37. International Chemistry Olympiad Taipei 2005

National German competition

Volume 11

Preface

To become a member of the German IChO-team you have to be successful in four rounds.
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 the students who solve about 70% 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, excursions to chemical plants or universities and cultural events there are two written theoretical tests of 5 hours each.
The top 15 of the 3rd round are the members 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 elected.

Acknowledgements

It is a great pleasure to thank the many people whose help and suggestions were so valuable in ceating and reviewing all the problems and in helping us to perform the third and the fourth round.
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Wolfgang Hampe

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Part 1

The problem set of the four rounds

First Round (homework)

Problem 1-1 Acid Rain

In contrast to pure water that has a pH of 7, rainwater reacts to show a slightly acid reaction because of dissolved carbon dioxide. Some of the reasons for this phenomenon are natural and some are caused by man. In air, sulfur dioxide and nitrogen monooxide are oxidized to sulfur trioxide and nitrogen dioxide reacting with water to form sulfuric acid and nitric acid. These reactions make the so-called acid rain form that has an average pH of 4.5 – values like 1.7, however, have already been measured as well.

Sulfur dioxide can be understood as a dibasic acid. The acidity constants at 25 °C are the following:

$$SO_{2(aq)} + 2H_2O_{(l)} \rightleftarrows HSO_3^-{}_{(aq)} + H_3O^+{}_{(aq)} \qquad K_{a1} = 10^{-1,92}\ molL^{-1}$$

$$HSO_3^-{}_{(aq)} + H_2O_{(l)} \rightleftarrows SO_3^{2-}{}_{(aq)} + H_3O^+{}_{(aq)} \qquad K_{a2} = 10^{-7,18}\ molL^{-1}.$$

The following questions refer to 25°C.

The solubility of sulfur dioxide is 33.9 L per 1 L of water at a sulfur-dioxide partial pressure of 1 bar (changes in volume by the dissolution of SO_2 are to be ignored).

a) What is the pH of such a solution?

b) Calculate the concentration of hydrogen ions in a solution of sodium sulfite (c = 0.010 molL^{-1}).

The dominating equilibrium in an aqueous sodium-hydrogensulfite solution is the following:

$$2\ HSO_3^-{}_{(aq)} \rightleftarrows SO_{2(aq)} + SO_3^{2-}{}_{(aq)} + H_2O_{(l)}$$

c) Calculate the equilibrium constant.

d) Calculate the concentration of $SO_{2(aq)}$ in a solution of sodium hydrogensulfite (c = 0.01 molL^{-1}) with the equilibrium constant of c).

Drops of bromine are added to a solution of sulfur dioxide (c = 0.01 molL^{-1}) until there is an excess of bromine. The total amount of sulfur dioxide is oxidized to sulfate ions. The excess of bromine is eliminated.

e) Give the reaction equation for this process and calculate the pH of the nascent solution. It can be assumed that none of the manipulations mentioned results in a change in volume; $pK_a(HSO_4^-) = 1.99$.

After a volcanic eruption, the pH of rain water is 3.2. Assume that only sulfuric acid causes this value.

f) Calculate the total concentration of sulfuric acid.

Problem 1-2 Fume - Fog - Smoke?

Some of the compounds listed below fume in air, for example, if the vessels in which they are stored are opened:

$BaCl_2 \cdot 2\ H_2O$, $AlCl_3$, NH_4Cl, $SiCl_4$, $TiCl_4$, $LiCl \cdot H_2O$, CCl_4 .

Which compounds are fuming compounds and what is the reasomn for this phenomenon? Write down their reaction equations. What does the smoke consist of?

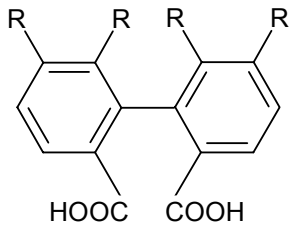
Problem 1-3 Composition of a coin

0.2000 g of a coin containing aluminium, copper, nickel and silver is dissolved in dilute hydrochloric acid. 119.8 cm^3 of hydrogen (p = 990 hPa, ϑ = 20°C) form.
The undissolved residue (m = 0,0500 g) is dissolved completely in nitric acid and electrolyzed after a certain treatment. The complete separation at the cathode takes 219.3 s at a current of 0.7 A and a current efficiency of 85%.

a) Give the reaction schemes of all dissolving processes.
b) Determine the percentage composition of the alloy (percent by weight).

Problem 1-4

There are two stereoisomers of the following compound:



R = Br, I

a) Give reasons for the stereoisomerism of the compositions of this type and draw "image and mirror image".

The two stereoisomers can be isolated from each other at room temperature, if R = iodine (compound A).
This separation will not be possible at room temperature, if R = bromine (compound B).

b) Give reasons for this difference by comparing the two structures and energy quanteties of stereoisomerism.

Problem 1-5

A yield as high as possible has to be produced of p-nitrophenol.
Two initial substances are available:

A: nitrobenzene B: phenol (hydroxybenzene)

a) Write down two reaction schemes describing the methods of producing the substances A and B.
b) Which of the two initial substances would you choose for the production of p-nitrophenol? Give reasons for your decision.

In alkaline solutions, p-nitrophenol is deeply yellow. In acid solutions, however, it has a pale greenish yellow colour.

c) Explain the different colours of p-nitrophenol in an acid and in an alkaline solution.
d) What are substances showing such an effect like p-nitrophenol used for? What advantage do many of these substances have over p-nitrophenol? Give examples.

Second Round (homework)

Problem 2-1: Liquid ammonia

Apart from water, other chemical solvents are frequently used as well. Liquid ammonia is one of them that has been investigated best. Like water molecules, ammonia molecules are polar as well. Thus, ammonia can dissolve ionic compounds well.

There is an autoprtolysis equilibrium in liquid ammonia:

$$2\ NH_3 \rightleftarrows NH_4^+ + NH_2^-$$

with the constant (at -33°C)

$$K_{Am} = c(NH_4^+) \cdot c(NH_2^-) = 10^{-30}\ mol^2 \cdot L^{-2}$$

Substances increasing the concentration of the NH_4^+ ions can be considered as acids. Those increasing the concentration of NH_2^- ions are bases. In analogy to aqueous solutions, a pH value can be defined in liquid ammonia as well as the negative common logarithm of the NH_4^+- ionic concentration: $pH = -\lg \frac{c(NH_4^+)}{c_0}$ $c_0 = 1\ mol \cdot L^{-1}$.

a) What is the pH of pure liquid ammonia?

b) Which of the following substances can be classified as acids or bases after they have been dissolved in liquid ammonia:

NH_4NO_3 / KNH_2 / CH_3COOH / $C_6H_5NH_2$ (aniline) / KI ?

Give reasons.

c) Give the equation for the reaction of NH_4Cl with KNH_2.
What kind of type is this reaction?

In liquid ammonia, the measuring of the pH value can be carried out with a platinum-hydrogen electrode consisting of a platinum wire that is surrounded by gaseous hydrogen at constant pressure ($p(H_2)$ = standard pressure). According to conventions, the potential of the platinum-hydrogen electrode is $E^0 = 0$ V for the activity of the NH_4^+ ions $a(NH_4^+) = 1\ mol \cdot L^{-1}$. An Ag/AgCl/KCl-electrode having the potential of $E^0 = 0.681$ V at - 40°C is used as a reference electrode.

In an ammoniacal solution of acetic acid having the concentration of $c(CH_3COOH) = 10^{-3}\ mol \cdot L^{-1}$ the potential difference of $\Delta E = 0.820$ V towards the reference electrode can be measured with the platinum-hydrogen electrode at –40°. The analogous measurement in a HCN solution having the concentration of $c(HCN) = 10^{-3}\ mol \cdot L^{-1}$ results in $\Delta E = 0.837$ V.

d) Calculate the degree of protolysis of the two acids in liquid ammonia and compare it (qualitatively) with the behaviour of these compounds in aqueous solutions.

e) *What is the pH of a solution of* HCN *in ammonia with c(*HCN*)= 0.01 mol·L^{-1} that 0.60 g·L^{-1} of ammonium cyanide are added to? Make use of the valuet pK_a = 3.5 for the protolysis constant of HCN in liquid ammonium.*

The ability of dissolving alkali- and alkaline-earth metals is one of the especially striking properties of liquid ammonia. Apart from metal cations, free electrons that are located in the interstitial sites of the solvent. These electrons lead to an absorption maximum at the wavelength of λ = 1500 nm.

f) Calculate the medium size (edge length) of the interstitial sites by considering the electrons as"particles in a three-dimensional box".

Problem 2-2: Rates of reaction

The course of the hydrolysis of para-nitrophenylacetate can be observed with the help of ultraviolet-absorption at 398 nm, because only the compounds with a nitrophenyl group show strong (but different) absorption at this wavelength. A solution of para-nitrophenylacetate (c_0 = 10^{-4} mol L^{-1}) in a phosphate buffer was hydrolysed at 25°C. The extinction of the solution was noted (series of measurements 1). The reaction was repeated with the same initial substances at 30°C (series of measurements 2). A phosphate buffer that 10^{-3} mol L^{-1} of imidazole had been added to was used at 25°C in the third series of measurements.
(Note that the initial concentration of the series of measurements 2 and 3 are not given.)
After the end of the reaction the solutions showed constant values of extinction that are marked with t = ∞ in the table. All measurements were carried out in a cuvette with the length l = 1 cm.

time in s	300	600	900	1200	1500	3000	4500	6000	∞
series 1 extinction	0.152	0.272	0.377	0.469	0.553	0.886	1.100	1.244	1.456
series 2 extinction	0.307	0.440	0.558	0.664	0.757	1.092	1.278	1.384	1.512
series 3 extinction	0.750	1.229	1.598	1.886	2.100	2.648	2.798	2.842	2.860

a) *Write down the equation for the hydrolysis of para-nitrophenylacetate.*
b) *Calculate the extinction coefficient of the reaction product at 398 nm for the first series of measurements.*

c) *Determine the reaction order and the rate constant for the hydrolysis under the conditions of the first series of measurements. Check for a reaction of zero, first and second order. How can the reaction order be harmonized with the reaction equation?*

d) *Calculate the rate constant for the second series of measurements. What is the activation energy of the hydrolysis?*

e) *What function does imidazole have in the third series of measurements? Make a proposal for a mechanism explaining the influence of imidazole on the hydrolysis of para-nitrophenylacetate. Start out from the fact that the same products will form and that there will be the same pH-value as in the experiments of the first two series of measurements.*

Problem 2-3: Metal hydrides

Metal **M** reacts in a hydrogen atmosphere to form the hydride $\mathbf{MH_x}$ (x = natural number). 1,000 g of $\mathbf{MH_x}$ react at 25°C and an atmospheric pressure of 99,50 kPa with water to form 3.134 L of hydrogen.

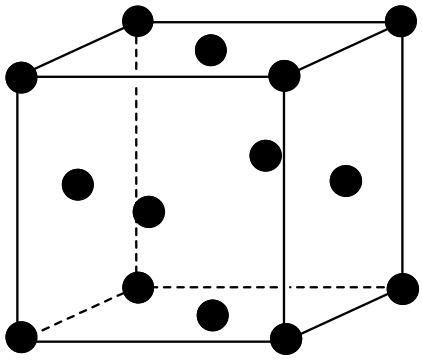
a) *Find the metal **M**?*

b) *Give a balanced reaction equation for the formation of $\boldsymbol{MH_x}$ and the decomposition of $\boldsymbol{MH_x}$ in water.*

$\mathbf{MH_x}$ crystallizes in a cubic face-centered packing (see illustration 1). The edge length of the unit cell is **a**. The marked positions symbolize the hydride ions, the ions M^{x+} are not illustrated.

illustration 1:

cubic face-centered unit cell



A unit cell contains **Z** hydride ions.

c) *Give the number **Z** of the hydride ions per unit cell.*

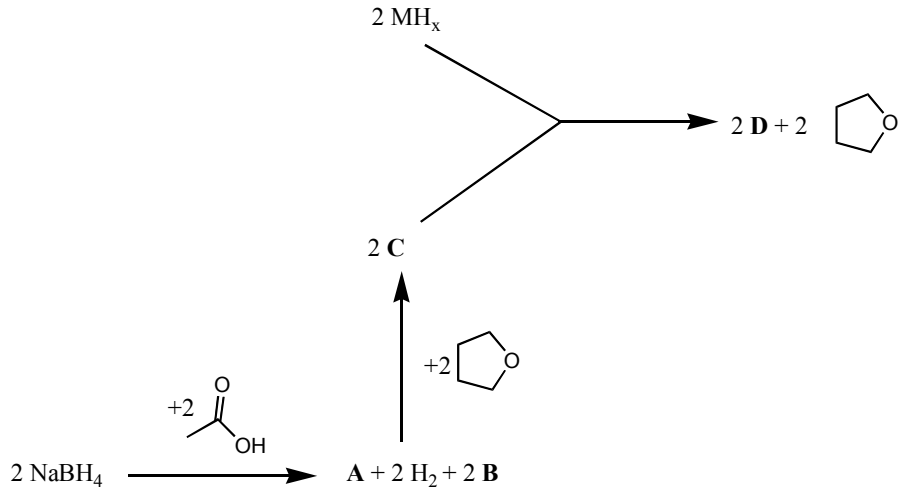
If crystals of $\mathbf{MH_x}$ are exposed to air, the hydride ions that are located on the surface of the crystal will react with atmospheric humidity. The result are crystals containing anion lattices

of which the interior consists of hydride ions H^-. Their surfaces, however, consist of hydroxide ions (OH^-).

A sample of **MH_x** (powdery, very small cubic crystals having the same size) was stored in air for a short time, so that the surface (and only that) is completely occupied with OH^- ions. This sample is investigated as a solid by ^{1}H-NMR-spectroscopy. There are two peaks (for H^- and OH^-) in the ratio of 150 : 1 in the resulting spectrum.

*d) Determine the edge length of the investigated crystals as a multiple of **a**.*

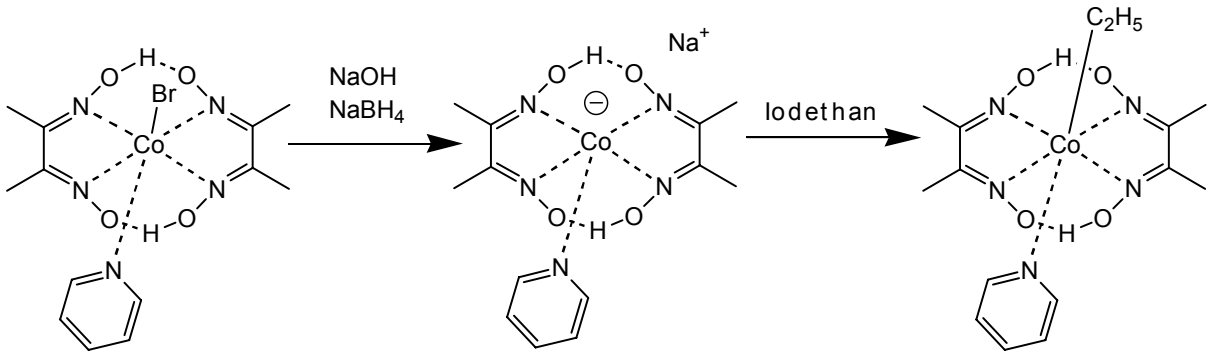
It is true that **MH_x** reacts violently with water, but can be stabilized in the form of a salt-like complex **D** that is soluble in water in its undecomposed state.
For this purpose, sodium borohydride, $NaBH_4$, reacts with dry acid in tetrahydrofuran (THF) to form **A** ($M(\mathbf{A}) = 27.67\ g \cdot mol^{-1}$). In addition to that, hydrogen and **B** form as well. **A** continues reacting with tetrahydrofuran to form the complex **C** that reacts with **MH_x** to form **D** while tetrahydrofuran is separated:



*e) Give the structural formulas of the compounds **A** and **C**. Give reasons for the molecular structure of **A**.*

*f) What compounds do **B** and **D** stand for? Give the three-dimensional structural formula of the anion of **D**.*

Hydrides (e.g. sodium borohydride, $NaBH_4$) are used for the synthesis of complex compounds:
Iodethan = ethyl iodide



I **II** **III**

*g) Give balanced reaction equations for the formation of **II** from **I** and of **III** from **II**.*

*h) Give the oxidation numbers of the central atoms in the complexes **II** and **III**.*

*i) Give reasons for the octahedral complexes **I** and **III** being diamagnetic.*

Problem 2-4: Synthesis with detours

Sometimes, direct syntheses do not lead to a successful reaction . „Detours“ make possible the formation of the desired product.

The following synthesis is carried out:

$HOCH_2CH_2CH_2Br$ + **X** $\xrightarrow{\text{spec. base}}$ **A** + base hydrochloride

A + **Y** $\xrightarrow{\text{ether}}$ **B**

B $\xrightarrow[\text{2.) } +H_2O]{\text{1.) } +\mathbf{Z}}$ **C** + **D**

C + H_2O $\xrightarrow{H_3O^+}$ $HOCH_2CH_2CH_2C(OH)HCH_3$ + **F**

E

The total formula of compound **B** could only partly be determined.

It contains 6 C-atoms, 15 H-atoms and a Mg-, a Br-, an O-atom and an atom of a further element **Q**.

The analysis of **F** led to the following results:

- Apart from carbon and hydrogen, **F** contains only oxygan and the element **Q**.
- The elemental analysis of **F** results in 39.94% of carbon and 11.19% of hydrogen.

- The molar mass of **F** is M = 90.22 g·mol^{-1}.
- **F** forms a dimeric compound by the separation of hydrogen. This compound is stable in air.

a) *Give the structural formulas of the compounds **A**, **B**, **C**, **D** and **F*** as well as their reaction schemes.
*What reagents and compounds **X**, **Y** and **Z** were used?*

b) *Give reasons for the function of compound **X** in the synthesis.*

Problem 2-5: Stereoselective reactions

The compound (1S,2S)-1,2-dibromo-1,2-diphenylethane separates hydrogen bromide in the presence of a strong base (e.g. RO$^-$).

a) *Give a reaction scheme showing the three-dimensional structures of the initial- and the final substance (see tips for the sketch).*
Give the complete name (E-Z-name) of the final substance.

b) *Draw a Newman-projection justifying the three-dimensional structure of the compound that has formed.*

c) *Explain why the same three-dimensional structure will form, if (1R,2R)-1,2-dibromo-1,2-diphenylethane is used as an initial substance under the same reaction conditions.*

In a further experiment, (1S)-1-bromo-1,2-diphenylethane reacts according to the same reaction conditions. **E** forms.

d) *What is/are the stereoisomeric structure(s) of **E** in this reaction?*
*Give the structur(s) of **E** and give reasons for it/them.*

Tips for the sketch:

Y-atoms above (in front of) the paper plane

Y-atoms below (behind) the paper plane

Third Round, Test 1

A formulary and a periodic table were made available for the two tests of the third round.

Problem 3-1 (multiple choice, more than one answer may be correct)

a) The formulas of sodium tungstate and lead phosphate are Na_2WO_4 and $Pb_3(PO_4)_2$ respectively. What is the formula of lead tungstate?

A	B	C	D
$PbWO_4$	$Pb_2(WO_4)_3$	$Pb_3(WO_4)_2$	$Pb_3(WO_4)_4$

b) Assign the pk values 1.3 / 2.8 / 4.1 / 4.8 to the acids below.

A) $Cl(CH_2)_2COOH$	B) $ClCH_2COOH$	C) CH_3COOH	D) $Cl_2CHCOOH$

c) Which element in its ground-state electronic configuration has the greatest number of unpaired electrons?

A) Fe	B) V	C) In	D) As	E) Br

d) The table below shows the successive ionisation energies I_n (n = 1,...,6) of elements X und Y in kJ/mol.

	I_1	I_2	I_3	I_4	I_5	I_6
X	590	1146	4941	6485	8142	10519
Y	1086	2352	4619	6221	37820	47260

E and F are the oxides of X and Y respectively, such that the elements X and Y are present in their highest oxidation states.
E reacts with F to form a compound with the empirical formula

A) X_2YO_2	B) X_2YO_3	C) XY_2O_3	D) XYO_3	E) X_2YO_4

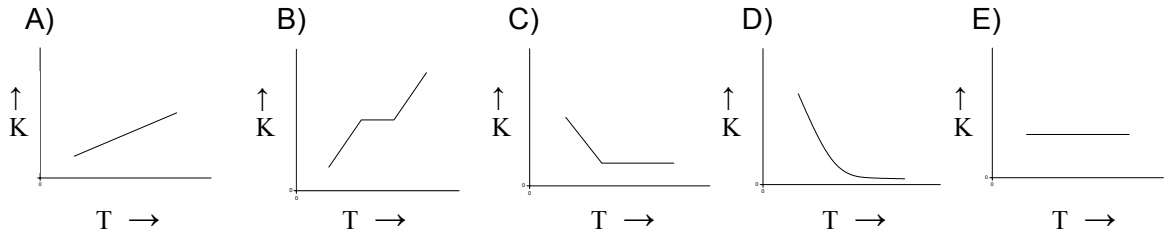
e) The anhydrides of the acids H_3PO_4, H_2SO_4, CH_3COOH are

A)	B)	C)	D)
P_2O_5, SO_2, CH_2CO	P_2O_3, SO_3, $(CH_3CO)_2O$	P_2O_3, SO_2, CH_2CO	P_2O_5, SO_3, $(CH_3CO)_2O$

f) The pH of an aquous solution at 60°C is found to be equal to 7. The solution is

A	B	C	D
neutral	basic	acidic	not possible to determine

g) Which could be a plot of the equilibrium constant vs. temperature for the condensation of ethanol vapor [C_6H_5OH (g) $\rightleftarrows$ C_6H_5OH (l)] ?



D

Problem 3-2

Toothpaste “with fluorine” contains sodium fluorophosphate, Na_2PO_3F, and sodium fluoride. The total amount of fluorine of 0,100 % (of mass) of a certain toothpaste consists of 0,050 % (of mass) of each compound.

a) Calculate the mass ratio of the two compounds.

b) Show a 3-D structure of the fluorophosphate ion.

c) Show 3-D structures of XeF_4, XeO_4, SF_4, XeF_2, und $SnCl_2$.
Use the VSEPR model by Gillespie.

Problem 3-3 Thermogravimetry

(adaptation of a problem from the Israeli Chemical Olympiad, Dr. Vitali Averbukh)

Thermogravimetry is an analytical method to determine the composition of solids which decompose on heating. The change in mass which is measured during the heating process provides information about the composition of the analyzed substance.
A mixture of calcium oxalate and magnesium oxalate was heated up to 900°C. During this process the mass of the mixture is measured continuously. It is known that there are two decomposition reactions around 400°C

MgC_2O_4 (s) $\rightleftharpoons$ MgO (s) + CO (g) + CO_2 (g)

CaC_2O_4 (s) $\rightleftharpoons$ $CaCO_3$ (s) + CO (g) .

At 700°C the third decompositon is observed.

a) Write the equation of the third decomposition reaction.

At 500°C the mass of a sample was 3.06 g, at 900°C 2.03 g.

b) Calculate the composition of the original sample prior to heating in mass percent.

The chemist who carried out the analysis in part b) wanted to check the accuracy of the gravimetric method. Therefore he attempted to determine the molar mass of carbon and compared it with the value given in literature.
The researcher heated 7.30 g calcium oxalate to obtain the following data:

temperature (°C)	90	250	500	900
mass (g)	7.30	6.40	5.00	2.80

c) *What is the reason for the first decrease in mass?*
Calculate the molar mass of carbon on the basis of the data above.

Sometimes the gravimetric method leads to the discovery of new compounds. For example, the thermogravimetry of boric acid, H_3BO_3, revealed the existence of a compund X.
The heating process of H_3BO_3 was accompanied by a two step loss of solid mass:

H_3BO_3 (s) $\rightleftharpoons$ X (s) + H_2O (g)
X (s) $\rightleftharpoons$ B_2O_3 (s) + H_2O (g)
(Note that the equations are not balanced!)

Results of the experiment:

temperature (°C)	40	100	250
mass (g)	6.2	4.4	3.5

d) Determine the empirical formula of X.

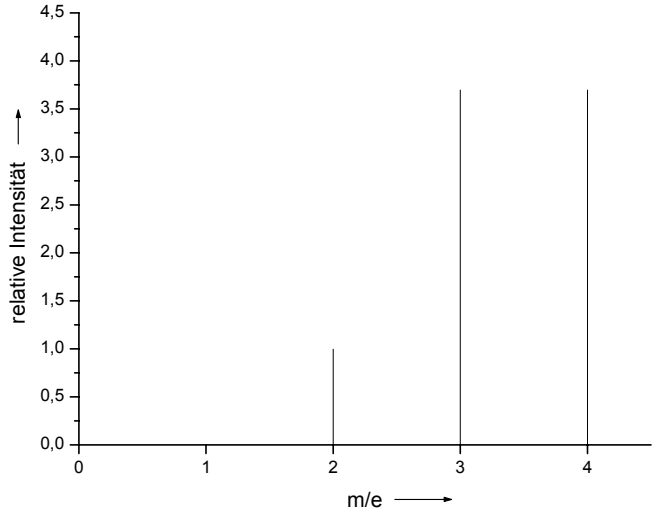
Problem 3-4 Equilibria

The following method is very helpful to determine the coordination number n and the formation constant K_f of the complex $[ML_n]^{2+}$ between a metal ion M^{2+} and a ligand L such as $H_2N\text{-}CH{=}CH\text{-}NH_2$.
A series of solutions is made in which the sum of the concentration of the metal ion and the concentration of the ligand is constant, $c(Me^{2+}) + c(L) = 1.00 \cdot 10^{-3}$mol/L.
The absorbance at 510 nm of these solutions is taken in a 1.00 cm cell. Both, M^{2+} and L do not absorb at 510 nm.
The absorbance A of each solution with the mole fraction X_M von M^{2+} is shown as follows:

X_M	A	X_M	A	X_M	A	X_M	A	X_M	A
0.10	1.12	0.20	0.22	0.30	0.28	0.40	0.31	0.50	0.34
0.60	0.32	0.70	0.26	0.80	0.22	0.90	0.12		

a) Determine the coordination number n and the molar absorption coefficient ε.
b) Calculate the formation constant K_f .

V_1 mL of hydrogen (H_2) were mixed with the double amount ($2 \cdot V_1$) of deuterium (D_2). After equilibrium established itself the mass spectrum given below was obtained.



c) Give the equation for the equilibrium.

d) Calculate the equilibrium constant.

e) Which assumptions do you make when analysing the data of the plot?

Problem 3-5 Electrochemistry

(Assume in all problems that activity is equal to concentration)

Given $E°_1(Fe^{3+}/Fe^{2+}) = 0.77$ V , and $E°_2(Fe^{3+}/Fe) = -0.036$ V.

a) Calculate the equlibrium constant for the reaction

$$2\ Fe^{3+} + Fe \rightleftharpoons 3\ Fe^{2+}.$$

The potential of an $Sb(s)/Sb_2S_3(s)/OH^-(aq)$ - electrode depends on the activity of OH^- ions.

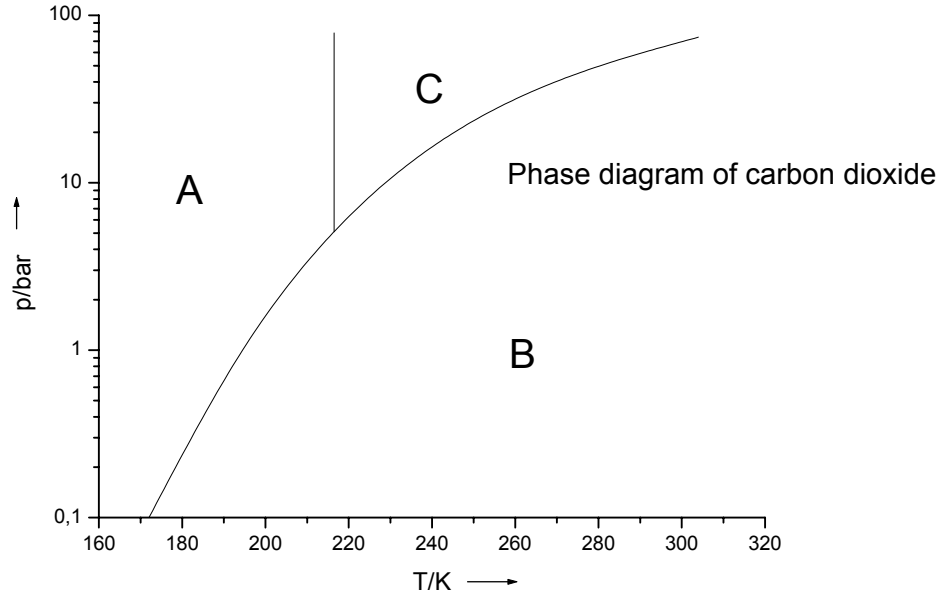
b) Write the electrode reaction.

c) How will the electrode potential change if the pH of the solution increases from 12.0 to 12.7?

Given $E°(Hg_2^{2+}/Hg) = 0.798$ V and $E°(Hg/Hg_2Cl_2(s)/ Cl^-(aq)) = 0.268$ V.

d) Calculate the solubility (in g/L) of Hg_2Cl_2 at 25°C.

Problem 3-6 Carbon dioxide



a) In which phase exists carbon dioxide in the areas A, B and C respectively.

b) Which state may carbon dioxide adopt at normal pressure?*

c) Up to which pressure has CO_2 at least to be compressed to become fluid?*

d) To which temperature has CO_2 at least to be cooled down in order to condense?*

e) Which temperature has dry ice (CO_2 (s)) at normal pressure if it is in equivalence with CO_2 (g)?*

f) A fire extinguisher contains fluid CO_2. Which pressure does it have to withstand at least at 20°C?*

* Draw relevant lines or dots in the diagram **on the answer sheet**!

g) The CO_2 gas container in a laboratory was delivered filled with fluid CO_2 and then used many times. How can one prove how much CO_2 it still contains?

Natural rain in slightly acid as carbon dioxide from air is solved.
Air contains 0.035 % (V/V) of CO_2, the normal pressure is 101.3 kPa.
Given the following constants:

CO_2 (g)	$\rightleftharpoons$ CO_2 (aq)	$K_H = 3.36 \cdot 10^{-7}$ mol·L^{-1}·Pa^{-1}
CO_2 (aq) + H_2O	$\rightleftharpoons$ H_2CO_3	$K = 2.58 \cdot 10^{-3}$

$pK_1(H_2CO_3) = 3.3$
$pK_2(HCO_3^-) = 10.4$

h) Calculate the pH of natural rain.

Problem 3-7 Solubility

Solubility of salts is an important item in chemistry. It varies greatly with the nature of the solute and the solvent, and the experimental conditions such as temperature and pressure, pH and complex formation also may have influence on the solubility.
An aquous solution contains both, $BaCl_2$ und $SrCl_2$, in a concentration of 0.01 mol/L each. The question is whether it will be possible so seperate the cations completely by adding a saturated solution of sodium sulfate. The criterion is that at least 99.9 % of Ba^{2+} has precipitated as $BaSO_4$ and that $SrSO_4$ may not be contaminated with more than 0.1% of $BaSO_4$.

Solubility products: $K_{sp}(BaSO_4) = 1.0 \cdot 10^{-10}$ $K_{sp}(SrSO_4) = 3.0 \cdot 10^{-7}$

a) Write equations for the formation of the precipitates.

b) Calculate the concentration of sulfate when $BaSO_4$ starts to precipitate.

c) Is the seperation complete? Calculate!

Complex formation may have an effect on the solubility of silver chloride in a solution of ammonia.
Solubility product: $K_{sp}(AgCl) = 1.7 \cdot 10^{-10}$
Equilibrium constant for the formation of the silver-ammonia-complex: $K = 1.5 \cdot 10^{+7}$

d) Give a balanced equation for the formation of the silver ammonia complex.

e) Calculate the solubility (in g/L) of silver chloride in water.

f) Calculate the solubility (in g/L) of silver chloride in an aquous solution of ammonia (c = 1.0 mol/L) and compare it with the solubility in water.

Problem 3-8 Isomeric Structures

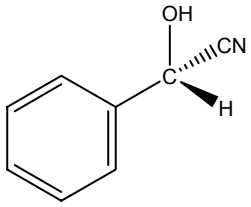
Given the compound with the molecular formula $BrCl_2C_2H$.

a) State the structures of all compounds with the given molecular formular and their names (use IUPAC rules).

b) Which kind of isomerism do you find among these compounds?

Problem 3-9 Synthesis of Cyanohydrin

Sulphuric acid is added to a mixture of benzaldehyde (C_7H_6O) and sodium cyanide.
Besides hydrogen cyanide two compounds A1 and A2 with the same melting point form.

A1 = 

a) Write the reaction equation with 3-D structures of the compounds A1 and A2.

b) Show the reaction mechanism of the formation A1 and explain it.

This reaction is used in the chemistry of sugars.

c) Draw a structure of any D-pentose (aldose in Fischer-projection, open-chain form).

Pentose reacts with sodium cyanide in sulphuric acid to yield two compounds B1 and B2 with different melting points.

d) Write the reaction equation of the formation of B1 and B2 using Fischer projections.

e) Which kind of isomerism do you find between B1 and B2?

Aufgabe 3-10 Catalytic Synthesis

2,2,4-Trimethylpentane is produce in a large scale from B (C_4H_8) and C (C_4H_{10}) by catalytic synthesis.
B reacts in the presence of acid with itself following the rule of Markownikow to form to isomeric alkenes D und E (C_8H_{16}).
Ozonolysis cleaves D and E to form four compound, among others acetone ($(CH_3)_2CO$) und formaldehyde (HCHO).

a) Give the structural formulas and the names of the compounds B and C.

b) Give the structural formulas and the names of the compounds D und E.

c) Which kind of isomerism do you find between D and E?

d) Show the mechanism of the cleavage by ozone (all intgermediates) - reaction with O_3 and Zn/H_3O^+ - of the compounds D and E

Third Round, Test 2

Problem 3-11 (multiple choice, more than one answer may be correct)

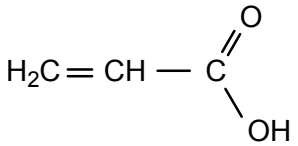
a) An analysis of an aquous solution has shown the presence of Na^+, Cl^- und SO_4^{2-} ions exclusively. The concentrations were determined to be $c(Na^+)$ = 1 mol/L, $C(Cl^-)$ = 0.2 mol/L. Give the concentration of the SO_4^{2-} ions.

A) 0.8 mol/L	B) 0.5 mol/L	C) 0.4 mol/L	D) 0.3 mol/L	E) 0.2 mol/L

b) A solution containing equal concentrations of a weak acid and its conjugate base is best described as

A) equivalent	B) dissociated	C) protolytic	D) buffered	E) neutralized

c) According to the Valence-Bond-Theory what are the states of hybridisation of the carbon atoms (reading from left to right) in the following compound?



A) sp sp^2 sp	B) sp^2 sp sp^3	C) sp^2 sp^2 sp^2	D) sp^3 sp^2 sp^3	E) sp^3 sp^3 sp^3

d) Given the electronegativities of the elements P, Q, R, S, T (no symbols of elements)

Element	P	Q	R	S	T
Electronegativity	0.7	1.1	1.6	2.5	1.7

Which is the bond with the most ionic character?

A) P - T	B) P - Q	C) R - S	D) T - S	E) Q - T

e) HeH^+ molecular ions are formed in a hydrogen-helium gas mixture under electron impact conditions. Which of the following dissociation processes is characterized by the smallest dissociation energy?

A	B	C	D
$HeH^+ \longrightarrow He + H^+$	$HeH^+ \longrightarrow He^+ + H$	$HeH^+ \longrightarrow He^{2+} + H^-$	A and B

f) The number of significant figures in 0.00407 is

A) 2	B) 3	C) 5	D) 6	E) 407

g) ½ $N_2(g)$ + $O_2(g)$ $\rightleftharpoons$ $NO_2(g)$ K_1

$2\ NO_2(g)$ $\rightleftharpoons$ $N_2O_4(g)$ K_2 .

The two reactions given above have the equilibrium constants K_1 and K_2 respectively. What would be the expression for the following reaction in terms of K_1 and K_2?

$N_2O_4(g)$ $\rightleftharpoons$ $N_2(g)$ + $2\ O_2(g)$

A) $K_1 \cdot K_2$	B) $K_1^2 \cdot K_2$	C) $K_1 \cdot K_2^2$	D) $\frac{1}{K_1 \cdot K_2^2}$	E) $\frac{1}{K_1^2 \cdot K_2}$

Problem 3-12 Acetic Acid

Vaporized acetic acid is a mixture of monomer and dimer molecules.
The vapor pressure of an unknown amount of acetic acid at 50°C in a 500 mL vessel is 5.92 kPa.
The vapor is condensed and the liquor then titrated with 22.60 mL of a solution of barium hydroxide (c = 0.0413 mol/L).

a) How would you explain the formation of the dimer molecules in the vapor?

b) Calculate the degree of dissociation (α) of the dimer under the conditions given above.

c) Calculate the equivalent constants K_c und K_p for the dissociation reaction under the conditions given above.

Problem 3-13 About nitrogen compounds

On addition of 0.560 g of sodium nitrate(III) (sodium nitrite) in water to a solution of 0.495 g of hydroxylammonium chloride ($HONH_3Cl$), a colourless odourless gas evolved.

After the reaction had ceased the solution was mixed with 20.0 mL of potassium manganate(VII) solution (c = 0.050 mol/L). After acidifying and heating the solution the excess manganate(VII) was titrated with sodium-oxalate solution. It was found that 11.94 mL (mean value of several titrations) of the originally added manganate(VII) solution had not been consumed.

a) Why is the oxidation with manganate(VII) performed?
Write a balanced equation for the reaction between sodium nitrate(III) and hydroxylammonium chloride and hence identify the gas evolved.

Aqueous solutions of nitric(III) acid (nitrous acid) are unstable and decompose rapidly when heated. Nitrogen(II) oxid is the only gaseous product of the decomposition.

b) Write a balanced equation for this decomposion.

c) Draw "dot and line" structures to show the bonding in the gases N_2O, NO, N_2O_2, NO_2 and N_2O_4. *Which of these molecules are free radicals?*

Problem 3-14 Kinetics

Within metabolism, for example of glucose, oxygen is reduced not only to water but also in a small amount to the radical O_2^-. Superoxidedismutase SOD (called E in this problem) is an enzyme to destroy this higly reactive, toxic radical by catalizing the following reaction:

$$2\ O_2^- + 2\ H^+ \xrightarrow{E} O_2 + H_2O_2$$

A kinetic study was made in a buffer solution with pH = 9.1 . The initial concentration of SOD was $0.400 \cdot 10^{-6}$ /L in each case. The initial rate r_0 of the disproportionation reaction

mentioned above was masured at room temperature with various initial concentrations of O_2^- ions:

$c_0(O_2^-)$ in mol/L	$7.69 \cdot 10^{-6}$	$3.33 \cdot 10^{-5}$	$2.00 \cdot 10^{-4}$
r_0 in mol L^{-1} s^{-1}	$3.85 \cdot 10^{-3}$	$1.67 \cdot 10^{-2}$	0.100

a) Determine the reaction order of the rate law $r = k \cdot c(O_2^-)^n$.

b) Calculate the rate constant k.

c) The following mechanism was proposed for the disproportionation reaction:

$$E + O_2^- \xrightarrow{k_1} E^- + O_2$$
$$E^- + O_2^- \xrightarrow{k_2} E + O_2^{2-} .$$

E^- is an intermediate and can be regarded as a free radical. The protonization of the superoxide ions is a rapid reaction.

Check whether this mechanism is consistent with the rate law observed. Write down any necessary assumption for your deduction.

d) Calculate the constants k_1 and k_2 if $k_2 = 2 \cdot k_1$.

Problem 3-15 Distillation

The table shows the vapour pressure of pure benzene and pure m-xylene at different temperatures. Under a pressure of 101.3 kPa the boiling temperature of benzene and m-xylene are 353 K and 412 K respectively.

T in K	363	373	383	393	403
p^0_{Benzol} in kPa	135.1	178.0	231.8	297.3	376.1
$p^0_{m\text{-}Xylol}$ in kPa	21.5	30.5	43.1	58.4	78.7

Benzene and m-xylene form ideal solutions (mixtures).

a) What is an „ideal mixture“? To answer this question name at least two properties of an ideal mixture and the conditions of the molecules of the compounds (which form such a mixture) which lead to these properties.

b) Draw a temperature-compositon diagram of the mixture which shows the composition of both, the vapor and the liquid, as a function of the overall mole fraction of benzene in the system. Show the necessary calculations and your score table.

To solve c, d, e and to make your solution clear use the diagram of b).

If you could not solve b) you can get an answer sheet with a similar temperature-compositon diagram to solve the problems c,d,e.

c) Which phases are present in the different regions in the temperature-compositon diagram?

Benzene and m-xylene are mixed in the mass ratio 1 : 1.5 and heated up to 388 K.

d) What is the compositon of the phases which are in equilibrium (result in mole fractions)?

In a laboratory a mixture of benzene and m-xylene with a boiling point of 395 K shall be seperated by fractional distillation. A distillation column with three plates is available for this process.

e) What is the purity of the recycled benzene (related to amounts in mole)? Assume that the composition of the original mixture does not change during distillation.

Problem 3-16 Solids & Surfaces

The accumulation of particles at a surface ist called adsorption. The substance that adsorbs is the adsorbate, the underlying material is the adsorbent or substrate.

The extend of surface coverage is expressed as the fractional coverage θ:

$$\theta = \frac{\text{number of adsorption sites occupied}}{\text{number of adsorption sites available}}.$$

Molecules and atoms can stick to surfaces in two ways.
In physisorption, there is a van der Waals interaction between the adsorbate and the substrate.
In chemisorption the particles stick to the surface by forming a chemical bond.

a) What do you understand by "van der Waals interaction"? Describe in short different types.

b) Chemisorption is a spontaneous process. Determine whether this process is exothermic or endothermic. Justify your decision.

c) Which of both types of adsorption has larger adsorption enthalpy (as to the absolute values). Justify your decision.

The Langmuir isotherme describes the coverage of a surface θ as a function of the pressure p of the gas in the dynamic equilibrium with the substrate:

$$\theta = \frac{K \cdot p}{1 + K \cdot p}$$ where K is a constant.

At constant θ you can use the slope m of the function lnp = f($\frac{1}{T}$), to determine the "isosteric adsorption enthalpy" (= adsorption enthalpy at constant coverage of the surface):

$$m = \frac{\Delta H^0_{ads}}{R}.$$

The vapour pressure of N_2 in a dynamic equilibrium with a layer of N_2 on rutile (TiO_2) at constant surface coverage of θ = 0.1 varies with the temperature as follows:

T in K	220	240	260	280	300
p in mbar	28	77	170	380	680

d) Plot the function (in a suitable scale, score table) and calculate the isosteric adsorption enthalpy ΔH^0_{ads} of N_2 on rutile at θ = 0.1.

Problem 3-17 Calorimetric Measurements

Naphthaline, anthracene and pentamethylbenzene were burnt in a constant volume bomb calorimeter. A certain amount of mass of each of the hydrocarbons are pressed together with an ignition primer to form a disk. This disk was brought into the calorimeter filled with more than sufficient oxygen. The ignition was electrically initiated.

The only results of the combustion are

- $H_2O_{(l)}$ ($\Delta_f H$ = -285.9 kJ/mol), $CO_{2(g)}$ ($\Delta_f H$ = -393.5 kJ/mol) and the combustion products of the ignition primer as substance, and
- the heat of combustion Q_c. Within Q_c there is the constant heat of combustion of the ignition primer, Q_c(primer) = -30.0 J.

Further experimental data are given in table 1.

All data as well as all calculations of this problem refer to 25°C.

Table 1

substance	m/g	Q_c/J
naphthalene	0.7002	-28237
anthracene	0.6653	-26381
pentamethylbenzene	0.6409	-27994

a) Draw a line-bond structure of the three hydrocarbons.
Write the three reaction equations for the combustion.
b) Calculate the molare combustion enthalpy $\Delta_c H$ of the three hydrocarbons.
c) Calculate the enthalpy of formation $\Delta_f H$ of these hydrocarbons.

Combustion enthalpies can be estimated by a special system of increments (see table 2). For that purpose the "individual combustion enthalpies" $\Delta_C H^i$ of the discrete bonds of the molecule are added. For benzene e.g. this calculation leads to
$3 \cdot \Delta_C H^i(C=C_{cis}) + 3 \cdot \Delta_C H^i(C\text{-}C) + 6 \cdot \Delta_C H^i(C\text{-}H) + 1 \cdot \Delta_C H^i$ (six-membered ring):
$\Delta_C H^i$ = [- 491.5 · 3 - 206.4 · 3 - 226.1 · 6 - 4.2] kJ/mol) = -3454.5 kJ/mol.
Furthermore the enthalpy of sublimation or of vaporisation respectively have to be added in order to get $\Delta_C H$.

Table 2

bond	$\Delta_C H^i$/kJmol^{-1}	bond	$\Delta_C H^i$/kJmol^{-1}
C-H	-226.1	$C=C_{(4\ groups)}$	-483.2
C-C	-206.4	six-membered ring	-4.2
$C=C_{(2\ H,\ 2\ groups,cis)}$	-491.5	branch point of a ring	+7.2
$C=C_{(1\ H,\ 3\ groups)}$	-484.4		

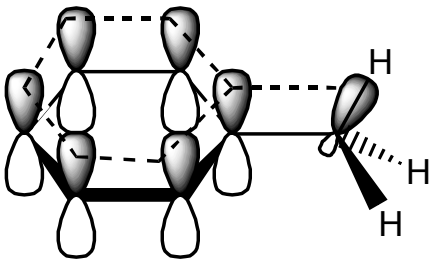
Enthalpies of sublimation $\Delta_S H$: naphthalene 66.5 kJ/mol, anthracene 93.4 kJ/mol, pentamethylbenzene 61.1 kJ/mol.

d) Calculate the enthalpies of combustion of the three hydrocarbons using the system of increments.

This system does not take into consideration that there exists something like "resonance stabilization" .

e) Using the practical (c) and the theoretical (d) values of enthalpie of naphthene and anthracene calculate the stabilizing (mesomeric) energy $\Delta_{mes}H$ per π electron.

Besides resonance stabilization the hyperconjugation gives stabilizing energy. Hyperconjugation is the overlapping of a σ bond (e.g. of a C-H of a methyl group) with a π electron system.



f) Calculate the energetic contribution of hyperkonjugation per methyl group using pentamethylbenzene as an example.

Problem 3-18 Determination of an Unknown Compound

Compound A is a white solid which contains only atoms of C, H and O.
It shows the following properties:

1. Heating of A with $Cu(OH)_2$ in alkaline solution leads to a red precipitate.
2. Tollens-reagent gives a silver mirror.
3. With an excess of methanol in the presence of catalytic acid a volatile optical inactive compound B forms.
4. The combustion of 60 mg of A in an excess of oxygen gives 44.8 mL of gas C (0°C, p = $1.013 \cdot 10^5$ Pa) with a molar mass of 44 g/mol - and 0.036 mL of a fluid D with the density of 1 g/cm^3.
5. Fluid D reacts with B (in the presence of traces of H^+) to give gas E. E is soluble in water, the solution is often used for medical applications. E may again convert to A.
6. From more measurements it's known that 0.036 g of fluid D have the same amount of oxygen atoms as 60 mg of compound A.

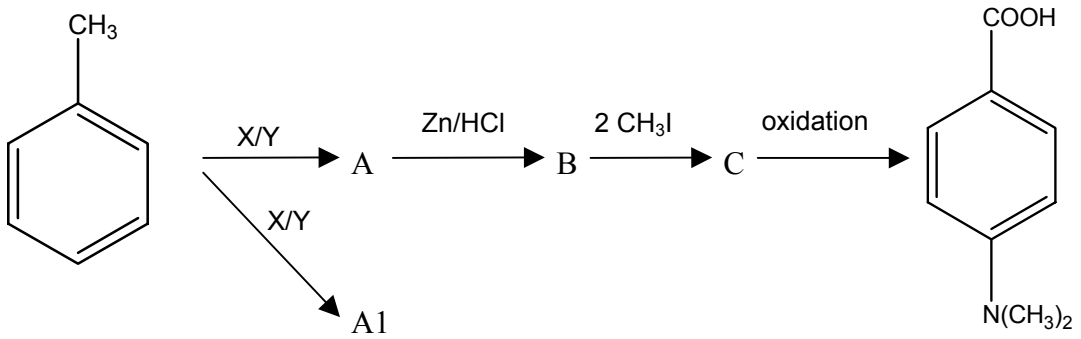
a) Determine the compounds A, B, C, D and E, write the formalas and the names.

b) Write balanced equations for the following reactions:

1. *Heating of A with $Cu(OH)_2$ (in NaOH solution).*
2. *Formation of B by reacting of A with methanol.*
3. *Combustion of A to yield compounds C and D.*
4. *Formation of A from E.*

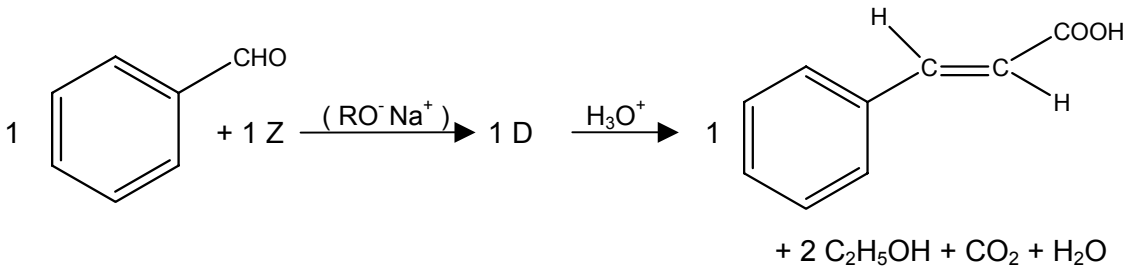
Problem 3-19 Synthesis of Aromatic Compounds

A. The following synthesis was carried out:



a) Determine the compounds A, B, C, X, Y and A1 (structural formulas).

B. Another synthesis was carried out:



b) Draw the structural formulas of Z and D. Give the reaction mechanism to form D from Z.

Problem 3-20 Stereoselective Reactions

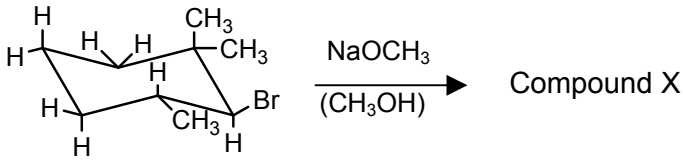
By converting an alkyl halide (e.g. bromoethane) with hydroxide ions (OH^-) or methoxy ions (CH_3O^-) the halogen is replaced by the hydroxy or methoxyl group.

a) Write the equation for the reaction of bromoethane with sodium methoxide, give the name of the product.

Compound (S)-2-bromobutane reacts with hydroxide ions.

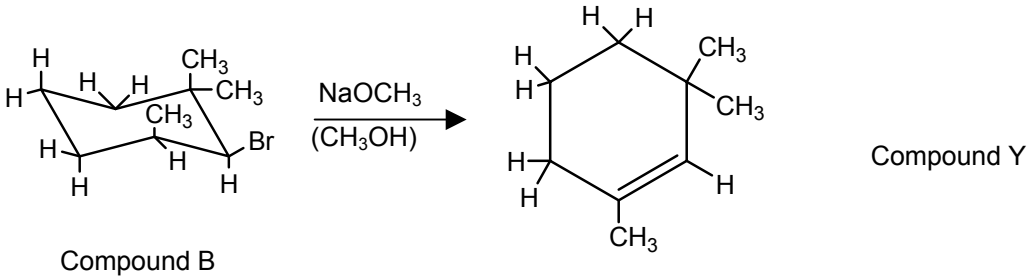
b) Write the reaction mechanism.
Pay attention to the steric situation of the substituents of reactant and product.
What is the total name of the product (R-, S-nomenclature)?

c) Show the spatial orientation of the substituents of compound X in the following reaction:



Compound A

Though under the same conditions, compound B reacts to give another main product Y.



Compound B

d) What kind of isomers are A und B?

e) Which kind of reaction happens the formation of Y to be?

Explain the different behaviour of A and B in the reations mentioned above.

Show the reaction mechanism of the formation of compound Y from compound B.

Fourth Round (Theoretical Problems)

Problem 4-1 Equilibrium

Halogens form a series of interhalogens, which are more or less stable. One of these is bromine chloride (BrCl) which decomposes at 500 °C into the elements. The equilibrium constant at this temperature is K_c = 32 related to the decomposition of 2 mol BrCl.

Inspect now a system 1 with c(BrCl) = c(Br_2) = c(Cl_2) = 0.25 mol/L.

a) Write the reaction equation for the decomposition.

b) Show by calculation that system 1 is not in equilibrium.

c) In which direction will the reaction in system 1 proceed?

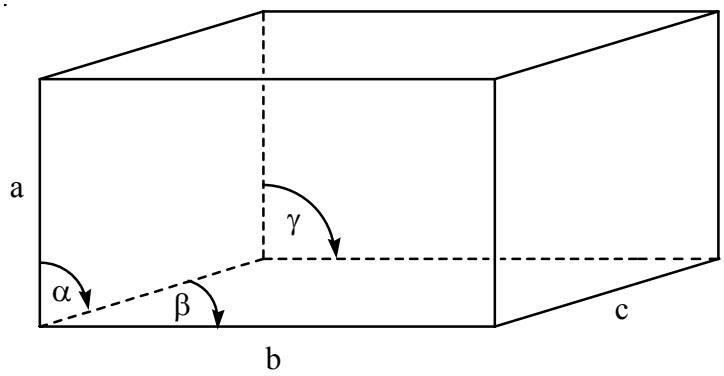
d) Calculate K_p for this reaction?

e) Calculate the equilibrium concentrations of BrCl, Br_2 and Cl_2 in system 1.

f) Determine the free reaction enthalpie for the reaction with the starting conditions mentioned above.

Problem 4-2

Paragonite, $NaAl_3Si_3O_{10}(OH)_2$, crystallizes in the monoclinic system. Its unit cell is shown below:



$a \neq b \neq c$

$\alpha = \gamma = 90^0$

$\beta \neq 90^0$

X-ray diffraction gives

a = 5.13 Å b = 8.89 Å c = 19.00 Å β = 95.00°. [1 Å = 0.1 nm]

a, b and c are real length between different parallel planes, which are equivalent referring to symmetry, of anions and/or cations.

The wavewlength of the x-rays omitted is 1.54 Å, the density of paragonite ρ = 2.90 g/cm^3.

a) Under which angle will you detect first-order diffraction for the distance a of the planes?
b) Derive a formula for the volume of a monoclinic cell as a function of a, b, c and sinβ
c) Calculate the number of aluminium atoms in the unit cell of paragonite.

Problem 4-3 Gases

Imagine you are in a laboratory with standard equipment: devices for heating, beakers, test tubes ect., demineralized water and 8 chemicals. Six of them are given

KOH, HCl (30%), $KMnO_4$, S, Zn und Cu.

You can choose a 7th and 8th chemical yourself. They have to be pure solid or liquid substance, no mixtures.

Show by writing chemical equations how to produce as many gases as possible (at least 8).

Hints:

- If heating is necessary mention it by "$\xrightarrow{\Delta H}$".
- To produce a gas you may use more than one step.
- Neither electrolysis is allowed nor parts of the equipment (glas, metals, wooden devices) as reactants.
- The compounds produced have to be gaseous at 25°C and standard pressure.
- No points will be awarded for mixtures unless you show a way to seperate them.

Problem 4-4 Potentials

All data of this problem refer to T = 298.15 K.

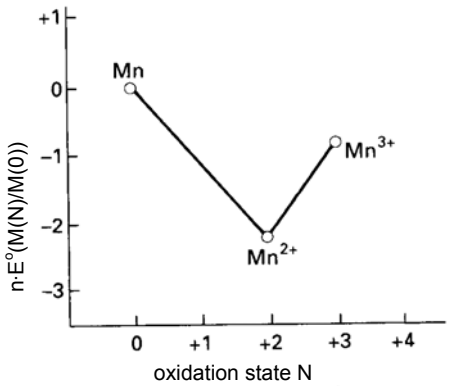
Some elements form compounds with different oxidation states N, ranging from N = 0 to N = 7. The standard potentials of e.g. $Mn^{2+} + 2\ e^- \rightleftarrows Mn$, E° = -1.18 V and $Mn^{3+} + e^- \rightleftarrows Mn^{2+}$, E° = 1.51 V can be expressed in the following way

$$Mn^{3+} \longrightarrow Mn^{2+} \xrightarrow{-1.18} Mn$$

The values of n·E° can be plotted in a Frost diagram as f(N) = n · E°[X(N)/X(0)] with

N: oxidation state n: number of electrons transferred.

Frost diagram of the example Mn^{3+} / Mn^{2+} / Mn



Given the data of different bromine compounds at different values of pH

pH = 0: $BrO_4^- \longrightarrow BrO_3^- \xrightarrow{1.45} HBrO \xrightarrow{1.61} Br_2 \xrightarrow{1.07} Br^-$

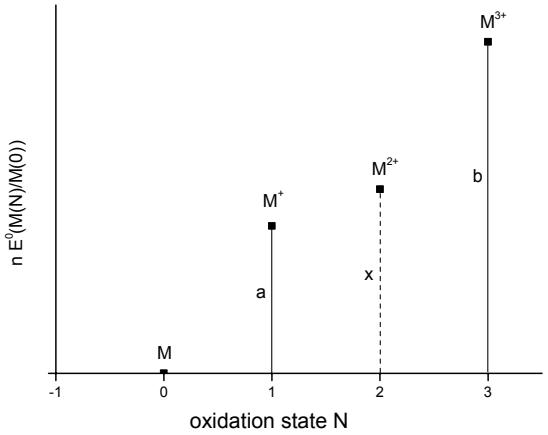
pH = 14: $BrO_4^- \longrightarrow BrO_3^- \xrightarrow{0.49} HBrO \xrightarrow{0.46} Br_2 \xrightarrow{1.07} Br^-$

a) *Calculate $E°(BrO_3^-/Br_2)$ at pH = 0 and at pH = 14. You will find different values. Account for this result.*
Describe why these values differ with the pH while the standard potential $E°(Br_2/Br^-)$ is not influenced by pH.
Use reaction equations for your explanations.

b) *Plot a Frost diagram of the bromine compounds at pH = 0 and at pH = 14 (both in the same figure).*

c) *How is the standard potential of the conversion of X(N) to the element X(0) connected with the free reaction enthalpie (ΔG°). Give an equation.*

Given the Frost diagram below



The values of a and b are regarded as fixed, x may have different values.

d) *Which conditon has x to fulfill if M^{2+} undergoes disproportionation into M^+ and M^{3+}?*
What happens if x does not fulfill this condition?
How can you read the different reactions form the Frost diagram?

e) *Evaluate the stability of bromine to disproportionation in acid and in alkaline solution respectively.*
Give an example for a disproportionation and for a comproportionation of three neighbouring species in alkaline solution (reaction equations).
Calculate the equilibrium constant for the disproportionation.

Problem 4-5 Superconductors

Superconductors based on lanthanum cuprate (La_2CuO_4) have the general composition of $La_xM_{(2-x)}CuO_4$ (M = Ca, Sr, Ba, in this problem M = Ba, barium).
For an analytical analysis to find out x you need standard solutions of sodium thiosulphate ($Na_2S_2O_3$) und Na_2H_2EDTA (ethylenediamine tetraacetate).

To produce a 0.01 M $Na_2S_2O_3$ - solution 2.450 g $Na_2S_2O_3 \cdot 5\ H_2O$ are dissolved and filled up to 1.000 L.

To determine the exact titer 0.108 g potassium iodate (KIO_3) are dissolved in water, 1 g of potassium iodide are added, the solution slightly acidified and filled up to 500 mL.
25 mL of this solution then are titrated with $Na_2S_2O_3$ - solution.
V($Na_2S_2O_3$ - solution) = 15.95 mL.

a) Write the reaction equation and calculate the exact concentration of the $Na_2S_2O_3$ solution.

The Na_2H_2EDTA solution is made by solving an exactly weighed mass of Na_2H_2EDTA.

b) Draw the structure of the EDTA anion und give the number of positons of the anion to coordinate.

c) Sketch the 3-D structure an EDT-metal complex. Are there isomers, if yes how many? Jusity your answer.

To analyse a certain amount of the superconductor is solved and the solution is filled up to 250 mL (parent solution). Two determinations are performed:

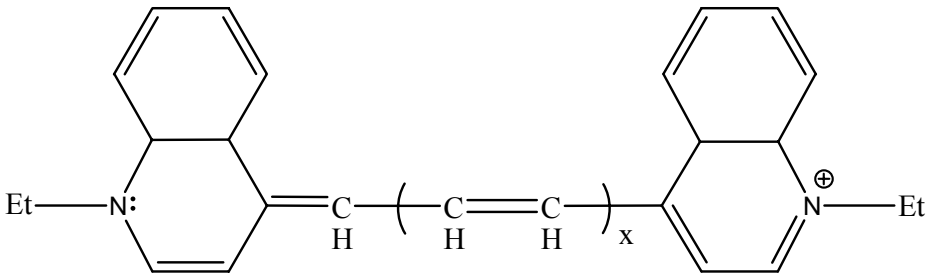
1. 25 mL of the parent solution are brought to pH = 6 and then titrated with Na_2H_2EDTA solution (c = 0.100 mol/L). Consumption:11.76 mL.
   (Hint: under these conditions ions of barium do not react with EDTA.)
2. 25 mL of the parent solution are tansferred into a volumetric flask and filled up to 100 mL.
   25 mL are taken thereof and 10 mL of a NaI solution are added. Then follows a titration with $Na_2S_2O_3$ solution (c = 0.010 mol/L, not the value from a)).
   Consumption: 10.50 mL .
   (Hint: under these conditions La^{3+} does not react with EDTA.)

d) Write reaction equations for the determinations #1. and #2.

e) Calculate the mass of copper and lanthanum in the parent solution.

f) Calculate the coefficient x in the formula $La_xBa_{2-x}CuO_4$.

Problem 4-6 Electrons in an 1-D Box



The molecules of the dyes shown above with x = 0, 1, 2... contain a system of conjugated π electrons. This system can be described by the “particle in the box theory“ in which a particle with the mass m is confined between two walls with the distance L.

In this model the energy of an electron is given by $E_n = \frac{h^2 \cdot n^2}{8 \cdot m \cdot L^2}$.

h = $6.63 \cdot 10^{-34}$ Js (Planck constant)
n = 1, 2, 3.... (quantum number)
m = $9.11 \cdot 10^{-31}$ kg (mass of an electron)

L is the length of the box between two N atoms:
L = b·l + γ
b = number of bounds in the chain between the N atoms
l = average bond length in the conjugated system
γ = empirical parameter for the extension of the π electron system beyond the bordering N atoms
l and γ are considered to be constant in the series of dyes.

a) Given x, determine the number of π electrons in the conjugated system between the N atoms, the number b of bondings and the number N of orbitals which are occupied by electrons in ground state.

b) The longest wavelength λ_{max} of the spectrum is set by the transition of electrons from the highest occupied (HOMO) to the lowest unoccupied orbital (LUMO).
Given x, determine an eqation for λ_{max} as a function of l and γ.

c) For the first two dyes of the series the longest wavelength is measured by λ_{max} = 592.2 nm and λ_{max} = 706.0 nm respectively. Calculate l and γ.

d) One of these dyes exhibits an absorption band at λ = 440.9 nm.
Show that x = 3 and that the electron transition is not carried out from HOMO to LUMO but to the next higher level.

Problem 4-7 Mass Spectrometry

(This problem refers to a low resolution spectrometer. Only peaks with z = 1 are taken into consideration, which implies m/z = m.)

Even with al low resolution mass spectrometer the same ionic fragment can generate multiple adjacent peaks of different nominal mass due to different isotopes of atoms involved. For example CH_3^+ generates fragments ranging from M = 15 ($^{12}C^1H_3^+$) up to M + 4 = 19 ($^{13}C^2H_3^+$).

Natural silicon consists of three stable isotopes ^{28}Si, ^{29}Si und ^{30}Si, whereas natural chlorine consists of ^{35}Cl and ^{37}Cl.

a) How many peaks do you expect from the fragment $SiCl_2^+$. Justify your answer.

The relative intensity of these “isotope peaks“ depends on the natural isotopic composition of the elements involved. Examples can be found in the following table.

element	% natural. abundance	element	% natural. abundance	element	% natural. abundance	element	% natural. abundance
^{12}C	98.90	^{1}H	99.985	^{35}Cl	75.77	^{16}O	99.762
^{13}C	1.10	^{2}H	0.015	^{37}Cl	24.23	^{17}O	0.038
^{10}B	19.90	^{14}N	99.634			^{18}O	0.200
^{11}B	80.10	^{15}N	0.366				

Because of the different occurance the most intense peak of the above mentioned fragment CH_3^+ can be found at M = 15 (according to $^{12}C^1H_3^+$), the intensity is much smaller at M+1 = 16 generated by $^{13}C^1H_3^+$ and $^{12}C^1H_2{}^2H^+$. The M+4 peak ($^{13}C^2H_3^+$) has practically zero intensity due to the extremely low probability of occurance.

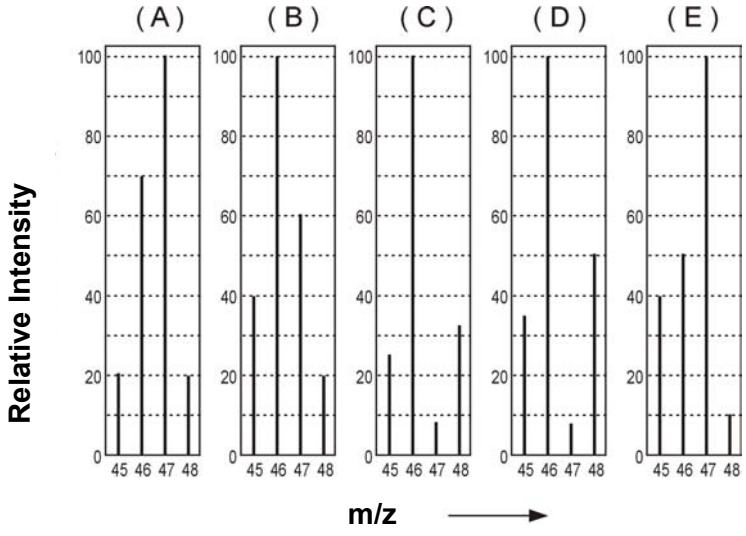
The relative intensity of a peak can be calculated from the probabilities of occurance of the elemts involved.

b) Calculate the relative intensity of M = 49 and of M+1 of the fragment CH_2Cl^+.

The most intense peak is called “base peak“ and the relative intensities of the other peaks are commonly reported as % of the base peak (base peak = 100%).

c) Report the base peak of part b) and calculate the intensities of the other fragments in % of this base peak.

d) Which of the following mass-spectrum patterns (A to E) corresponds to the fragment BCl^+? Justify your decision.

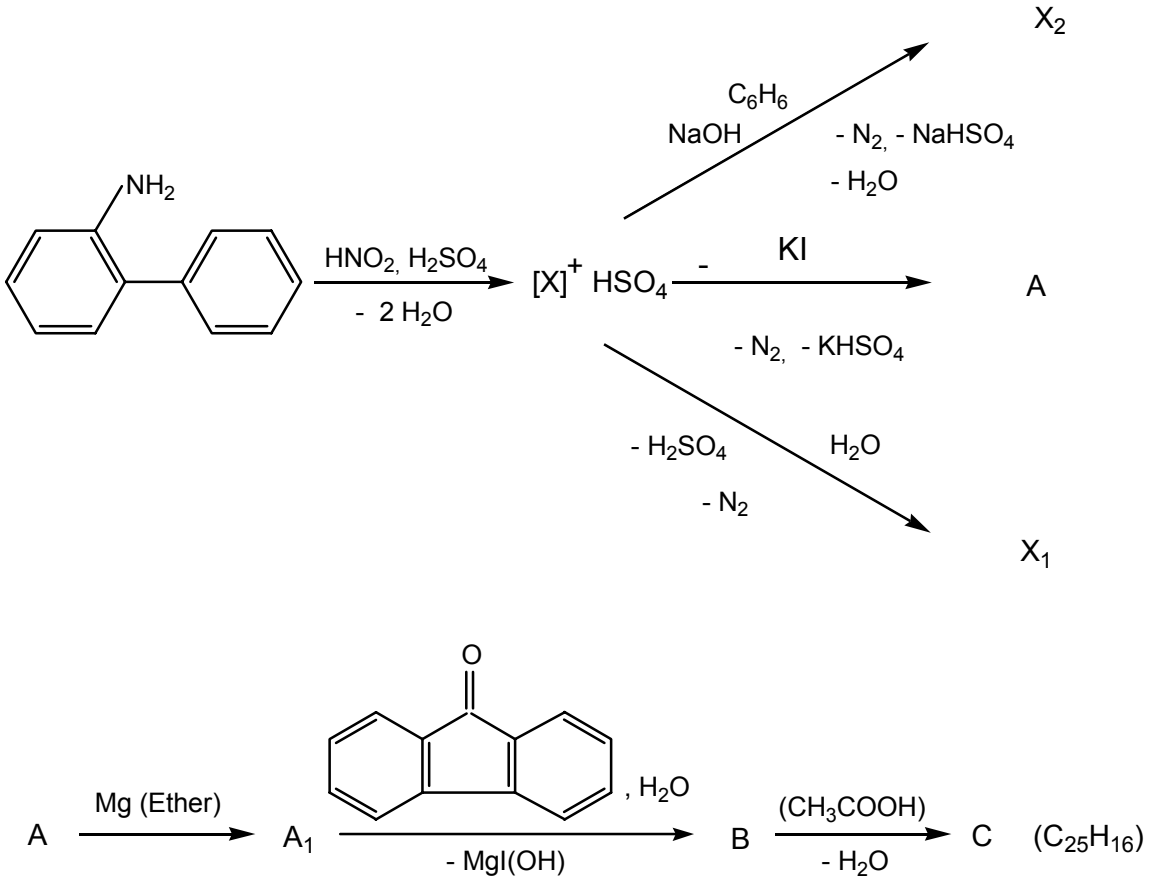


All the following fragments N_2^+, CO^+, CH_2N^+ have the same nominal mass of M = 28. With a low resolution spectrometer they cannot be resolved. However, based on the relative intensity of the M+1 peaks an identification still can be achieved.

e) Identify the ionic fragment (s) whose relative intensity of the M+1 peak is 1.15%.

Problem 4-8 Reactions given - Compounds wanted

Given the following reaction equations:

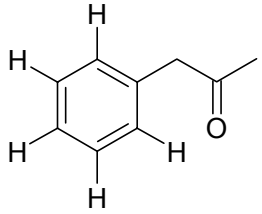


Find the missing compounds X, X_1, X_2, A, A_1, B und C and draw their structural formulars.

Keep in mind that - the reaction equations are not balanced,
- compounds in brackets are solvents.

Problem 4-9 NMR

Given NMR spectrum I (page 37) of the following compound:



a) Assign the protons to the peaks.

In a solution of potassium dichromate in diluted sulphuric acid a monomeric, primary aromatic alcohol A (spektrum II, page 38) reacts to form compound B.

b) Write the structural formulas and the names of the compounds A and B.

Compound C is an aliphatic saturated monoketone (spectrum III, page 39).

c) Write the structural formula and the name of compound C.

Compound C exists in two tautomeric forms C1 and C2.

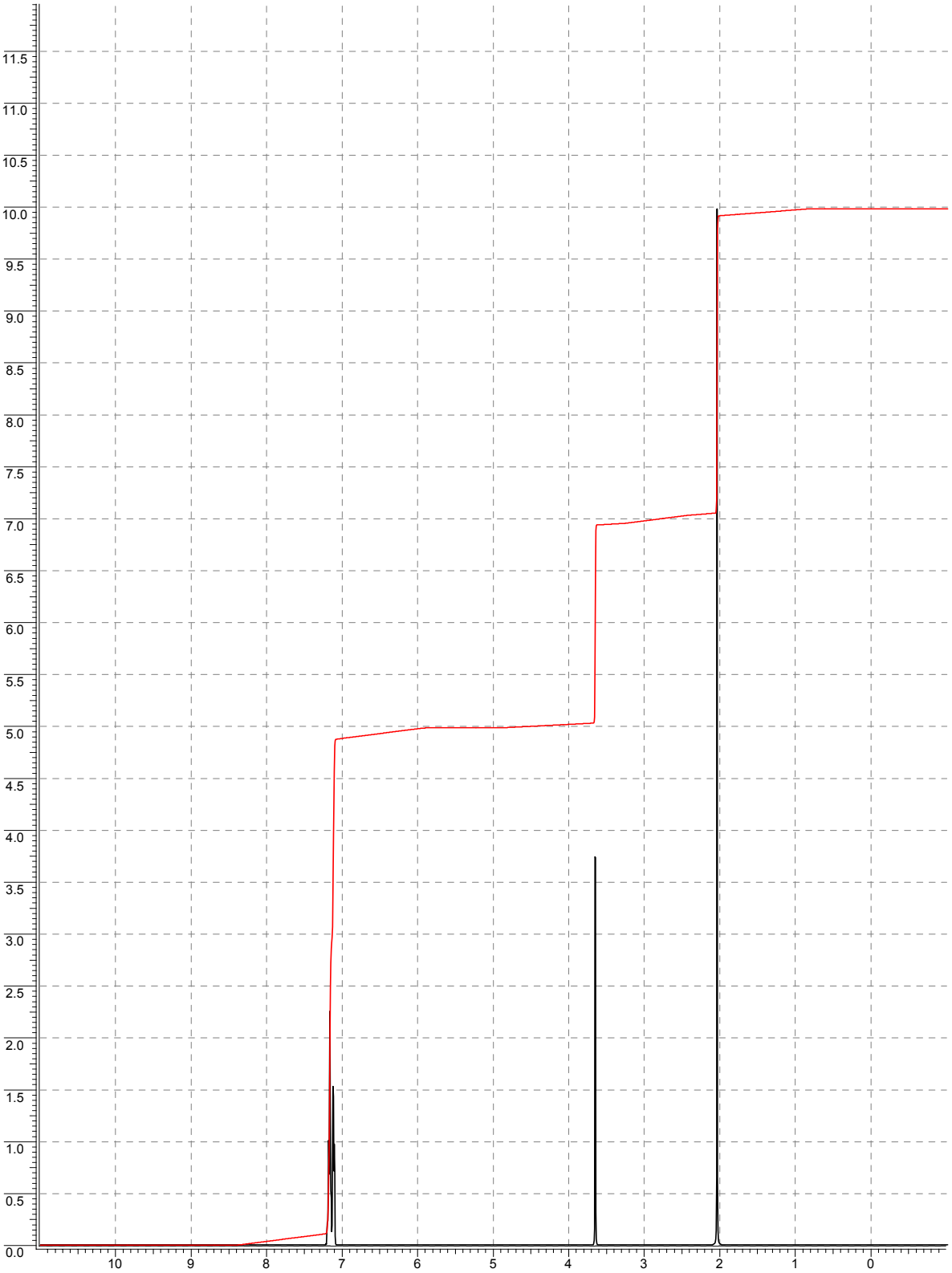
d) Draw the structural formulas of C1 and C2.

Compound C reacts with B in the presence of sodium ethoxide splitting off water. Starting from the different tautomers of C two different product, D and E, form.

e) Draw the structural formulas of D and E.

f) Assign one of the compounds D or E to spectrum IV (page 40). Justify your decision using the spectrum.

Spectrum I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11.0
10.5
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8.5
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2.0
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10
9
8
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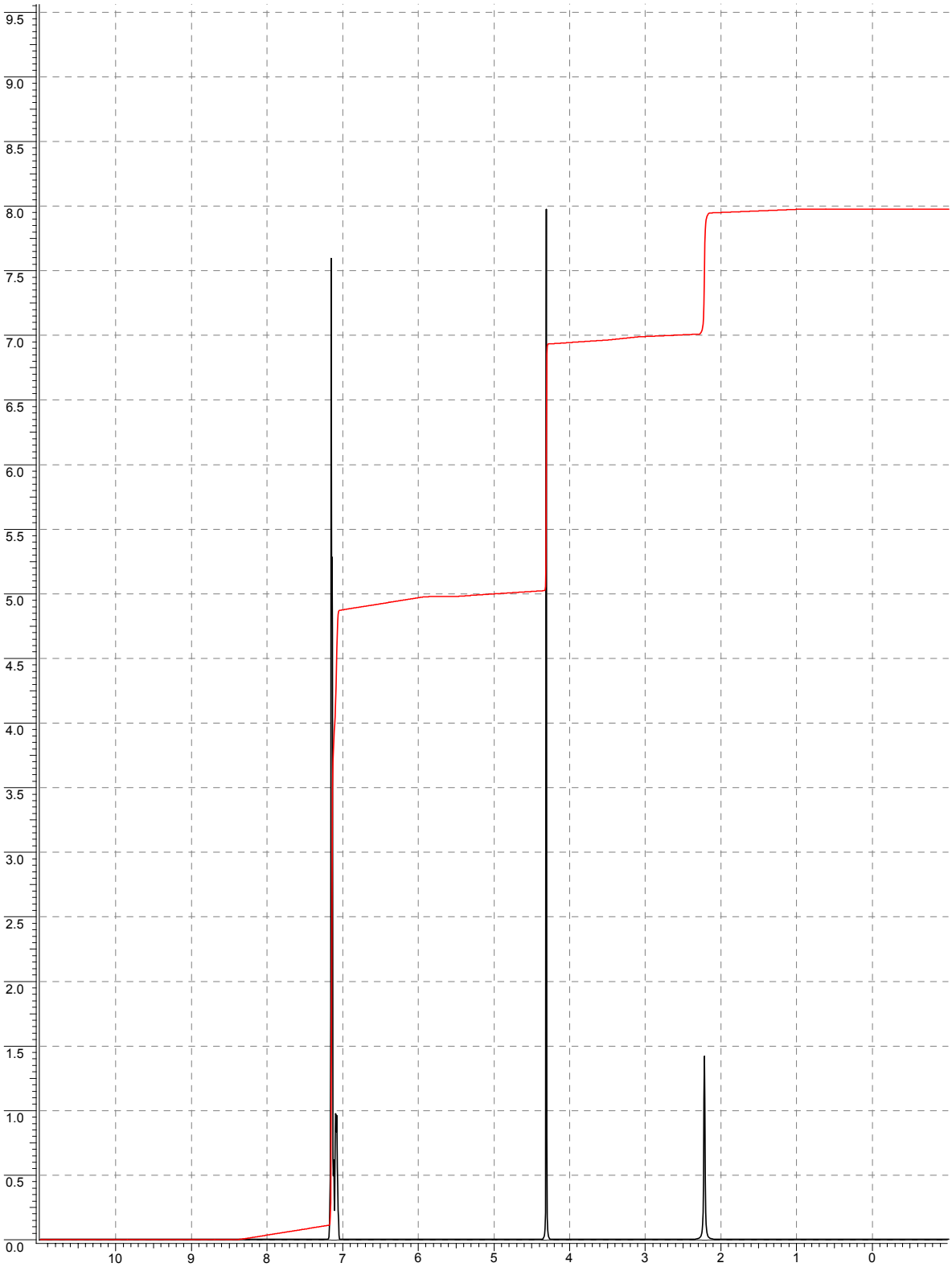
0

Spectrum II


9.5
9.0
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10
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2
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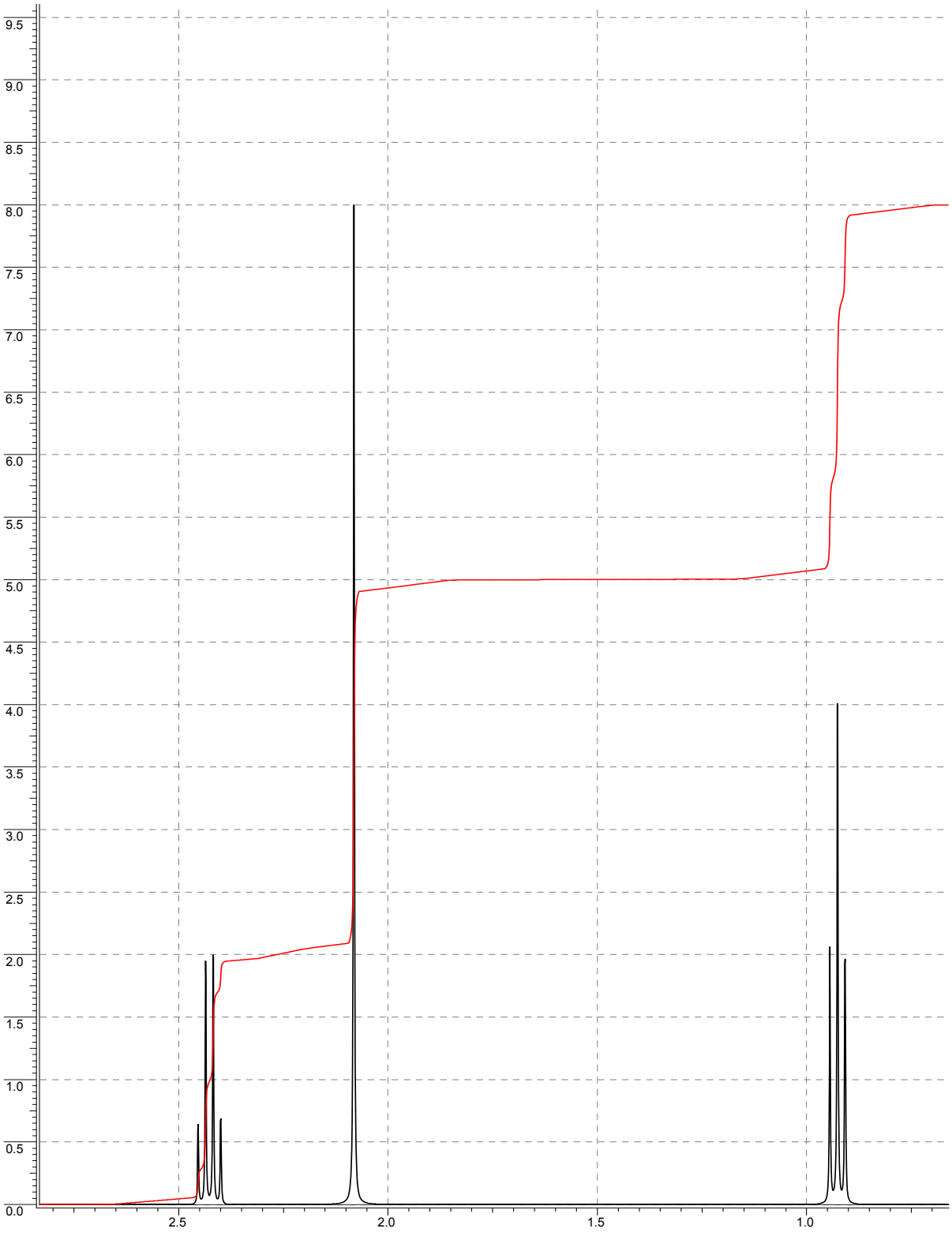
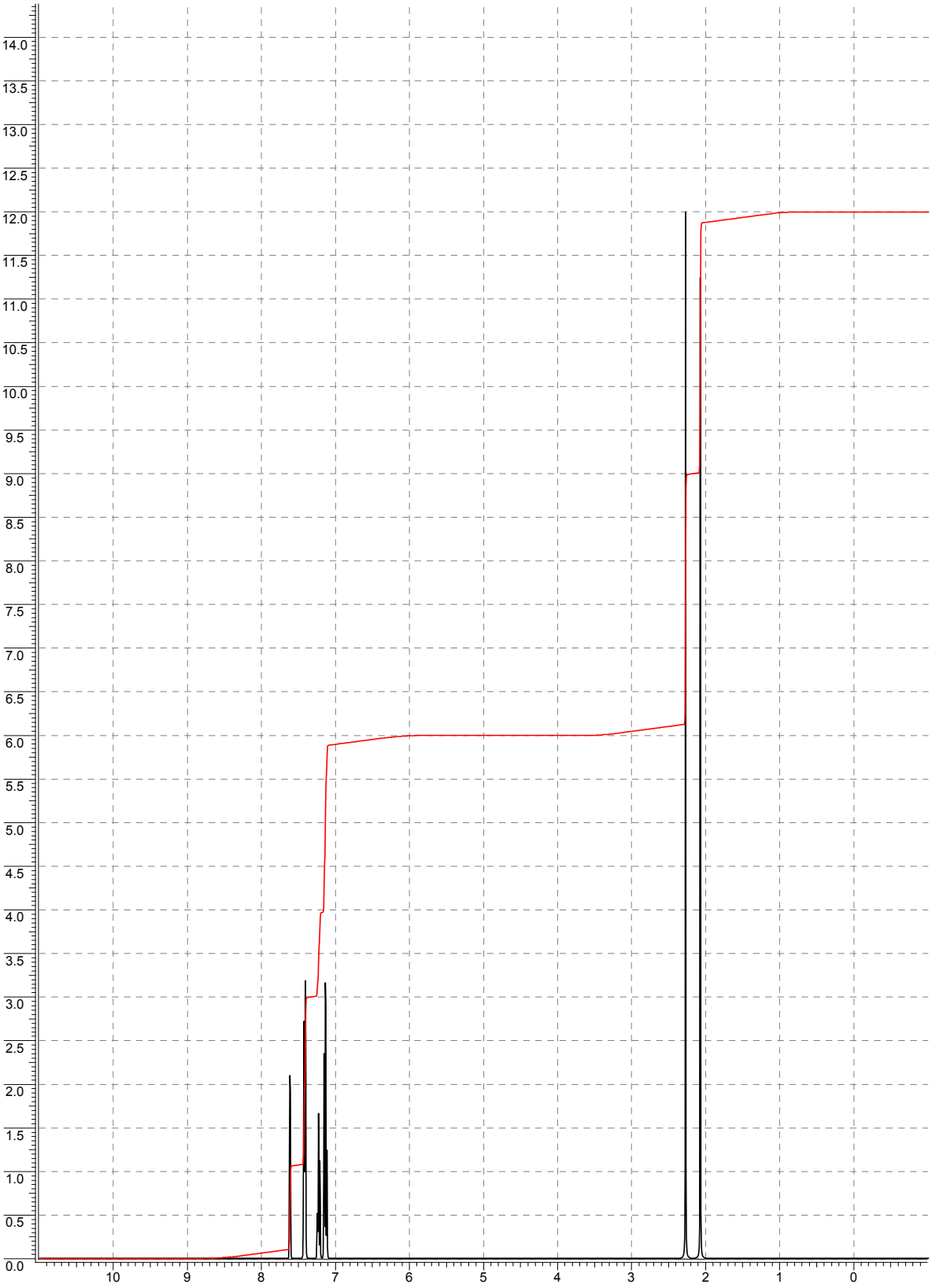
0

Spectrum III



Spectrum IV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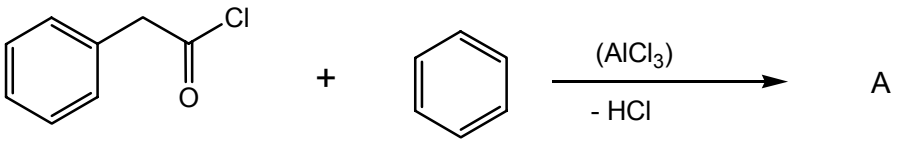
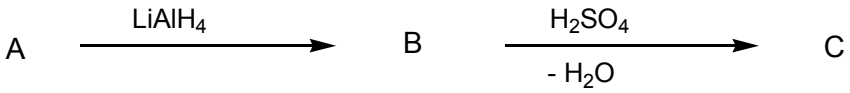
Problem 4-10

Given the following reactions:





Principally there are two possibilities to eliminate water from B to give two different products. Only one of these products, C, will form.

a) Draw the structural formulas of the compounds A to C. Give the reason of the only formation of C.

b) Map out a possible reaction mechanism of the formation of A.

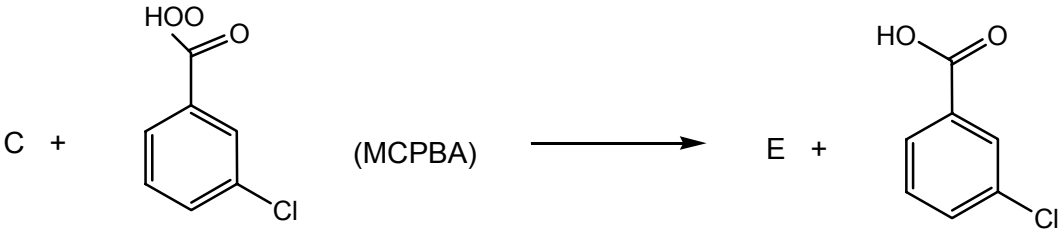
Two reactions of C are described below.

1. Reaction of C:
Compound C reacts with a solution of potassium permanganate to form D1 and D2.

c) Draw a 3-D structure of D1 and D2.

d) Which kind of isomerism is present?

2. Reaction of C:
Compound C reacts with MCPBA:



e) Draw the 3-D stucture of compound E.

Acidic hydrolysis of E leads to compound E1.

f) Show the mechanism to form E1 by drawing 3-D structures.

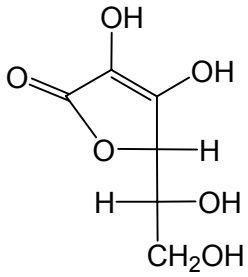
g) Write the special name of this kind of compounds and verify, whether E1 is optically active or not.

Fourth Round (Practical Problems)

Practical problem 4-11 Ascorbic Acid in a Vitamin C Tablet

Find out the amount of vitamin C in mg/tablet in a tablet in different ways.
Compare the results and account for the variations.

The main ingredient of a vitamin C tablet is ascorbic acid:



- Ascorbic acid is a weak monoprotic acid

  $C_6H_8O_6 + OH^- \rightleftarrows C_6H_7O_6^- + H_2O$
- Ascorbic acid can be oxidised with e.g. iodine to form dehydroascorbic acid:

  $C_6H_8O_6 + I_2 \longrightarrow C_6H_6O_6 + 2\ I^- + 2\ H^+$

Procederes:

1. Preparation of a solution of vitamin C:
   Weigh a tablet and solve it in a small beaker with about 20 mL of water. Filtrate the solution into a 100 mL volumetric flask and fill up with water.

2. Standardizing the solutions:
   a) Determine the concentration of the given sodium-hydroxide solution by titration with standardized sulphuric acid (concentration see supply bottle).
   b) Determine the concentration of the given iodine solution by titration with standardized sodium-thiosulphate solution (concentration see supply bottle).
   (Hint: $S_2O_3^{2-}$ is oxidised to $S_4O_6^{2-}$).

3. Determination of the amount of vitamin C:
   a) Titrate 20 ml of the solution prepared in #1. with the given sodium-hydroxide solution. Use phenolphthalein as indicator.
   b) Titrate 10 ml of the solution prepared in #1. with the given iodine solution. Use 2 mL starch solution as indicator.
   (The blue colour has to be constant for at least 20 s).

Practical problem 4-12 Synthesis of an Organic Compound

An organic acid reacts with an acid anhydride to form an ester in the presence of concentrated sulphuric acid.

Procedures:

a) Preparation:
The given 100 mL Erlenmeyer flask conrtains 3.5 g of acetic anhydride. Add 3.5 g of salicylic acid. Use a dropping pipette to add 5 drops of concentrated sulphuric acid, be cautious! Heat the mixture for 10 minutes in boiling water, stir while heating.
A clear solution is obtained. Add 15 ml of ice water to the reaction mixture. The product precipitates while cooling the flask in an ice bath.
Collect the crystals by suction filtration, wash twice with ice water.

b) Recrystallization:
Transfer the crystals to an Erlenmeyer flask and add 8 mL of ethanol. Heat the flask in a water bath until the solid is dissolved.
Add 20 mL of hot water to the flask and heat for 5 more minutes.
Cool the flask again in an ice bath. Collect the crystals formed by filtration and wash them three times with ice water.
Allow the product to dry for about 1 hour in a drying oven (110 °C).

c) Analysis of the product:
1) Calculate the theoretical yield and determinate the practical yield.
2) Determine the melting point of the product.
3) Carry out a thin-layer chromatography of the product and of the starting solution.
Use the given plates with silica gel and the provided mixture as solvent.
After drying the plates in the drying oven spray them with a solution of iron(III) chloride.
4) Comment on your results with regard to yield and purit

Part 2

The answers to the problems of the four rounds

Answers Round 1

Solution to problem 1-1

a) Conversion into amount of substance:

$p \cdot V = n \cdot R \cdot T$ $\quad n = \frac{1.000 \cdot 10^5\,Pa \cdot 33.9 \cdot 10^{-3}\,m^3}{8.314\,J mol^{-1} K^{-1} \cdot 298.15\,K}$ $\quad n = 1.368$ mol

1.368 mol of SO_2 dissolve per 1 L of water.

Because of the big difference only the first protolysis constant has to be considered for the calculation of the pH-value.

$SO_{2(aq)} + 2H_2O_{(l)} \rightleftarrows HSO_3^-{}_{(aq)} + H_3O^+_{(aq)}$ $\quad c(HSO_3^-) = c(H_3O^+) = x$ molL^{-1}

$K_{a1} = \frac{c(HSO_3^-) \cdot c(H^+)}{c(SO_2) \cdot}$ $\quad 10^{-1.92} = \frac{x^2}{1{,}368 - x}$ $\quad x = 0.122$

$c(H_3O^+) = 0.122$ molL^{-1} $\quad$ **pH = 0.91**

b) $SO_3^{2-}{}_{(aq)} + H_2O_{(l)} \rightleftarrows OH^-_{(aq)} + HSO_3^-{}_{(aq)}$ $\quad c(OH^-) = c(HSO_3^-) = y$ molL^{-1}

$K_b = 10^{-14}$ mol^{2}L^{-2}/K_{a2} $\quad K_b = 10^{-6.82}$ molL^{-1}

$10^{-6.82} = \frac{y^2}{0{,}01 - y}$ $\quad y = 3.88 \cdot 10^{-5}$ $\quad c(OH^-) = 3.88 \cdot 10^{-5}$ molL^{-1}

$c(H_3O^+) = 10^{-14}$ mol^{2}L^{-2}/$c(OH^-)$ $\quad$ **$c(H_3O^+) = 2.58 \cdot 10^{-10}$ molL^{-1}**

c) $K = \frac{c(SO_2) \cdot c(SO_3^{2-})}{c(HSO_3^-)^2}$ $\quad K = \frac{c(SO_2)}{c(HSO_3^-) \cdot c(H_3O^+)} \cdot \frac{c(SO_3^{2-}) \cdot c(H_3O^+)}{c(HSO_3^-)} = K_{a2}/K_{a1}$

$K = 10^{-5.26}$ $\quad$ **$K = 5.50 \cdot 10^{-6}$**

d) $c(SO_2) + c(HSO_3^-) + c(SO_3^{2-}) = 0.01$ molL^{-1} $\quad$ and $\quad c(SO_2) = c(SO_3^{2-})$

$5.50 \cdot 10^{-6} = \frac{c(SO_2)^2}{[0.01\,molL^{-1} - 2 \cdot c(SO_2)]^2}$ $\quad$ **$c(SO_2) = 2.33 \cdot 10^{-5}$ molL^{-1}**

e) Reactions: $6\,H_2O + SO_2 + Br_2 \longrightarrow SO_4^{2-} + 2\,Br^- + 4\,H_3O^+$

$HSO_4^- + H_2O \rightleftarrows SO_4^{2-} + H_3O^+$ $\quad (K_a = 10^{-1.99}$ molL$^{-1})$

$c(HSO_4^-) + c(SO_4^{2-}) = 0.01$ molL^{-1} $\quad c(H_3O^+) + c(HSO_4^-) = 0.04$ molL^{-1}

$c(HSO_4^-) = 0.04$ molL^{-1} - $c(H_3O^+)$ $\quad c(SO_4^{2-}) = c(H_3O^+) - 0.03$ molL^{-1}

$K_a = \frac{c(SO_4^{2-}) \cdot c(H_3O^+)}{c(HSO_4^-)}$ $\quad 10^{-1.99}$ molL^{-1} $\quad = \frac{[c(H_3O^+) - 0.03\ molL^{-1}] \cdot c(H_3O^+)}{0.04\ molL^{-1} - c(H_3O^+)}$

$c(H_3O^+) = 0.0324$ molL^{-1} $\quad$ **pH = 1.49**

f) $c(H_3O^+) = 10^{-3.2}\ molL^{-1}$ $\qquad 10^{-1.99} = \frac{c(SO_4^{2-}) \cdot 10^{-3,2}}{c(HSO_4^-)}$

$c(HSO_4^-) = c(SO_4^{2-}) \cdot 10^{-1.21}$

$c(H_3O^+) = c(HSO_4^-) + 2 \cdot c(SO_4^{2-})$

$10^{-3.2}\ molL^{-1} = c(SO_4^{2-}) \cdot 10^{-1.21} + 2 \cdot c(SO_4^{2-})$

$c(SO_4^{2-}) = 3.06 \cdot 10^{-4}\ molL^{-1}$ $\qquad c(HSO_4^-) = 1.89 \cdot 10^{-5}\ molL^{-1}$

$c(H_2SO_4)_{total} = c(HSO_4^-) + c(SO_4^{2-})$ $\qquad$ **$c(H_2SO_4)_{total} = 3.25 \cdot 10^{-4} molL^{-1}$**

Solution to problem 1-2

$AlCl_3$, $SiCl_4$, $TiCl_4$ fume in air because of hydrolysis with water from the surrounding air.

$AlCl_3 + H_2O \rightleftarrows HCl\uparrow + AlOHCl_2$ (in the first step)

$SiCl_4 + 4\ H_2O \rightleftarrows 4\ HCl\uparrow + H_4SiO_4$ (in the first step)

$TiCl_4 + H_2O \rightleftarrows HCl\uparrow + TiOCl_2$ (in the first step)

A fog of drops of hydrochloric acid in air can be observed.

Solution to problem 1-3

a) Dissolution in hydrochloric acid:

$2\ Al + 6\ H_3O^+ \rightleftarrows 2\ Al^{3+} + 6\ H_2O + 3\ H_2$

$Ni + 2\ H_3O^+ \rightleftarrows Ni^{2+} + 2\ H_2O + H_2$

Dissolution in nitric acid.

$3\ Cu + 2\ NO_3^- + 8\ H_3O^+ \rightleftarrows 3\ Cu^{2+} + 2\ NO + 12\ H_2O$

$3\ Ag + NO_3^- + 4\ H_3O^+ \rightleftarrows 3\ Ag^+ + NO + 6\ H_2O$

Because the concentration of nitric acid is not indicated in the problem, the reaction equations describing the formation of NO_2 are to be rated as well as correct:

$Cu + 2\ NO_3^- + 4\ H_3O^+ \rightleftarrows Cu^{2+} + 2\ NO_2 + 6\ H_2O$

$Ag + NO_3^- + 2\ H_3O^+ \rightleftarrows Ag^+ + NO_2 + 3\ H_2O$

b) Determination of the aluminium- and nickel content.

Hydrogen forms by dissolution: $n(H_2) = \frac{p \cdot V}{R \cdot T}$

$n(H_2) = \frac{99000\ \text{Pa} \cdot 119.8 \cdot 10^{-6}\ \text{m}^3}{8.314\ \text{Jmol}^{-1}\text{K}^{-1} \cdot 293.15\ \text{K}}$ $n(H_2) = 4.8662 \cdot 10^{-3}$ mol

$n(H_2) = 1.5 \cdot n(Al) + n(Ni)$ $n(Ni) = n(H_2) - 1.5 \cdot n(Al)$

$m(Al) + m(Ni) = 0.1500$ g $n(Al) \cdot M(Al) + n(Ni) \cdot M(Ni) = 0.1500$ g

$n(Al) = \frac{0.1500\text{g} - M(Ni) \cdot n(H_2)}{M(Al) - 1.5 \cdot M(Ni)}$ $n(Al) = \frac{0.1500 - 58.69 \cdot 4.8662 \cdot 10^{-3}}{26.98 - 1.5 \cdot 58.69}$ mol

$n(Al) = 2.2209 \cdot 10^{-3}$ mol

$m(Al) = 0.0599$ g **Al: 29.95 %**

$m(Ni) = 0.1500\text{g} - 0.0599\text{g} = 0.0901$ g **Ni: 45.05%**

Determination of the copper- and silver content

Necessary charge: $0.7\ \text{A} \cdot 219.3\ \text{s} \cdot 0.85 = 130.48\ \text{C}$

This corresponds to: $130.48\ \text{C} / 96485\ \text{Cmol}^{-1} = 1.3524 \cdot 10^{-3}$ mol

$2 \cdot n(Cu) + n(Ag) = 1.3524 \cdot 10^{-3}$ mol $n(Ag) = 1.3524 \cdot 10^{-3}\ \text{mol} - 2 \cdot n(Cu)$

$m(Cu) + m(Ag) = 0.0500$ g $n(Cu) \cdot M(Cu) + n(Ag) \cdot M(Ag) = 0.0500$ g

$n(Cu) = \frac{0.05\text{g} - M(Ag) \cdot 1.3524 \cdot 10^{-3}\text{mol}}{M(Cu) - 2 \cdot M(Ag)}$ $n(Cu) = 6.3000 \cdot 10^{-4}$ mol

$m(Cu) = 0.0400$ g **Cu: 20.00 %**

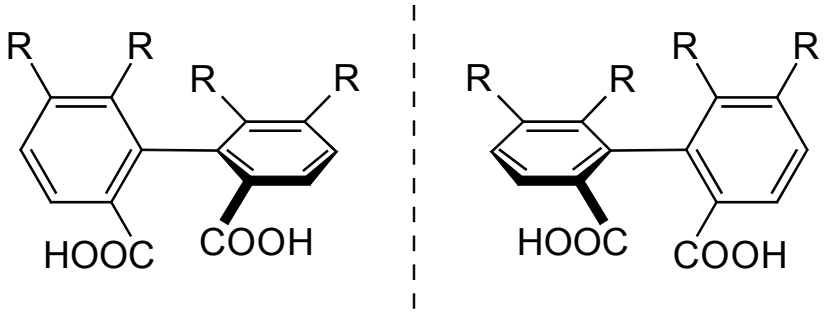
$m(Ag) = 0.0100$ g **Ag: 5.00 %**

Solution to problem 1-4

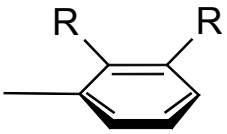
a) The free rotation of the two phenyl rings is hindered by the bulky iodine- or rather bromine- and acid residues. The two ring planes with their groups form an angle of about 90°C.

In this spatial arrangement, the energies of each compound have minimum values. The result are two structures behaving like image and mirror image (enantiomers):

mirror plane



R = I, Br respectively



ring is vertical
to the paper plane

b) The comparison of the spatial extensions of the different substituents iodine and bromine shows that the iodine atom needs much more space. Thus, compound A is more strongly hindered in its free rotation than compound B.

The energy that can be interpreted as a rotational barrier is higher in compound A than in compound B.

That means: ΔG_{rot} (A) > ΔG_{rot} (B)

The two spatial arrangements (image and mirror image) of compound B can be transformed into each other already at room temperature (about 20°C).

Thus, an isolation of the enantiomers is not possible.

Solution to problem 1-5

a) Preparation of nitrobenzene (A):

Nitrobenzene forms by the nitration of benzene. The reaction takes place according to the following scheme:

$$C_6H_6 + HNO_3 \xrightarrow{(H_2SO_4)} C_6H_5NO_2 + H_2O$$

The nitronium ion NO_2^+ is the agent. It forms from nitrating acid according to the following reaction:

$$HNO_3 + 2H_2SO_4 \rightleftarrows NO_2^+ + H_2O + 2HSO_4^-$$

At higher temperatures and if there is an excess of nitrating acid, a dinitro product (e.g. an m-dinitrobenzene) will form.

Preparation of phenol (B) (only one preparation is rated):

Example 1: Halogenation of benzene and a later reaction with alkali-hydroxide solution (X = halogen):

$$C_6H_6 + X_2 \longrightarrow C_6H_5X + HX$$

$$C_6H_5X \xrightarrow{NaOH(H_2O)} C_6H_5OH + NaX$$

high pressure, high temperature, technically a DOW-process

Example 2: Sulfonation of benzene and a later reaction alkali-hydroxide solution:

$$C_6H_6 + HOSO_3H \xrightarrow{SO_3} C_6H_5SO_3H + H_2O$$

$$C_6H_5SO_3H \xrightarrow{NaOH(H_2O)} C_6H_5OH + NaHSO_3$$

Example 3: Isopropylbenzene (cumene) is oxidized in air. Cumene hydroperoxide forms and is decomposed into phenol and acetone in an dilute acid:

$$C_6H_5(C_3H_7) \xrightarrow{O_2} C_6H_5(C_3H_7O_2)$$

$$C_6H_5(C_3H_7O_2) \xrightarrow{(H_2O(H^+))} C_6H_5OH + CH_3COCH_3$$

b) Substance B (phenol) has to be preferred absolutely to the other substance as an initial substance for the preparation of p-nitrophenol.

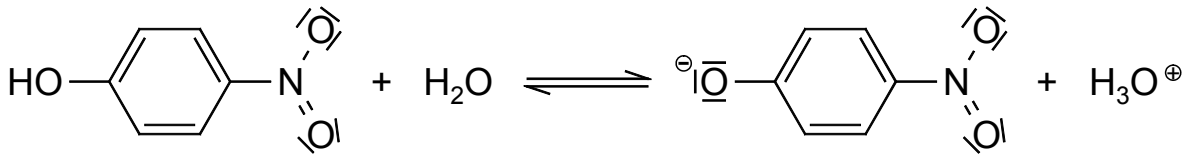
Reasons:

1) Phenol activates the second substitution altogether and

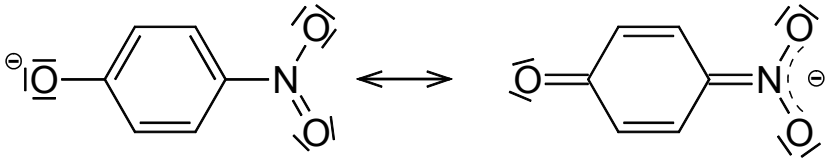
2) phenol directs the nitro group into the ortho- and para-position. These two substances still have to be separated then.

Nitrobenzene, however, would inactivate a second substitution altogether and then direct the second substituent into the meta-position.

c) P-nitrophenol is a weak acid protolysing according to the following scheme:



In basic solutions, the π-electron system is extended by the additional lone electron pair at the negatively charged oxygen atom:



This delocation of the electrons in a basic medium leads to a lowering of the first excited electron state. The absorption maximum shifts towards a higher wavelength (lower energy) and thus into the visible range. The compound is intensively coloured (yellow).

d) Substances like p-nitrophenol are used as acid-base indicators. The indicators that are frequently used in practice show a more distinct and more intensive change in colour than p-nitrophenol (e.g. phenolphthalein, methyl orange or litmus).

Answers Round 2

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

Solution to problem 2-1

a) The pH of pure ammonia can be determined by the following formula:

$c(NH_4^+) = c(NH_2^-) = \sqrt{K_{Am}} = 10^{-15}$ mol·L^{-1} ➜ pH = 15.

b) The following dissociation reactions take place in solution [(am.) means the solvation of the ions in liquid ammonia]:

NH_4NO_3	⟶	$NH_4^+{}_{(am.)} + NO_3^-{}_{(am.)}$	acid
KNH_2	⟶	$K^+{}_{(am.)} + NH_2^-{}_{(am.)}$	base
$CH_3COOH + NH_3$	⟶	$NH_4^+{}_{(am.)} + CH_3COO^-{}_{(am.)}$	acid
KI	⟶	$K^+{}_{(am.)} + I^-{}_{(am.)}$	neither acid nor base

Aniline is a weaker base than ammonia (pK_b (aniline) = 9.4, pK_b (NH_3) = 4.7), but a stronger acid (pK_a (aniline) = 27, pK_a (NH_3) = 34), so that aniline shows a weak acid reaction in liquid ammonia:

$C_6H_5NH_2 + NH_3 \longrightarrow C_6H_5NH^-{}_{(am.)} + NH_4^+{}_{(am.)}$

c) It is a neutralization reaction.

$NH_4Cl + KNH_2 \longrightarrow KCl + 2\ NH_3$ or

$NH_4^+{}_{(am.)} + NH_2^-{}_{(am.)} \longrightarrow 2\ NH_3$.

d) The half-cell reaction at the hydrogen-platinum:

$H_2 + 2\ NH_3 \rightleftarrows 2\ NH_4^+ + 2\ e^-$.

Its potential:

$$E(NH_4^+/H_2) = E^0(NH_4^+/H_2) + \frac{RT}{2F}\ln\frac{c^2(NH_4^+)/c_0^2}{p(H_2)/p_0}$$ with $E^0(NH_4^+/H_2) = 0$ V.

In contrast to the Ag/AgCl-electrode, the hydrogen electrode is an anode (otherwise the value of $c(NH_4^+)$ would be absurd).

ΔE = E(cathode) - E(aode) 0.820 V = 0.681 V - $E(NH_4^+/H_2)$

➜ $E(NH_4^+/H_2)$ = - 0.139 V

$$\ln(c(NH_4^+)/c_0)) = \frac{-0{,}139 \cdot 96485}{8{,}314 \cdot 233{,}15}$$ $c(NH_4^+) = 9.9 \cdot 10^{-4}$ mol·L^{-1}.

Acetic acid is practically completely protolysed in liquid ammonia (degree of protolysis: α = 0.99). thus it behaves as a strong acid.

In analogy to that. we obtain the following values for ΔE = 0.837 V:

$E(NH_4^+/H_2)$ = - 0.156 V $c(NH_4^+) = 4.22 \cdot 10^{-4}$ mol L^{-1}.

42.2% of hydrogen cyanide are protolysed. It behaves like a moderately weak acid.

In aqueous solution. acetic acid is a moderately weak acid (pK_a = 4.75) and hydrogen cyanide is a very weak acid (pK_a = 9.25); the higher basicity of the solvent ammonia increases the acidity of the dissolved substances.

e) $c(NH_4CN) = \frac{0{,}60}{44{,}06}$ mol·L^{-1} = $1.36 \cdot 10^{-2}$ mol·L^{-1}.

Ammonium cyanide is an ionic compound and thus completely dissociated in solution.

	$NH_3 + HCN \rightleftarrows NH_4^+ + CN^-$	
c before equilibrium in mol·L^{-1}	0.01	0.6/44.06 mol·L^{-1} each
c in equilibrium in mol·L^{-1} each	0.01 - x	0.6/44.06 mol·L^{-1} + x

In equilibrium. the following equation can be applied:

$$K_a = \frac{c(NH_4^+)c(CN^-)}{c(HCN)} = 10^{-3.5} \text{ mol·L}^{-1} = 3.16 \cdot 10^{-4} \text{ mol·L}^{-1}$$

$$10^{-3.5} \text{ mol·L}^{-1} = \frac{(0.6/44.06 \text{ mol·L}^{-1} + x)^2}{0.01 \text{ mol·L}^{-1} - x}$$

The quadratic equation leads to the solutions

x_1 = -0.0110 mol·L^{-1} and x_2 = -0.0165 mol·L^{-1}, but x_2 does not make any sense [$c(NH_4^+) < 0$]:

$c(NH_4^+)$= 0.6/44.06 - 0.0110 mol·L^{-1} , $c(NH_4^+) = 2.62 \cdot 10^{-3}$ mol·L^{-1}, pH = 2.58

(Ammonium cyanide is nothing else than only HCN in ammonia. Assigning the value of $2.36 \cdot 10^{-2}$ mol·L^{-1} to c_0(HCN) and calculating the pH of this acid then would be a simple approach as well).

f) The energy adequate to the wavelength λ = 1500 nm is the following:

$$\Delta E = h \cdot \nu = \frac{hc}{\lambda} = 1.33 \cdot 10^{-19} \text{ J}.$$

The following is true for the energy levels of the particle in the three-dimensional box:

$$E_{n_x,n_y,n_z} = \frac{h^2}{8m \cdot L^2}\left(n_x^2 + n_y^2 + n_z^2\right)$$

with m = $9.11 \cdot 10^{-31}$ kg (mass of an electron)

h = $6.63 \cdot 10^{-34}$ Js (Planck`s constant)

L = edge length of the box that is assumed to be cubic.

The quantum numbers n_x, n_y and n_z specify the state of the electron.

If we assume the transition from the lowest state

$n_x = n_y = n_z = 1$ into e.g. the state $n_x = 2$, $n_y = n_z = 1$ for the absorption at 1500 nm, we will obtain the following value:

$$\Delta E = \frac{(6-3)\cdot h^2}{8m\cdot L^2} \quad \rightarrow \quad L = 1.17\cdot 10^{-9}\ m = 1.17\ nm$$

(in contrast to d(N-H) = 0.10 nm in the NH_3-molecule)

Solution problem 2-2

a) Reaction equation of the hydrolysis:

$$O_2NC_6H_4OCOCH_3 + H_2O \longrightarrow O_2NC_6H_4OH + CH_3COOH.$$

b) If a complete reaction is taken as a basis, the absorbing substance will be only the product para-nitrophenol (NP) for t = ∞. The extinction for t = ∞ is
$E_\infty = \varepsilon(NP)\cdot c_0\cdot l$; $\varepsilon(NP)$ is the extinction coefficient of para-nitrophenol.

$$\varepsilon(NP) = \frac{1.456}{10^{-4}\ mol\,L^{-1}\cdot 1cm} = 14560\ mol^{-1}\,L\cdot cm^{-1}.$$

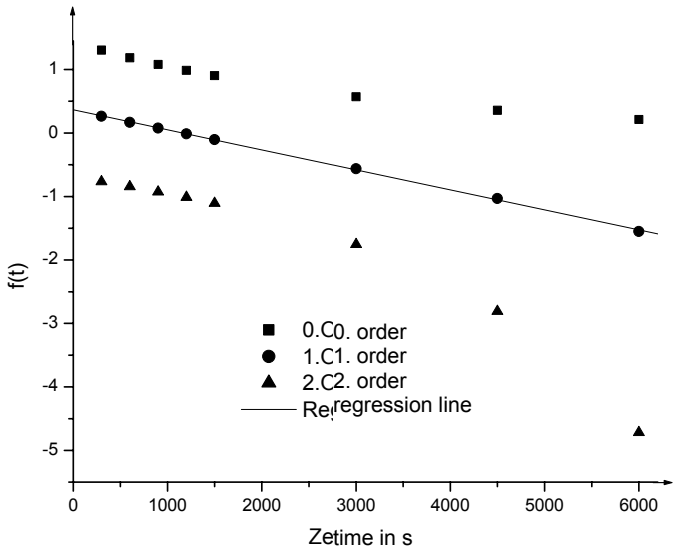
c) At the wavelength of 398 nm, the starting material para-nitrophenylacetate (NPA) as well as the product para-nitrophenol (NP) absorb, so that the following formula can be established:

$$E = [\varepsilon(NPA)\cdot c(NPA) + \varepsilon(NP)\cdot c(NP)]\cdot l = [\varepsilon(NPA)\cdot c(NPA) + \varepsilon(NP)\cdot (c_0 - c(NPA))]\cdot l =$$
$$= \varepsilon(NP)\cdot c_0\cdot l + [\varepsilon(NPA) - \varepsilon(NP)]\cdot c(NPA)\cdot l = E_\infty + [\varepsilon(NPA) - \varepsilon(NP)]\cdot c(NPA)\cdot l.$$

$$E - E_\infty = [\varepsilon(NPA) - \varepsilon(NP)]\cdot c(NPA)\cdot l$$

The expression $E - E_\infty$ is directly proportional to c(NPA) and can be used for the determination of the reaction order. The extinction increases in the course of the reaction, so that $\varepsilon(NPA) < \varepsilon(NP)$.
$-(E(t) - E_\infty)$ is plotted against t (for zero order), $\ln(-(E(t) - E_\infty)$ is plotted against t (for first order) and $1/(E(t) - E_\infty)$ is plotted against t (for second order) for the determination of the reaction order.

time in s	300	600	900	1200	1500	3000	4500	6000
E(t)	0.152	0.272	0.377	0.469	0.553	0.886	1.100	1.244
$-(E(t) - E_\infty)$	1.304	1.184	1.079	0.987	0.903	0.570	0.356	0.212
$\ln(-(E(t) - E_\infty))$	0.265	0.169	0.076	-0.013	-0.102	-0.562	-1.033	-1.551
$1/(E(t) - E_\infty)$	-0.767	-0.845	-0.927	-1.013	-1.107	-1.754	-2.809	-4.717



Only the plotting for the first order results in a line. The rate constant k is the negative slope of the line, $k = 3.154 \cdot 10^{-4}\ s^{-1}$.

Apart from para-nitrophenylacetate, water as well takes place in the hydrolysis. Because there is an excess of water as a solvent, its concentration does approximately not change, so that the reaction takes place according to a pseudo-first order.

d) The table below shows the analysis of the kinetic data at 30°C:

time in s	300	600	900	1200	1500	3000	4500	6000
E(t)	0.307	0.440	0.558	0.664	0.757	1.092	1.278	1.384
$-(E(t) - E_\infty)$	1.205	1.072	0.954	0.848	0.755	0.420	0.234	0.128
$\ln(-(E(t) - E_\infty))$	0.186	0.070	-0.047	-0.165	-0.281	-0.868	-1.452	-2.056

They lead to the determination of the rate constant: $k = 3.925 \cdot 10^{-4}\ s^{-1}$.

The temperature dependency of the rate constant can be determined by the Arrhenius` equation:

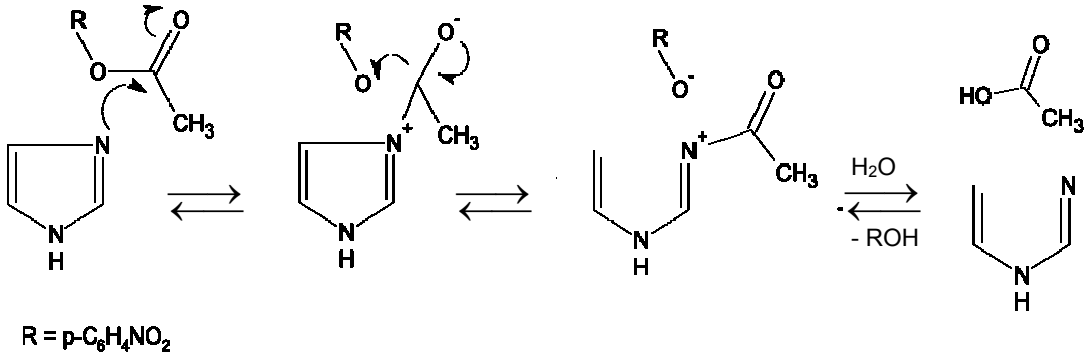
$$k = A\, e^{-\frac{E_A}{RT}}.$$

$$E_A = \frac{R \ln \frac{k_2}{k_1}}{\frac{1}{T_1} - \frac{1}{T_2}} = 32.87\ \text{kJ·mol}^{-1}$$

e) The rate constant of the hydrolysis in the presence of imidazole (series of measurement 3) is $8.359 \cdot 10^{-4}$ s^{-1}.

Imidazole has a catalytic effect on this reaction.

Proposal for a mechanism showing the catalytic effect of imidazole:



R = p-$C_6H_4NO_2$

(if necessary, protolytic equilibrium of the acid in the following)

Solution problem 2-3

a) $\mathbf{MH_x} + x\ H_2O \longrightarrow \mathbf{M}(OH)_x + x\ H_2$

$$n(H_2) = \frac{p \cdot V}{R \cdot T} = \frac{99.50 \cdot 10^3 Nm^{-2} \cdot 3.134 \cdot 10^{-3} m^3}{8.314 NmK^{-1}mol^{-1} \cdot 298.15 K}$$

$n(H_2) = 0.1258$ mol ➜ n(1g $\mathbf{MH_x}$) = 0.1258 mol/x

x	M($\mathbf{MH_x}$) = 1g·x/0.1258 mol	M(**M**)	**M**
1	7.95 g·mol^{-1}	6.94 g·mol^{-1}	lithium
2	15.90 g·mol^{-1}	13.88 g·mol^{-1}	-
3	23.85 g·mol^{-1}	20.82 g·mol^{-1}	-
4	31.80 g·mol^{-1}	27.76 g·mol^{-1}	-

M = lithium

b) $2\ Li + H_2 \longrightarrow 2\ LiH$

$LiH + H_2O \longrightarrow H_2 + 2\ LiOH$

c) Z = 4

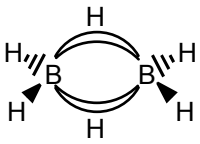
d) x is the number of elementary cells towards each axial direction of the crystal.
The undecomposed crystal contains about $4 \cdot x^3$ hydride ions. $6[(x-1)^2 + x^2]$ of them are located on the planes (without edges), $12(x-1)$ are located on the edges (without angles) as well as 8 that are located on the angles.
There are $4 \cdot x^3 - [6(x-1)^2 + 6x^2 + 12(x-1) + 8]$ hydride ions in the interior of the crystal.

$6(x-1)^2 + 6x^2 + 12(x-1) + 8 = 12x^2 + 2 \approx 12x^2$

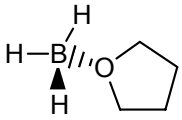
$$\frac{4x^3 - 12x^2}{12x^2} = \frac{150}{1} \quad \rightarrow \quad x = 453$$

The edge length of the crystal is $453 \cdot \mathbf{a}$.

e) **A**:



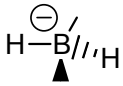
C:



(2)

Borane (BH_3) is a dimer (diborane), because BH_3 is an electron-deficient compound in which the B-atom has only 6 electrons in its valence shell. Both B-atoms fulfill the octet rule by the formation of diborane by B-H-B 2-electron-3-centre bonds. Because each B-atom is surrounded by 4 H-atoms, the result is an almost ideal-tetrahedral coordination environment around the B-atoms (sp^3-hybridized).

f) **B**: CH_3-COONa, sodium acetate (one indication is enough)
D: $LiBH_4$, lithium borohydride, lithium tetrahydridoborate, (one indication is enough)



The borohydride-anion has a tetrahedral structure

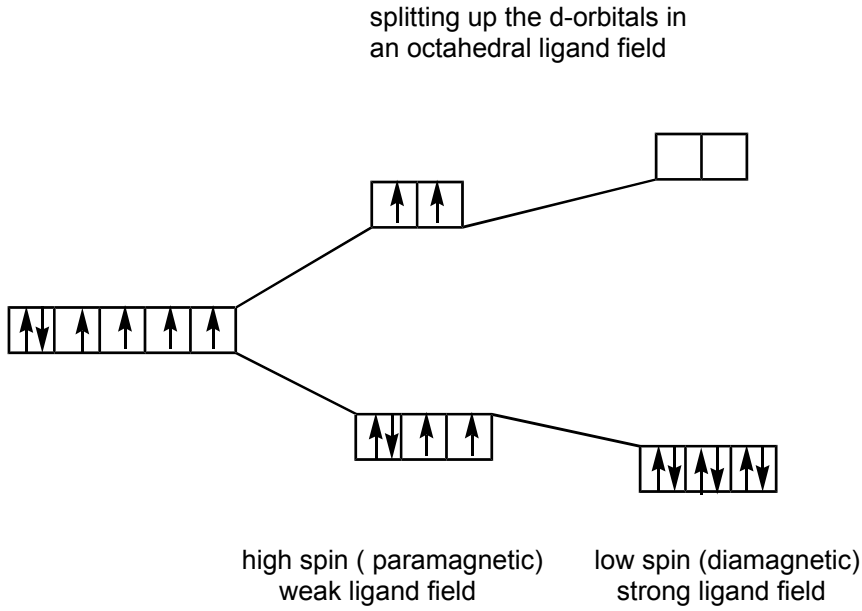
g) $4\ \mathbf{I} + 8\ NaOH + NaBH_4 \longrightarrow 4\ \mathbf{II} + 4\ NaBr + 4\ H_2O + Na[B(OH)_4]$

(The equation can vary according to the B-containing reaction product (H_3BO_3, $Na[B(OH)_4]$, $Na_2B_4O_7$...).)

$\mathbf{II} + C_2H_5I \longrightarrow \mathbf{III} + NaI$

h) OZ(Co in **II**) = +1; OZ(Co in **III**) = +3

i) OZ(Co in **I**) = +3; OZ (Co in **III**) = +3; the two complexes are d^6-systems in the octahedral ligand field.



There is low-spin configuration in almost all octahedral Co(III) complexes.

Solution problem 2-4

a) Structural formulas of the compounds **A** to **F** and of the compounds and reagents **X**, **Y** and **Z** as well as the reaction schemes:

$$HOCH_2CH_2CH_2Br + (CH_3)_3SiCl \xrightarrow{\text{spec. base}} (CH_3)_3SiOCH_2CH_2CH_2Br + \text{base hydrochloride}$$

(reagent **X**) (compound **A**)

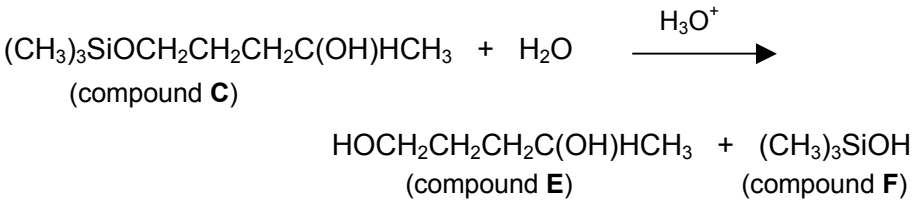
$$(CH_3)_3SiOCH_2CH_2CH_2Br + Mg \xrightarrow{\text{ether}} (CH_3)_3SiOCH_2CH_2CH_2MgBr$$

(compound **A**) (reagent **Y**) (compound **B**)

$$(CH_3)_3SiOCH_2CH_2CH_2MgBr \xrightarrow[2.)\ +H_2O]{1.)\ +CH_3CHO\ (\mathbf{Z})} (CH_3)_3SiOCH_2CH_2CH_2C(OH)HCH_3 + MgBr(OH)$$

(compound **B**) (compound **C**) (compound **D**)

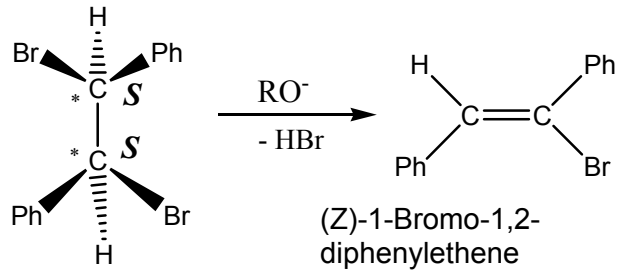
After the Grignard-reaction with e.g. an aldehyde (CH_3CHO) the Si-compound is separated again in an acid medium:



b) Compound **X** (trimethylsilylchloride: TMS) is a protective group of the HO-group, so that the Grignard-reaction of a compound of the type HORBr can be carried out. Otherwise it would only come to a protonation of the Grignard-reagent by the acid HO-group and thus to its destruction. Finally, it would lead to a reduction of the bromoalkane to an alkane.

Solution problem 2-5

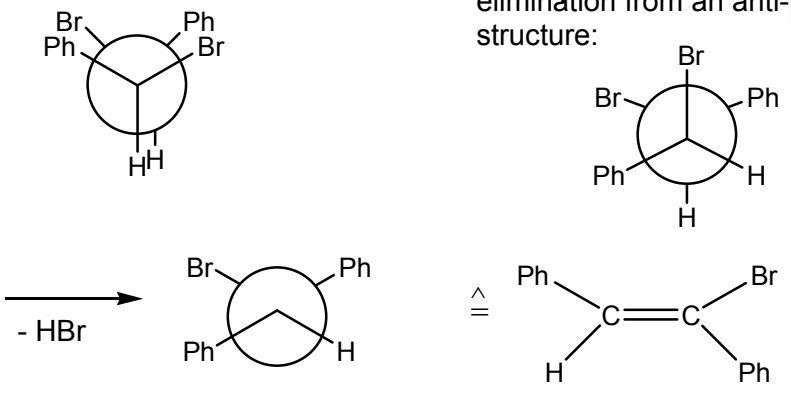
a)



(Z)-1-Bromo-1,2-diphenylethene

b)

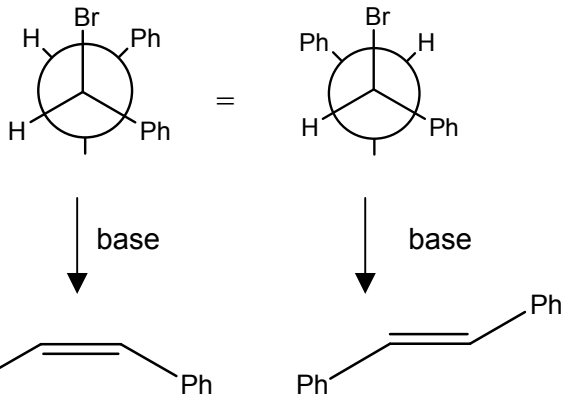
elimination from an anti-periplanar structure:



(Z-configuration)

c) The compounds (1S,2S)-1,2-dibromo-1,2-diphenylethane and (1R,2R)-1,2-dibromo-1,2-diphenylethane are enantiomers (mirror-image isomers).
Thus, they have the same "inner" configuration, so that the same (achiral) olefin must form by the separation of HBr from the anti-periplanar structure.
Or explanation by drawing a scheme like in b).

d)

(1S)-1-Bromo-1,2-diphenylethane ≡ 

The E-configuration forms preferentially. The elimination of HBr from the anti-periplanar educt conformation is energetically favoured. In this conformation the phenyl rings are in trans-position.

Answers Round 3 Test 1

Solution to problem 3-1

a) A) b) A) $pK_S = 4.1$ B) $pK_S = 2.8$ C) $pK_S = 4.8$ D) $pK_S = 1.3$

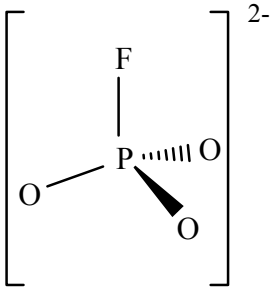
c) A) d) D) , E) e) D) f) B) g) D)

Solution to problem 3-2

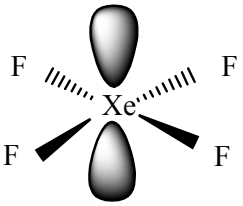
a) **m(NaF) =** $\frac{0.050 \cdot 10^{-2}\,\text{g}}{19.00\ \text{g/mol}} \cdot 42.00\ \text{g/mol} = 1.11\ \text{mg}$ **0.111 %**

m(Na_2PO_3F) = $\frac{0.050 \cdot 10^{-2}}{19{,}00} \cdot 143.97\ \text{g} = 3.79\ \text{mg}$ **0.379 %**

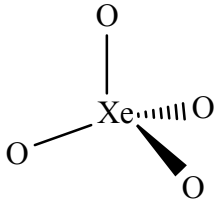
b)



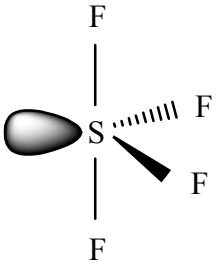
c)



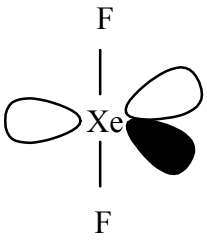
XeF_4, planar



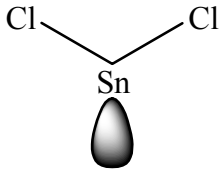
XeO_4, tetrahedral



SF_4



XeF_2, linear



$SnCl_2$, V-shape

Solution to problem 3-3

a) $CaCO_3 \longrightarrow CaO + CO_2$

b) **m(MgC_2O_4)** = 2.01 g **40.1 %** **m(CaC_2O_4)** = 3.00 g **59.9 %**

c) First decrease in mass: loss of water

CaC_2O_4 (s) $\longrightarrow$ $CaCO_3$ (s) + CO (g) $\Delta m_1 = 1.40$ g

$CaCO_3$ (s) $\longrightarrow$ CaO (s) + CO_2 (g) $\Delta m_2 = 2.20$ g

	C	CaO	$CaCO_3$	CaC_2O_4	CO_2
molare mass M in g/mol	X	56.08	40.08 + X + 48.00	40.08 + 2·X + 64.00	X + 32.00

$n(CaO) = m_{900°}/M(CaO) = 2.80/56.08$ mol (= 0.0499 mol)

$\Delta m_2 = M(CO_2) \cdot n(CaO)$ $2.20 = (X + 32)\cdot 2.80/56.08$

X = 12.06 (12.09)

$m_{500°} = m(CaCO_3) = M(CaCO_3) \cdot n(CaO)$ **X = 12.06** (12.12)

$m_{250°} = m(CaC_2O_4) = M((CaC_2O_4) \cdot n(CaO)$ **X = 12.05** (12.09)

d) $n(H_3BO_3) = m_{40°}/M(H_3BO_3)$ $n(H_3BO_3) = 6.2/61.84$ mol = 0.100 mol

(6.2-4.4) g = 1.8 g H_2O (0.1 mol) are released,

⇨ 1 mol H_2O per 1 mol H_3BO_3 are released,

suggestion: X = HBO_2

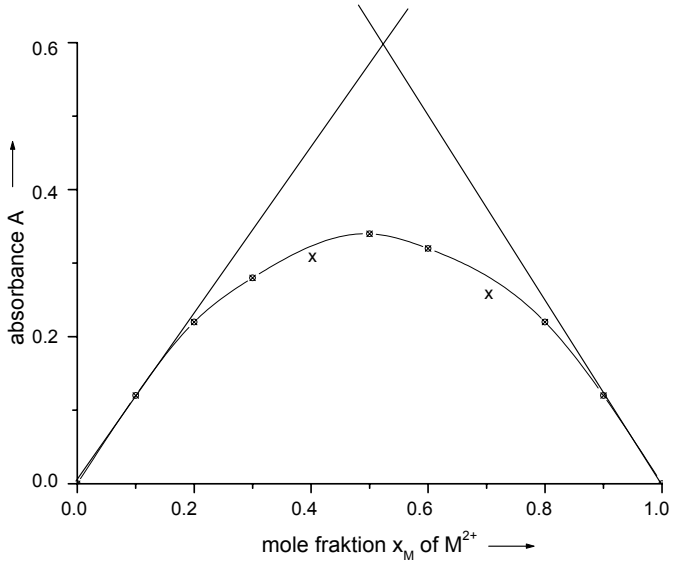
verification $m_{100°} = n(H_3BO_3)\cdot M(HBO_2)$ $m_{100°} = 4.4$

$m_{250°} = 0.5\cdot n(H_3BO_3)\cdot M(B_2O_3)$ $m_{250°} = 3.5$ q.e.d.

X = HBO_2

Solution to problem 3-4

a)



⇨ n = 1 $\varepsilon = 1.2 \cdot 10^3$ L·mol^{-1}·cm^{-1}.

b) $x_M = 0.5$ A = 0.34 ⇨ c(complex) = 0.34/(1.2 · 10^3 L/mol) = 2.83 · 10^{-4} mol/L

c(L) = c(Me^{2+}) = 0.5 · 10^{-3} mol/L - 2.83 · 10^{-4} mol/L = 2.17 · 10^{-4} mol/L

$K_f = \frac{2.83 \cdot 10^{-4}}{(2.17 \cdot 10^{-4})^2}$ L/mol **K_f = 6.01 · 10^3 L/mol.**

c) $H_2 + D_2 \rightleftarrows 2\ HD$

d)

	H_2	HD	D_2
rel. intensity	1	3.7	3.7

⇨➜ $p(HD) = p(D_2) = 3.7 \cdot p(H_2)$

$K_p = \frac{[3{,}7 \cdot p(H_2)]^2}{p(H_2) \cdot 3{,}7\ p(H_2)}$ **K_p = 3.7**

e) Assumptions: The relative intensity is proportional to the concentration in the sample and there are not any consecutive reactions in the mass spectrometer.

Solution to problem 3-5

a) $E°_1(Fe^{3+}/Fe^{2+})$ = 0.77 V : $Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$ $\Delta G_1 = -F \cdot E°_1$ (1)

$E°_2(Fe^{3+}/Fe)$ = - 0.036 V: $Fe^{3+} + 3\ e^- \rightleftharpoons Fe$ $\Delta G_2 = -3 \cdot F \cdot E°_2$ (2)

3·(1) - (2): $2\ Fe^{3+} + Fe \rightleftharpoons 3\ Fe^{2+}$ $\Delta G_R = 3 \cdot \Delta G_1 - \Delta G_2$

$\Delta G_R = 3 \cdot \Delta G_1 - \Delta G_2$ $\Delta G_R = -3 \cdot F \cdot (0.77\ V + 0.036\ V)$ ΔG_R = -233.3 kJ/mol

$\ln K = -\Delta G_R/(R \cdot T)$ lnK = 94.1 **$K = 7.5 \cdot 10^{40}$**

b) $2\ Sb + 6\ OH^- \rightleftharpoons Sb_2O_3 + 3\ H_2O + 6\ e^-$

c) pH = 12.0 ➜ $c(OH^-) = 10^{-2}$ mol/L pH = 12.7 ➜ $c(OH^-) = 10^{-1.3}$ mol/L

$E = E° + \frac{R \cdot T}{6 \cdot F} \ln \frac{1(mol/L)^6}{c^6(OH^-)}$, $E_{12.7} - E_{12.0} = \frac{R \cdot T}{F} \ln \frac{10^{-2}}{10^{-1,3}}$ $E_{12.7} - E_{12.0}$ = - 0.041 V

d) (1) $Hg_2^{2+} + 2\ e^- \rightleftharpoons 2\ Hg$ $E = E°(Hg_2^{2+}/Hg) + \frac{R \cdot T}{2 \cdot F} \ln c(Hg_2^{2+})$

for $c(Cl^-)$ = 1 mol/L:

$E°(Hg/Hg_2Cl_2(s)/\ Cl^-(aq)) = E°(Hg_2^{2+}/Hg) + \frac{R \cdot T}{2 \cdot F} \ln c(Hg_2^{2+})$

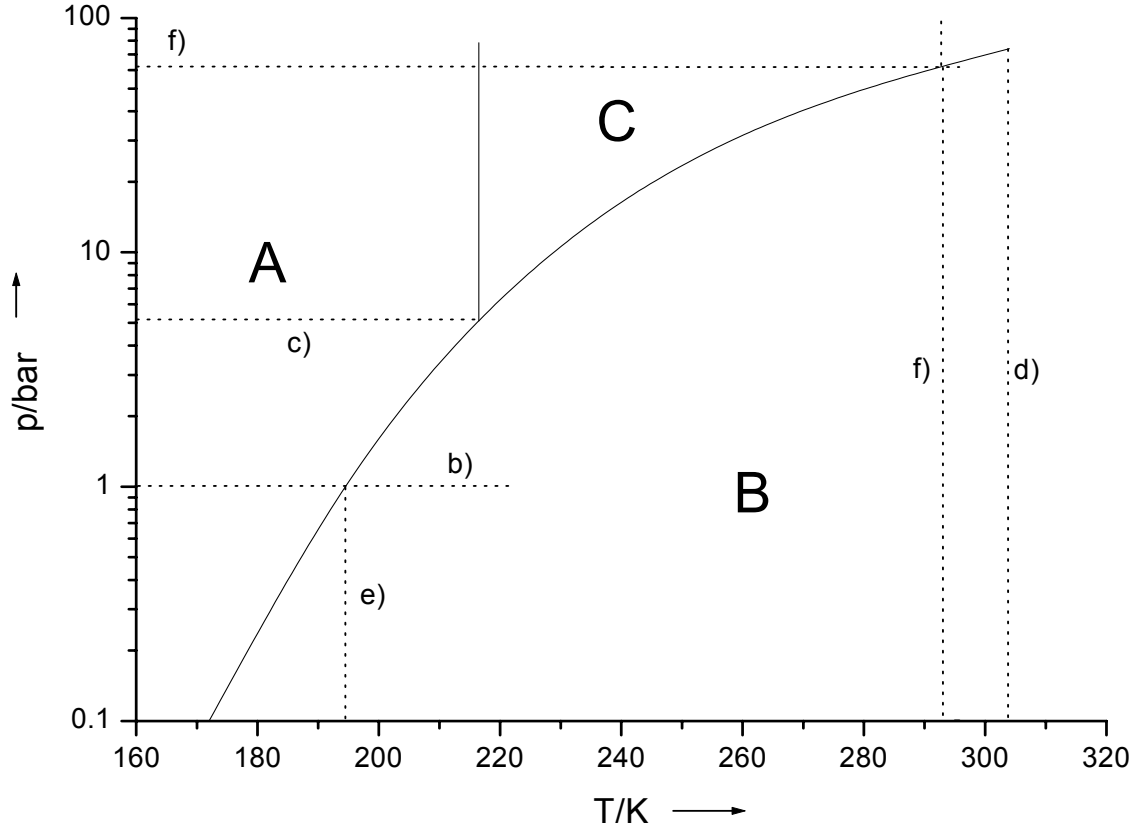
0.268 V = 0.798 V + 8.314·298.15/(2·96485) V · ln $c(Hg_2^{2+})$

ln $c(Hg_2^{2+})$ = - 41.26 $c(Hg_2^{2+}) = 1.206 \cdot 10^{-18}$ mol/L

	using $c(Cl^-) = 1$ mol/L:	$K_L = 1.206 \cdot 10^{-18}$ $(mol/L)^3$
(2)	$Hg_2Cl_2 \rightleftharpoons Hg_2^{2+} + 2\ Cl^-$	$K_L = c(Hg_2^{2+}) \cdot c(Cl^-)^2$
	in a solution over solid Hg_2Cl_2:	
	$c(Cl^-) = 2 \cdot c(Hg_2^{2+})$ ➜	$K_L = 4 \cdot c(Hg_2^{2+})^3$
	solubility $S = c(Hg_2^{2+}) = \sqrt[3]{K_L / 4}$	$S = 6.71 \cdot 10^{-7}$ mol/L
	$M(Hg_2Cl_2) = 472.08$ g/mol	**$S = 3.17 \cdot 10^{-4}$ g/L**

Solution to problem 3-6

a) A: solid B: gasous C: fluid
b) solid and gasous
c) read: 5.1 bar (exactly: 5.1 bar)
d) read: 304 K (exactly: 304 K)
e) read: 194 K (exactly: 194.7 K)
f) read: 61 bar (exactly: 57.5 bar)



g) Weighing the container and comparing with the weight of the empty container.

h) Because K_2 is so small $c(CO_2^{2-})$ can be neglected.

$H_2CO_3 + H_2O \rightleftarrows HCO_3^- + H_3O^+$ $\quad K_1 = 10^{-3.3}$ mol/L

$c(H_3O^+) = K_1 \cdot c(H_2CO_3)/c(HCO_3^-)$ and $c(H_3O^+) = c(HCO_3^-)$

$\Rightarrow \; c(H_3O^+)^2 = K_1 \cdot c(H_2CO_3)$

$K_H = c(CO_{2\,(aq)})/p(CO_{2\,(g)}) \quad \Rightarrow \quad c(H_3O^+) = \sqrt{K_1 \cdot K \cdot K_H \cdot p(CO_{2(aq)}}$

$$c(H_3O^+) = \sqrt{10^{-3.3}\,\text{mol/L} \cdot 2.58 \cdot 10^{-3} \cdot 3.36 \cdot 10^{-7}\,\text{mol/(L}\cdot\text{Pa)} \cdot 101.3\ \text{Pa} \cdot 35 \cdot 10^{-2}}$$

$c(H_3O^+) = 3.9 \cdot 10^{-6}$ mol/L $\qquad$ **pH = 5.4**

Solution to problem 3-7

a) $Ba^{2+}(aq) + SO_4^{2-}(aq) \longrightarrow BaSO_4\,(s)$

$Sr^{2+}(aq) + SO_4^{2-}(aq) \longrightarrow SrSO_4\,(s)$

b) $c(SO_4^{2-}) = \dfrac{K_{sp}(BaSO_4)}{c(Ba^{2+})}$ $\qquad$ **$c(SO_4^{2-}) = 1.0 \cdot 10^{-8}$ mol/L**

c) Precipitation of strontium sulfate starting at $c(SO_4^{2-}) = \dfrac{K_{sp}(SrSO_4)}{c(Sr^{2+})} = 3.0 \cdot 10^{-5}$ mol/L

In that moment $c(Ba^{2+}) = \dfrac{K_{sp}(BaSO_4)}{3.0 \cdot 10^{-5}\,\text{mol/l}}$ $\qquad c(Ba^{2+}) = 1/3 \cdot 10^{-5}$ mol/L

Remaining concentration in the solution $\dfrac{1/3 \cdot 10^{-5}\,\text{mol/L}}{0.01\ \text{mol/L}} \cdot 100\% = 0.033$ % of the original concentration of Ba^{2+}-ions, thus the criterion of seperation is fulfilled.

d) $Ag^+(aq) + 2\,NH_3(aq) \rightleftarrows Ag(NH_3)_2^+(aq)$

e) $c(Ag^+) \cdot c(Cl^-) = K_{sp}(AgCl)$ $\qquad c(Ag^+) = \sqrt{1.7 \cdot 10^{-10}}$ mol/L

$c(Ag^+) = 1.3 \cdot 10^{-5}$ mol/L $\qquad$ M(AgCl) = 143.32 g/mol $\qquad$ **$m(AgCl) = 1.9 \cdot 10^{-3}$ g/L**

f) $AgCl\,(s) \rightleftarrows Ag^+(aq) + Cl^-(aq)$

$\underline{Ag^+(aq) + 2\,NH_3(aq) \rightleftarrows Ag(NH_3)_2^+(aq)}$

total $AgCl\,(s) + 2\,NH_3(aq) \rightleftarrows Ag(NH_3)_2^+(aq) + Cl^-(aq)$.

$K_{total} = \dfrac{c(Ag(NH_3)_2^+) \cdot c(Cl^-)}{c(NH_3)^2} \cdot \dfrac{c(Ag^+)}{c(Ag^+)} = K_{sp} \cdot K$ $\qquad K_{total} = 2.55 \cdot 10^{-3}$

with x = molar solubuility of AgCl (in mol/L)

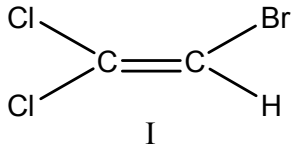
	$AgCl\ (s) + 2\ NH_3\ (aq) \rightleftharpoons Ag(NH_3)_2^+\ (aq) + Cl^-\ (aq)$		
begin	1,0 mol/L	0,0 mol/L	0,0 mol/L
change	- 2·x mol/L	+ x mol/L	+ x mol/L
in equilibrium	(1,0 - 2·x) mol/L	x mol/L	x mol/L

$K_{total} = \frac{x^2}{(1.0-2x)^2}$ $\frac{x}{(1.0-2x)} = \sqrt{2.55 \cdot 10^{-3}}$ x = 0.046

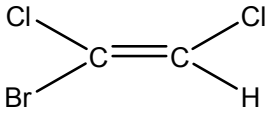
Solution of AgCl in 1 M ammonia solution: 0.046 mol/L· 143.32 g/mol = 6.59 g/L AgCl, ≈ 3500 times more than in pure water.

Solution to problem 3-8

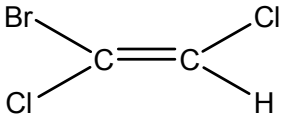
a)



I
2-Bromo-1,1-dichloroethene



II
(E)-1-Bromo-1,2-dichloroethene

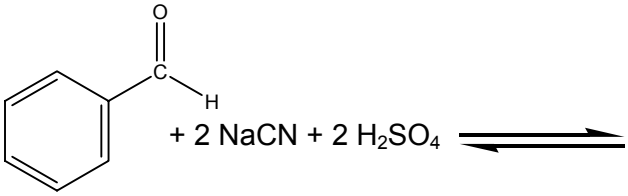


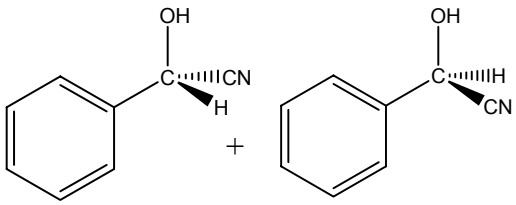
III
(Z)-1-Bromo-1,2,-dichloroethene

b)
- constitutional isomers: I und II / III
- diastereomers (cis-trans isomers): II und III

Solution to problem 3-9

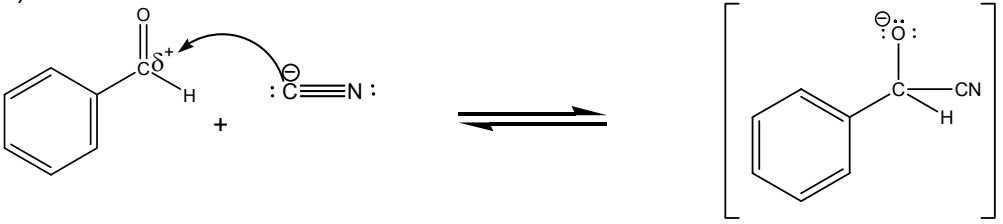
a)

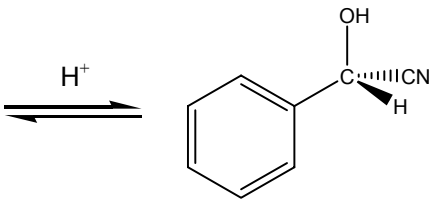




+ 2 $NaHSO_4$

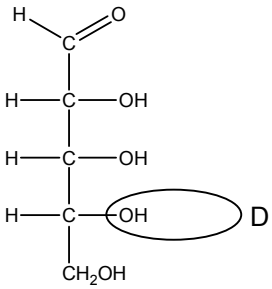
b)



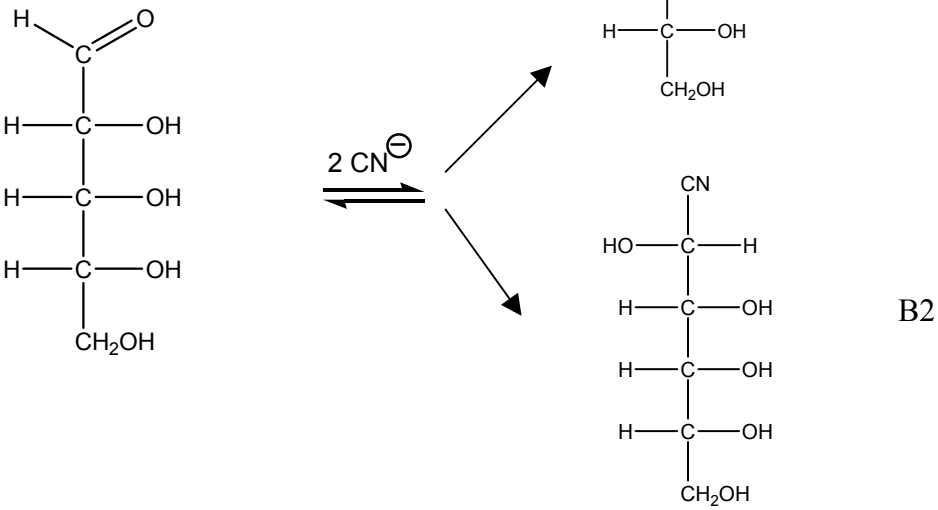


Nucleophilic addition of the cyanide ions to the carbonyl group of ketones and aldehydes.

c)



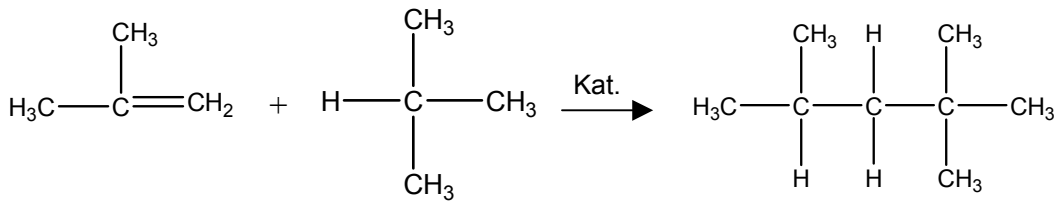
d)



e) B1 and B2 are diastereomers, more accurately epimers.

Solution to problem 3-10

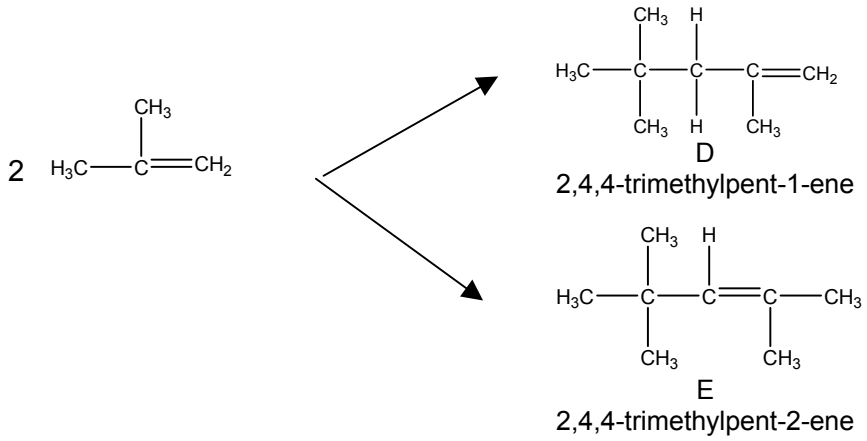
a)



B
2-methylprop-1-ene

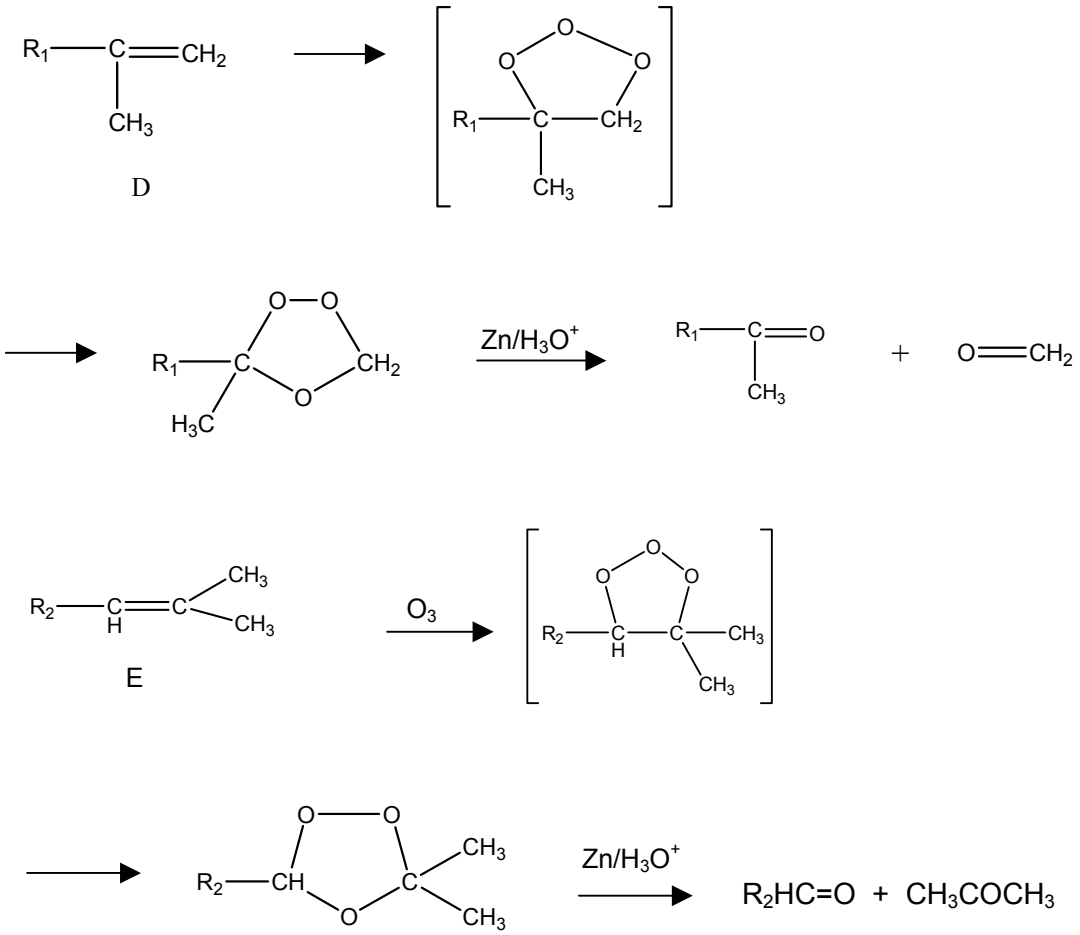
C
2-methylpropane

b)



c) D and E are constitutional isomers.

d)



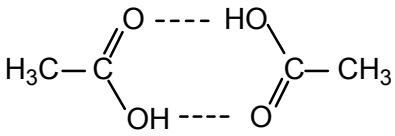
Answers Round 3 Test 2

Solution to problem 3-11

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

Solution to problem 3-12

a) 2 hydrogen bonds:



b) Total amount of acetic acid (HAc):

$Ba(OH)_2 + 2\ HAc \longrightarrow Ba(Ac)_2 + 2\ H_2O$

$n_0(HAc) = 0.0413\ mol/L \cdot 2 \cdot 22.60 \cdot 10^{-3}\ L = 1.867 \cdot 10^{-3}\ mol\ HAc$

or $9.334 \cdot 10^{-4}\ mol\ (HAc)_2$ respectively

Amount in the gas phase $n(HAc) + n((HAc)_2) = \frac{5.92 \cdot 10^3 Pa \cdot 0.5 \cdot 10^{-3} m^3}{8.314 JK^{-1}mol^{-1} \cdot 323.15 K}$

$n(HAc) + n((HAc)_2) = 1.102 \cdot 10^{-3}\ mol$

x = amount of decomosed dimer:

$n((HAc)_2) = n_0((HAc)_2) - x$ $\quad n(HAc) = 2 \cdot x$

$n_0((HAc)_2) - x + 2 \cdot x = 1.102 \cdot 10^{-3}\ mol$ $\quad x = 1.686 \cdot 10^{-4}\ mol$

$n((HAc)_2) = 7.648 \cdot 10^{-4}\ mol$ $\quad n(HAc) = 3.372 \cdot 10^{-4}\ mol$

$\alpha = \frac{n_0((HAc)_2) - n((HAc)_2)}{n_0((HAc)_2)}$ $\quad$ **α = 0.181 bzw. 18.1 %**

c) $(HAc)_2 \rightleftharpoons 2\ HAc$

$p((HAc)_2) = \frac{n((HAc)_2)}{n((HAc)_2) + n(HAc)} \cdot p_{gesamt}$ $\quad p(HAc) = \frac{n(HAc)}{n((HAc)_2) + n(HAc)} \cdot p_{gesamt}$

$p((HAc)_2) = 5.92 \cdot 10^3\ Pa \cdot (7.648 \cdot 10^{-4}\ mol / 1.102 \cdot 10^{-3}\ mol)$ $\quad p((HAc)_2) = 4109\ Pa$

$p(HAc) = 5.92 \cdot 10^3\ Pa \cdot (3.372 \cdot 10^{-4}\ mol / 1.102 \cdot 10^{-3}\ mol)$ $\quad p(HAc) = 1811\ Pa$

$K_p = \frac{p^2(HAc)}{p((HAc)_2)}$ $\quad$ **K_p = 798 Pa**

$c = n/V$ $\quad c((HAc)_2) = 7.648 \cdot 10^{-4}\ mol/0.5\ L$ $\quad c((HAc)_2) = 15.30 \cdot 10^{-4}\ mol/L$

$c(HAc) = 3.372 \cdot 10^{-4}\ mol/0.5\ L$ $\quad c(HAc) = 6.744 \cdot 10^{-4}\ mol/L$

$K_c = 2.97 \cdot 10^{-4}$ mol/L

(Or $K_c = K_p \cdot (R \cdot T)^{-\Delta n}$, $K_c = 798\ Pa \cdot (8.314\ JK^{-1}mol^{-1} \cdot 323.15\ K)^{-1} = 0.297\ mol/m^3$)

Solution to problem 3-13

a) $M(NaNO_2) = 69.00$ g/mol $\quad n_0(NaNO_2) = 0.560/69.00$ mol $= 8.12 \cdot 10^{-3}$ mol

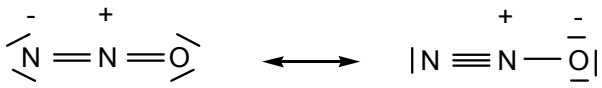
$M(HONH_3Cl) = 69.50$ g/mol $\quad n(HONH_3Cl) = 0.495/69.50$ mol $= 7.12 \cdot 10^{-3}$ mol

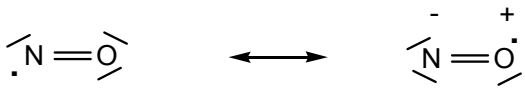
Oxidation: $2\ MnO_4^- + 5\ NO_2^- + 6\ H_3O^+ \longrightarrow 2\ Mn^{2+} + 5\ NO_3^- + 9\ H_2O$

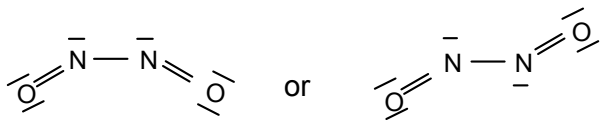
$2.5 \cdot (20.00 - 11.94) \cdot 10^{-3}$ L $\cdot$ 0.05 mol/L $= 1.0075 \cdot 10^{-3}$ mol of NO_2^- did not react. Thus sodium nitrite) and hydroxylammonium chloride reacted in a 1 : 1 ratio.

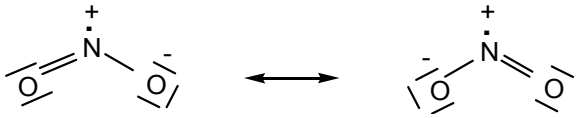
$NaNO_2 + HONH_3Cl \longrightarrow NaCl + N_2O + 2\ H_2O$

b) $3\ HNO_2 \longrightarrow 2\ NO + HNO_3 + H_2O$

c) N_2O 

NO 

N_2O_2 

NO_2 

NO and NO_2 are free radicals.

Solution to problem 3-14

a) $3.85 \cdot 10^{-3} = k \cdot (7.69 \cdot 10^{-6})^n$

$1.67 \cdot 10^{-2} = k \cdot (3.33 \cdot 10^{-5})^n$

$0.100 = k \cdot (2.00 \cdot 10^{-4})^n$

$\frac{3.85 \cdot 10^{-3}}{1.67 \cdot 10^{-2}} = (\frac{7.69 \cdot 10^{-6}}{3.33 \cdot 10^{-5}})^n$ $\quad 0.231 = (0.231)^n$ ⇨ **n = 1**

$\frac{1.67 \cdot 10^{-2}}{0.100} = (\frac{3.33 \cdot 10^{-5}}{2.00 \cdot 10^{-4}})^n$ $\quad 0.167 = (0.167)^n$ ⇨ **n = 1**

b) $r = k \cdot c(O_2^-)$ $\quad k = r / c(O_2^-)$

$k = 3.85 \cdot 10^{-3} / 7.69 \cdot 10^{-6}$ $\quad k = 501\ s^{-1}$

$k = 1.67 \cdot 10^{-2} / 3.33 \cdot 10^{-5}$ $\quad k = 502\ s^{-1}$

$k = 0.100 / 2.00 \cdot 10^{-4}$ $\quad k = 500\ s^{-1}$

average $\quad$ **$k = 501\ s^{-1}$** .

c) $E + O_2^- \xrightarrow{k_1} E^- + O_2$ $\qquad E^- + O_2^- \xrightarrow{k_2} E + O_2^{2-}$

if $k_2 > k_1$ then E^- is a rather short living intermediate and thus $c(E^-)$ is constant and then c(E), too.

⇨ $r = k_1 \cdot c(E) \cdot c(O_2^-)$

with $k_1 \cdot c(E) = k$, this mechanism is consistent with the rate law observed .

d) $r = k_1 \cdot c(E) \cdot c(O_2^-)$ $\quad r = k_1 \cdot [c_0(E) - c(E^-)] \cdot c(O_2^-)$ (*)

steady state of the intermediates:

$k_1 \cdot c(E) \cdot c(O_2^-) - k_2 \cdot c(E^-) \cdot c(O_2^-) = 0$

$k_1 \cdot [c_0(E) - c(E^-)] \cdot c(O_2^-) - 2 \cdot k_1 \cdot c(E^-) \cdot c(O_2^-) = 0 \quad \Rightarrow \quad c(E^-) = 1/3 \cdot c_0(E)$

in (*): $r = 2/3 \cdot k_1 \cdot c_0(E) \cdot c(O_2^-)$

on the other hand $r = k \cdot c(O_2^-)$

$\Rightarrow$ $2/3 \cdot k_1 \cdot c_0(E) = k$

$k_1 = 3/2 \cdot 501\ s^{-1} / (0.400 \cdot 10^{-6}\ mol/L)$ $\quad$ **$k_1 = 1.88 \cdot 10^9$ L mol^{-1} s^{-1}**

$k_2 = 3.76 \cdot 10^9$ L mol^{-1} s^{-1}

Solution to problem 3-15

a) Preparing an ideal solution no effects related to the mixing will occur i.e. the volume of the mixture is the sum of the original volumes of the components. The same is valid for the internal energy, there is no enthalpy of mixing. The vapour pressure of the mixture follows Raoult's law.

To achieve these properties the interactions between different molecules have to be the average of those between the molecules of each of the components.

b) Calculation of the composition at different temperatures:

$p_{total} = 101.3$ kPa $\quad p_{benzene}(T) + p_{xylene}(T) = 101.3$ kPa (1)

Raoult's law:

$p_{benzene}(T) = p^0_{benzene}(T) \cdot x_{benzene.l}(T)$ $\quad p_{xylerne}(T) = p^0_{xylene}(T) \cdot x_{xylene.l}(T)$ (2)

(1), (2) and $x_{benzene.l} + x_{xylene.l} = 1$:

$101.3\ kPa = p^0_{benzene}(T) \cdot x_{benzene.l} + p^0_{Xylol}(T) \cdot (1 - x_{benzene.l}(T))$

$$x_{benzene,l}(T) = \frac{101.3\ kPa - p^0_{xylene}(T)}{p^0_{benzene}(T) - p^0_{xylene}(T)}$$

Analogous for the composition of the vapour above the liqid phase:

$$x_{benzene,g}(T) = \frac{p_{benzene}(T)}{p_{total}} = \frac{p^0_{benzene}(T) \cdot x_{benzene,l}(T)}{1.013\ kPa}$$

T in K	$x_{benzene}$ in the liquid phase	$x_{benzene}$ in the gas phase
353	1.00	1.00
363	0.70	0.94
373	0.48	0.84
383	0.31	0.71
393	0.18	0.53
403	0.08	0.28
412	0	0

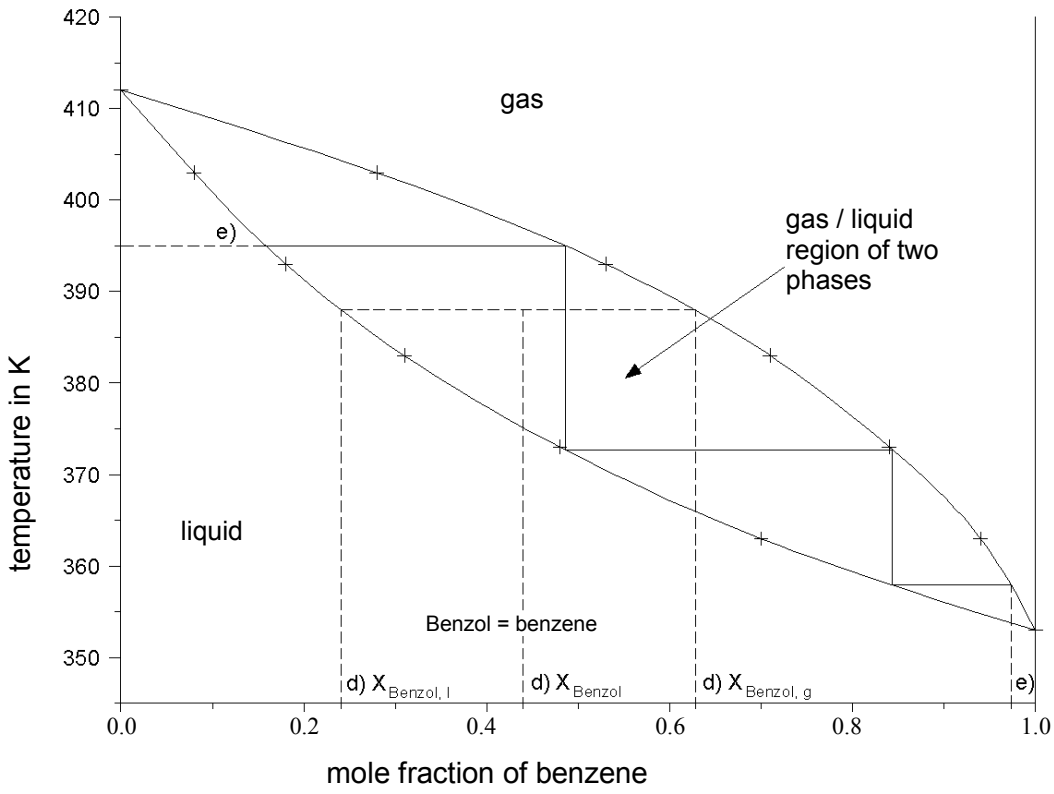
c) see diagram

d) $M_{benzene}$ = 78.10 g/mol M_{xylol} = 106.15 g/mol

$$x_{benzene} = \frac{n_{benzene}}{n_{benzene} + n_{xylole}} \qquad x_{benzene} = \frac{\frac{1}{M_{benzene}}}{\frac{1}{M_{benzene}} + \frac{1,5}{M_{xylole}}} \qquad x_{benzene} = 0.475$$

From the diagram: $x_{benzene, l}$ = 0.24 $x_{benzene,g}$ = 0.63

e) From the diagram: $x_{benzene\ after\ distillation}$ = 0.97 ($x_{xylene\ after\ distillation}$ = 0.03)
Purity: 97 % of molar amount.



Solution to problem 3-16

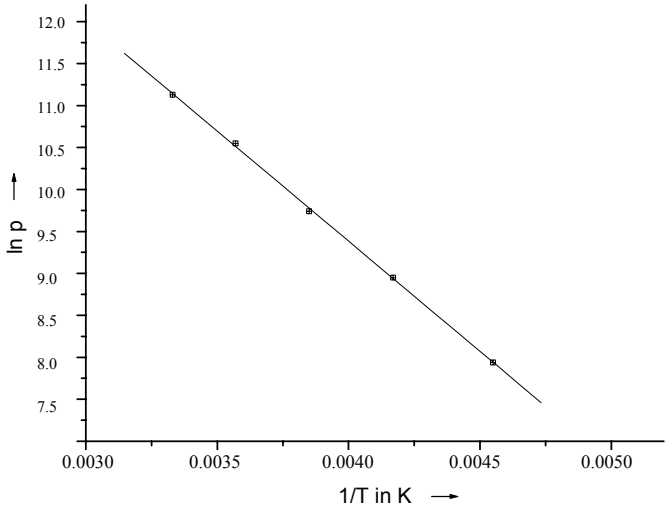
a) Van der Waals forces are forces between particles besides covalent and ionic bonds. Types:
- particles may stick together because they are permanent polar,
- permanent polar particels may stick together with non polar ones by inducing polarity on them,
- in case of non polar molecules the rapid fluctuations of the electron clouds give rise to instantaneous electric dipoles to result in forces between the molecules.

b) A spontaneous process requires a negative *ΔG*. Since the translational freedom of the adsorbate is reduced when it is adsorbed *ΔS* is negative. Therefore, in order for $\Delta G = \Delta H - T \cdot \Delta S$ to be negative, *ΔH* must be negative, too ⇨ chemisorption is an exothermic process.

c) To break chemical bonds one needs about 300 kJ/mol while intermolecular bond energies of van der Waals forces lie in most cases under 20 kJ/mol. Thus the (absolute) energy of chemisorption is higher.

d)

T in K	220	240	260	280	300
p in Pa	2800	7700	17000	38000	68000
ln p	7.94	8.95	9.74	10.55	11.13
1/T in K^{-1}	$4.55 \cdot 10^{-3}$	$4.17 \cdot 10^{-3}$	$3.85 \cdot 10^{-3}$	$3.57 \cdot 10^{-3}$	$3.33 \cdot 10^{-3}$



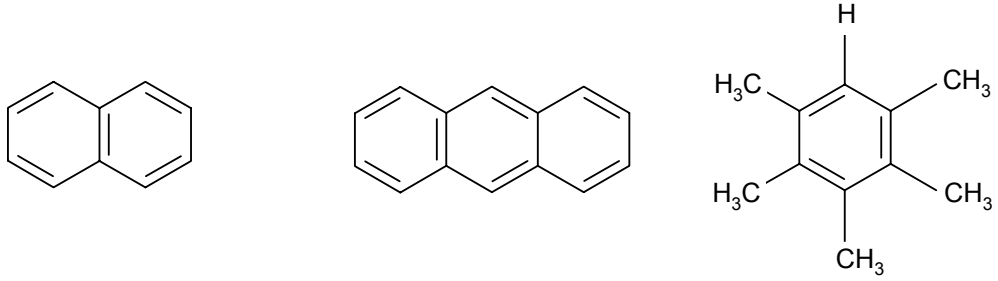
$$m \approx \frac{11.13 - 7.94}{3.33 \cdot 10^{-3} - 4.55 \cdot 10^{-3}} K$$

$$\Delta H^0_{ads} / R \approx -2615 \text{ K}$$

$$\Delta H^0_{ads} \approx -21.7 \text{ kJ}$$

Solution to problem 3-17

a)



(or mesomeric structures)

Naphthalene: $C_{10}H_8(s) + 12\ O_2(g) \rightleftharpoons 10\ CO_2(g) + 4\ H_2O(l)$

Anthracene: $C_{14}H_{10}(s) + 16{,}5\ O_2(g) \rightleftharpoons 14\ CO_2(g) + 5\ H_2O(l)$

Pentamethylbenzene: $C_{11}H_{16}(s) + 15\ O_2(g) \rightleftharpoons 11\ CO_2(g) + 8\ H_2O(l)$

b) As the volume in the calorimeter is constant the change of the internal energy $\Delta_C U$ is measured as heat of reaction Q_C. Computing the enthalpy of combustion $\Delta_C H$(aromatic) you have to take the work of expansion into account. The changings of the amount of gases, $\Delta n(g)$, related to the combustion of 1 mole hydrocarbon are:
naphthalene -2 mol, anthracene -2,5 mol, pentamethylbenzene -4 mol.

Q_C - Q_C(primer) is the change of internal energy by combustion of the hydrocarbon.

$$\Delta_C U = \frac{Q_C - Q_C(\text{primer})}{n(\text{hydrocarbon})} = \Delta_C H(\text{hydrocarbon}) - p \cdot V_C \qquad p \cdot V_C = \Delta n(g) \cdot R \cdot T$$

$$\Delta_C H(\text{hydrocarbon}) = \frac{Q_C - Q_C(\text{primer})}{n(\text{hydrocarbon})} + \Delta n(g) \cdot R \cdot T$$

n(naphthalene)	= 0,7002 g/128.18 g/mol	= $5.463 \cdot 10^{-3}$ mol
n(anthracene)	= 0.6653 g/178.24 g/mol	= $3.733 \cdot 10^{-3}$ mol
n(pentamethylbenzene)	= 0.6409 g/148.27 g/mol	= $4.323 \cdot 10^{-3}$ mol

$\Delta_C H$(naphthalene) = [(- 28190 + 30)/$5.463 \cdot 10^{-3}$ - 2·8.314·298.15] J/mol = **-5159.6 kJ/mol**
$\Delta_C H$(anthracene) = **-7052.8 kJ/mol**
$\Delta_C H$(pentamethylbenzene) = **-6459.1kJ/mol**

c) **$\Delta_f H$(naphthalene)** = $-\Delta_C H + 10 \cdot \Delta_f H(CO_2) + 4 \cdot \Delta_f H(H_2O)$ = **81.0 kJ/mol**
$\Delta_f H$(anthracene) = $-\Delta_C H + 14 \cdot \Delta_f H(CO_2) + 5 \cdot \Delta_f H(H_2O)$ = **114.3 kJ/mol**
$\Delta_f H$(pentamethylbenzene) = $-\Delta_C H + 11 \cdot \Delta_f H(CO_2) + 8 \cdot \Delta_f H(H_2O)$ = **-156.6 kJ/mol**

d) Using the system of increments you get:

$\Delta_C H^i$/kJmol^{-1}	C-H (-226.1)	C-C -206.4	C=C$_{(2\ gr)}$ -491.5	C=C$_{(3\ gr)}$ -484.4	C=C$_{(4\ gr)}$ -483.2	6-Rg -4.2	br.pt. +7.2	$\Delta_S H$	$\Delta_C H$
naphthalene	8	6	4		1	2	2	66.5	- 5423.9
mesomeric n.	8	6	3	2		2	2	66.5	- 5418.0
anthracene	10	9	4	2	1	3	4	93.4	- 7427.0
mesomeric a.	10	9	3	4		3	4	93.4	- 7421.1
pentamethylb.	16	8		1	2	1		61.1	- 6662.7

mean value $\Delta_C H$(naphthalene) = - 5421.0 kJ/mol (- 5423.9 / - 5418.0)

mean value $\Delta_C H$(anthracene) = - 7424.1 kJ/mol (- 7427.0 / - 7421.1)

$\Delta_C H$(Pentamethylbenzol) = - 6662.7 kJ/mol

e) The practical combustion enthalpy of naphthalene is 261.4 (264.3 / 258.4) kJ/mol higher than that of the increment system. This is the contribution of the stabilizing (mesomeric) energy$\Delta_{mes}H$, 26.1 (26.4 / 25.8) kJ/mol per π electron.
Anthracene: difference 371.3 (374.2 / 368.3) kJ/mol. 26.5 (26.7 / 26.3) kJ/mol per π electron.
Mean Value -26.3 kJ/mol per π electron.

f) The difference between practical and theoretical combustion enthalpy of pentamethyl-benzene is 203.6 kJ/mol instead of 26.3 kJ/mol ·6 = 157.8 kJ/mol, contributed by 6 π electrons. This difference is generated (45.8 kJ/mol) by hyperconjugation of 5 methyl groups, ~9 kJ/mol stabilization of each of them.

Solution to problem 3-18

a) $n(CO_2) = n(C_A)$, $n(H_2O) = 2n(H_A)$, $n(O_A) = n(H_2O)$
$n(O_A) : n(C_A) : n(H_A) = 1 : 1 : 2$ **A: (CH_2O)**

A = $(CH_2O)_n$ paraformaldehyde B = $CH_2(OCH_3)_2$ dimethoxymethane
C = CO_2 carbon dioxide D = H_2O water
E = CH_2O formaldehyde

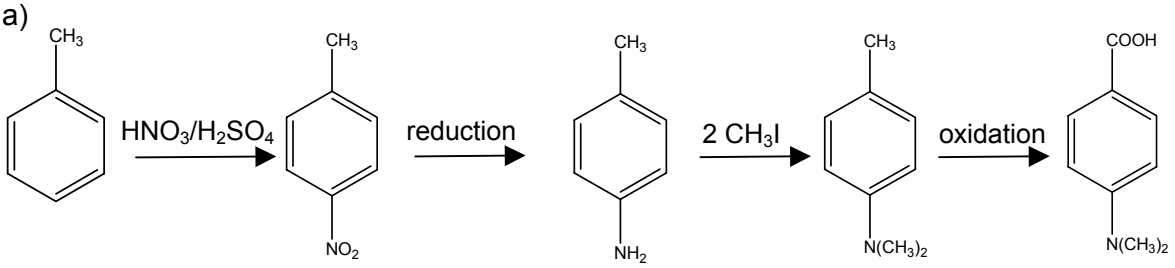
b)

1. $(CH_2O)_n + 4n\ Cu(OH)_2 + 2n\ NaOH \longrightarrow 2n\ Cu_2O\downarrow + n\ Na_2CO_3 + 6n\ H_2O$
2. $(CH_2O)_n + 2n\ CH_3OH \longrightarrow n\ H_2C(OCH_3)_2 + n\ H_2O$
3. $(CH_2O)_n + n\ O_2 \longrightarrow n\ CO_2 + n\ H_2O$
4. $n\ (CH_2O) \longrightarrow (CH_2O)_n$ polymerisation

e.g. n=3

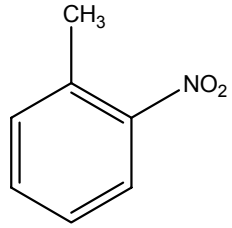
Solution to problem 3-19

a)

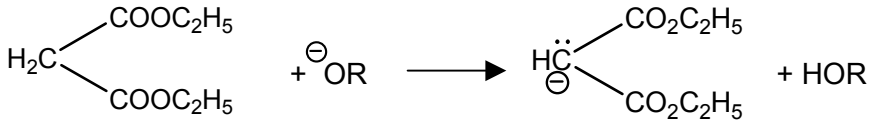


A B C

A1:

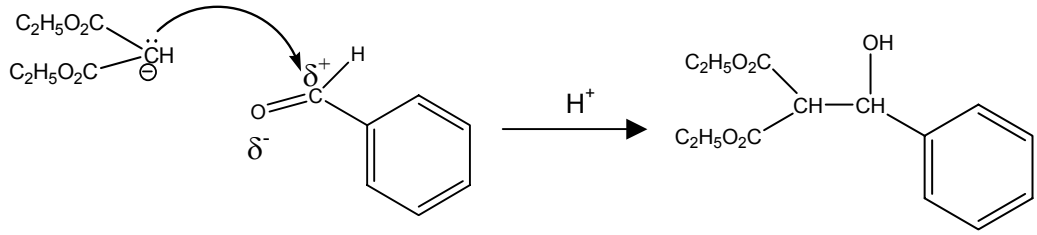


b) Formation of a carbanion:



compound Z

The carbanion is nucleophilic and adds to the partial positiv C atom of the carbonyl group:



compound D

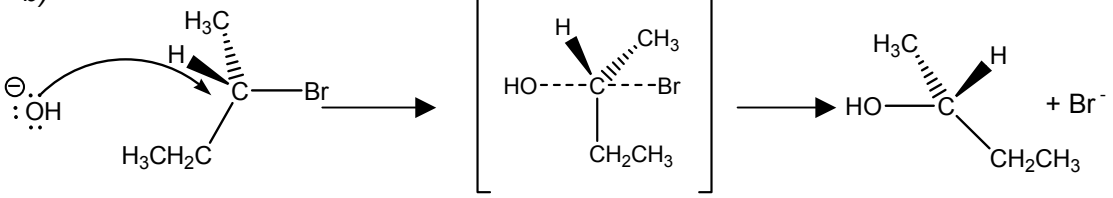
Solution to problem 3-20

a)

$CH_3CH_2Br + NaOCH_3 \xrightarrow{(CH_3OH)} CH_3CH_2OCH_3 + NaBr$

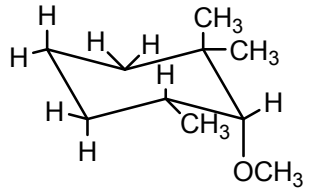
Ethoxymethane

b)



(S)-2-Bromobutane (R)-2-Butanol

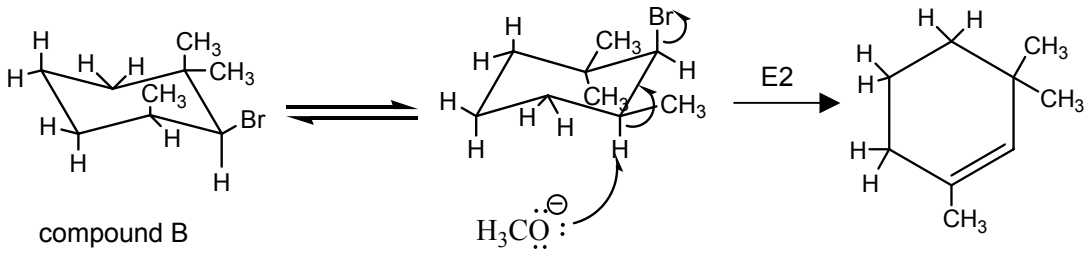
c)



compound X

d) Diastereomers.

e) Elimination (E2) took place to form Y from B.
This is possible (in contrast to the reaction of compound A) because compound B can undergo an anti-periplanar position to eliminate HBr.



compound B

+ CH_3OH + Br^-

Answers Round 4

Solution to problem 4-1

a) $2\ BrCl \longrightarrow Br_2 + Cl_2$

b) $Q = \frac{0.25 \cdot 0.25}{0.25^2} = 1 \neq K_c$

c) $Q < K_c$ ⇨ in direction of the products.

d) $K_c = \mathbf{K_p = 32}$ $(= K_{th})$

e) Concentrations in equilibrium:

$c(BrCl) = 0.25\ mol/L - 2 \cdot y$ $\qquad c(Br_2) = c(Cl_2) = 0.25\ mol/L + y$

$32 = \frac{(0.25 mol/L + y)^2}{(0.25 mol/L - 2y)^2}$ $\qquad y = 0.0945\ mol/L$

$c(BrCl) = 0.061\ mol/L$ $\qquad$ **$c(Br_2) = c(Cl_2) = 0.345\ mol/L$**

f) $\Delta G° = - RT \cdot \ln K_p$

$\Delta G = \Delta G° + RT \cdot \ln Q.\ \ Q = 1$ $\qquad ⇨ \qquad \Delta G = RT \cdot \ln \frac{Q}{K_{th}}$

$\Delta G = 8.314\ J/(mol \cdot K) \cdot 773.15\ K \cdot \ln (1/32)$ $\qquad$ **$\Delta G = - 22.3\ kJ/mol$**

Solution to problem 4-2

a) $n \cdot \lambda = 2a \cdot \sin\vartheta$; with n = 1 $\qquad \sin\vartheta = 1 \cdot \lambda/(2a) \qquad$ **$\vartheta = 8.63°$**

b) **$V = a \cdot b \cdot c \cdot \sin\beta$.**

c) $density = \frac{m(unit\ cell)}{V(unit\ cell)} \qquad ⇨ \qquad m(unit\ cell) = \rho \cdot a \cdot b \cdot c \cdot \sin\beta$

$m(unit\ cell) = 2.9\ g/cm^3 \cdot 5.13 \cdot 10^{-8}\ cm \cdot 8.89 \cdot 10^{-8}\ cm \cdot 19.00 \cdot 10^{-8}\ cm \cdot \sin 95°$

$m(unit\ cell) = 2.50 \cdot 10^{-21}\ g$.

On the other hand $\qquad m(unit\ cell) = \frac{M(paragonite)}{N_L} \cdot z$

with M(paragonite) = molar mass(paragonite) = 382.22 g/mol ,
z = number of $[NaAl_3Si_3O_{10}(OH)_2]$ - units per cell,
$N_L = 6.022 \cdot 10^{23}\ mol^{-1}$

$2.51 \cdot 10^{-21}\ g = \frac{382.22 g/mol}{6.022 \cdot 10^{23} mol^{-1}} \cdot z$ $\qquad z = 3.94 \approx 4.$

Number of Al-atoms in a unit cell = $3 \cdot z$ $\qquad$ **n = 12**.

Solution to problem 4-3

In this example HNO_3 and NH_4CN are choosen as additional chemicals.

No.	Gas	reactants	products
1	HCl	$HCl_{(aq)}$	$\xrightarrow{\Delta H}$ **$HCl_{(g)}\uparrow$**
2	Cl_2	16 $HCl_{(aq)}$ + 2 $KMnO_4$	$\longrightarrow$ **5 $Cl_2\uparrow$** + 2 $MnCl_2$ + 8 H_2O + 2 KCl
3	H_2	2 $HCl_{(aq)}$ + Zn	$\longrightarrow$ **$H_2\uparrow$** + $ZnCl_2$
4	HCN	$HCl_{(aq)}$ + NH_4CN	$\longrightarrow$ **HCN$\uparrow$** + NH_4Cl
5	H_2S	Zn + S ZnS + 2 $HCl_{(aq)}$	$\longrightarrow$ ZnS $\longrightarrow$ **$H_2S\uparrow$** + $ZnCl_2$
6	SO_2	3 S + 4 $KMnO_4$	$\xrightarrow{\Delta H}$ 3 **$SO_2\uparrow$** + 4 MnO_2 + 2 K_2O
7	O_2	$KMnO_4$	$\xrightarrow{\Delta H}$ $\frac{1}{2}$ **$O_2\uparrow$**+ K_2O + MnO_2
8	NO	4 Cu + 4 $HNO_{3\,(aq)}$ 2 NO_2 + 2 NO + 2 $KOH_{(aq)}$	$\longrightarrow$ 2 $NO_2\uparrow$ + 2 NO$\uparrow$ + 4 CuO + 2 H_2O $\longrightarrow$ KNO_3 + KNO_2 + 2 **NO$\uparrow$** + H_2O
9	NO_2	2 NO_2 + 2 NO (from # 8) + O_2 (from # 7)	$\longrightarrow$ 4 **$NO_2\uparrow$**
10	NH_3	NH_4CN + KOH	$\longrightarrow$ **$NH_3\uparrow$** + KCN + H_2O
11	N_2O	NH_3 (from # 10) + HNO_3 NH_4NO_3	$\longrightarrow$ NH_4NO_3 $\xrightarrow{\Delta H}$ **$N_2O\uparrow$** + 2 H_2O
12	NOCl	2 NO (from # 8) + Cl_2 (from # 2)	$\longrightarrow$ 2 **NOCl** $\uparrow$

Solution to problem 4-4

a) Oxidation states: BrO_3^- (+V), BrOH (+I), Br_2 (0), Br^- (-I)

pH = 0: $E°(BrO_3^-/Br_2) = \frac{1.61\ V \cdot 1 + 1.45\ V \cdot 4}{5} = 1.48\ V$

pH = 14: $E°(BrO_3^-/Br_2) = \frac{0.46\ V \cdot 1 + 0.49\ V \cdot 4}{5} = 0.48\ V$

(The multipliers 1, 4 and 5 refer to the number of electrons transferred)

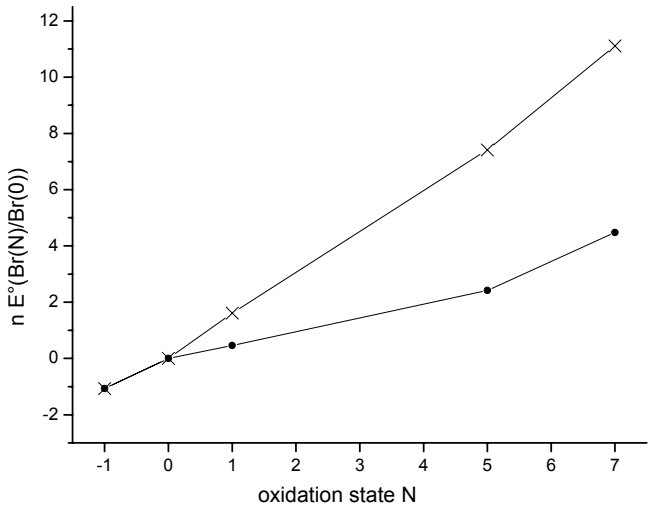
$$Br_2 + 2\ e^- \rightleftharpoons 2\ Br^-$$

$$2\ BrO_3^- + 12\ H^+ + 10\ e^- \rightleftharpoons Br_2 + 6\ H_2O$$

The first equilibrium is not influenced by $c(H^+)$, so pH does not influence E°.
In the second equilibrium the concentration of $c(H^+)$ is different under the conditions of E° (10^0 and 10^{-14} respectively) while the other concentrations do not differ. Thus $\Delta G°$ and E° have different values at different pH.

b)

	(BrO_4^-/Br_2) = (Br(7)/Br(0))	(BrO_3^-/Br_2) = (Br(5)/Br(0))	(BrO^-/Br_2) = (Br(1)//Br(0))	(Br_2/Br_2) = (Br(0)//Br(0))	(Br^-/Br_2) = (Br(-1)//Br(0))
N	7	5	1	0	-1
n	7	5	1	0	1
E° at pH=0	1.59	1.48 V	1.61 V	0	- 1.07 V (!)
n·E° at pH=0	11.11	7.41 V	1.61 V	0	- 1.07 V
E° at pH=14	0.64	0.48 V	0.46 V	0	- 1.07 V
n·E° at pH=14	4.48	2.42 V	0.46 V	0	- 1.07 V



c) $\Delta G° = - n \cdot F \cdot E°(X(N)/X(0))$

d) 1) $M^+ + e^- \rightleftarrows M$ $\quad E°_{1)} = a$ $\quad \Delta G°_{1)} = - F \cdot a$

2) $M^{2+} + 2e^- \rightleftarrows M$ $\quad E°_{2)} = x/2$ $\quad \Delta G°_{2)} = - F \cdot x$

3) $M^{3+} + 3e^- \rightleftarrows M$ $\quad E°_{3)} = b/3$ $\quad \Delta G°_{3)} = - F \cdot b$

⇨ 4) [2) - 1)]: $M^{2+} + e^- \rightleftarrows M^+$ $\quad \Delta G°_{4)} = \Delta G°_{2)} – \Delta G°_{1)} = -F \cdot (x – a)$

5) [3) - 2)]: $M^{3+} + e^- \rightleftarrows M^{2+}$ $\quad \Delta G°_{5)} = \Delta G°_{3)} – \Delta G°_{2)} = -F \cdot (b - x)$

⇨ 4) – 5): $2\ M^{2+} \rightleftarrows M^{3+} + M^+$ $\quad \Delta G° = \Delta G°_{4)} – \Delta G°_{5)}$

$= -F \cdot (2x – (a+b))$

Disproportionation $\Leftrightarrow$ $\Delta G° < O$ $\Leftrightarrow$ $2x > (a + b)$ $\Leftrightarrow$ **$x > (a + b)/2$**

if $x < (a + b)/2$ comproportionation is favoured

if $x = (a + b)/2$ no reaction will be observed

You can read these cases from the Frost diagram by the position of x:

x above the line from a to b	disproportionation
x below the line from a to b	comproportionation
x on the line from a to b	nothing observed.

e) Using the criterions of d) you find disproportionation of bromine in an alkaline but not in an acidic solution.

Disproportionation:

(i) $Br_2 + 2\ OH^- \longrightarrow Br^- + BrO^- + H_2O$

Comproportionation:

(ii) $2\ BrO_4^- + BrO^- \longrightarrow 3\ BrO_3^-$

Equilibrium constant for (i):

7) $Br_2 + 2\ e^- \rightleftarrows 2\ Br^-$ $E° = 1.07\ V$ $\Delta G°_7 = -2F\cdot 1.07\ V$

8) $2\ BrO^- + 2\ e^- + 2\ H_2O \rightleftarrows Br_2 + 4\ OH^-$ $E° = 0.46\ V$ $\Delta G°_8 = -2F\cdot 0.46\ V$

(i) = [½· 7) – ½· 8)] gives $\Delta G° = -F\cdot(1.07 - 0.46) = -58.86$ kJ/mol

$K = e^{\frac{-\Delta G^0}{RT}}$ $K = 2.05\cdot 10^{10}$

Soljution to problem 4-5

a) $IO_3^- + 5\ I^- + 6\ H^+ \longrightarrow 3\ I_2 + 3\ H_2O$

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

$M(KIO_3) = 214$ g/mol $n(KIO_3) = 0.108/214$ mol

leads to $n(I_2) = 3\cdot n(KIO_3) = 3\cdot 0.108/214$ mol

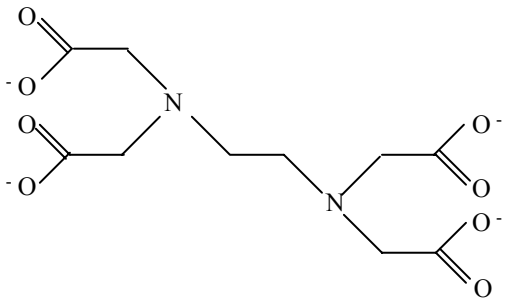
which use $n(S_2O_3^{2-}) = 2\cdot n(I_2) = 2\cdot 3\cdot 0.108/214$ mol

which are found in 20·15.95 mL solution:

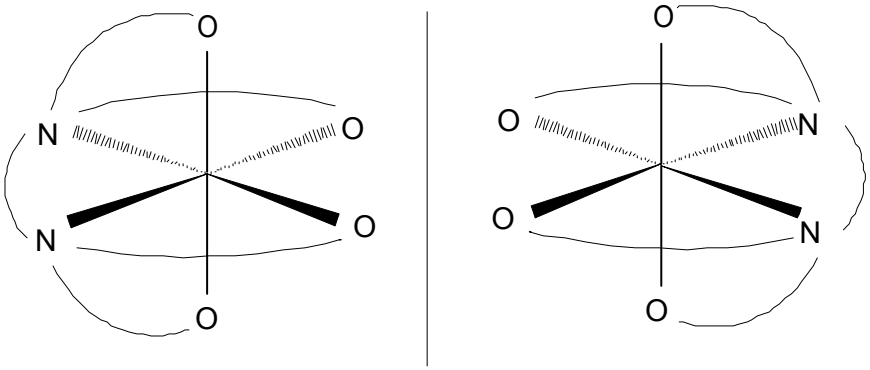
$20\cdot 15.95\cdot 10^{-3}$ L · $c(Na_2S_2O_3$ - solution) = $2\cdot 3\cdot 0.108/214$ mol

$c(Na_2S_2O_3$ - solution) = 0.00949 mol/L ≈ $9.5\cdot 10^{-3}$ mol/L

b) 6 positions to coordinate
(2·N and 4·O^-)



c)



(curved lines between to N atoms: - CH_2 - CH_2 - ,
between an N and an O-atom: - CH_2 - CO -)

As image and mirror image differ the complex is chiral, two enantiomers exist.

d) Determination # 1: $EDTA^{4-} + Cu^{2+} \longrightarrow CuEDTA^{2-}$

$EDTA^{4-} + La^{3+} \longrightarrow LaEDTA^{-}$

determination # 2: $2\ Cu^{2+} + 4\ I^{-} \longrightarrow I_2 + 2\ CuI$

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

e) Determination # 2 leads to the amount of copper, determination # 1 to the sum of copper and lanthanum. (M(Cu) = 63.55 g/mol). M(La) = 138.91 g/mol).

Mass of copper in the parent solution:
$10.50 \cdot 10^{-3}$ L · 0.01 mol/L · 4 · 10 · 63.55 g/mol = **0.267 g copper**

Mass of lanthanum in the parent solution:
$(11.76 \cdot 10^{-3}$ L · 0.1 mol/L - $10.50 \cdot 10^{-3}$ L · 0.01 mol/L · 4) · 10 · 138.91 g/mol
= **1.050 g lanthanum**

f) n(La) = $(11.60 \cdot 10^{-3}$ L · 0.1 mol/L - $10.50 \cdot 10^{-3}$ L · 0.01 mol/L · 4) · 10 = $7.56 \cdot 10^{-3}$ mol

n(Cu) = $10.50 \cdot 10^{-3}$ L · 0.01 mol/L · 4 · 10 = $4.2 \cdot 10^{-3}$ mol

n(La) : n(Cu) = 7.56 : 4.2 = x : 1 **x = 1.8** **$La_{1,8}Ba_{0,2}CuO_4$**

Solution to problem 4-6

a) Number of π electrons: **= 2·x + 10**

Number der bonds: **b = 2·x + 8**

Number of occupied orbitals : **N = (2·x + 10)/2 = x + 5**

b) $\Delta E = E_{N+1} - E_N = \frac{h^2}{8 \cdot m \cdot L^2} \cdot \left[(N+1)^2 - N^2\right] = \frac{h^2 \cdot (2N+1)}{8 \cdot m \cdot (b \cdot I + \gamma)^2}$

$N = x + 5 \qquad b = 2 \cdot x + 8$

$\lambda_{max} = \frac{h \cdot c}{\Delta E}$ $\qquad$ $\boldsymbol{\lambda_{max} = \frac{8 \cdot m \cdot c \cdot \left[(2x+8) \cdot I + \gamma\right]^2}{h \cdot (2x+11)}}$

c) x = 0: $\quad 592.2 \text{ nm} = \frac{8 \cdot m \cdot c \cdot \left[8 \cdot I + \gamma\right]^2}{h \cdot 11} \quad \Leftrightarrow \quad 8 \cdot I + \gamma = 1.405 \text{ nm}$

x = 1: $\quad 706.0 \text{ nm} = \frac{8 \cdot m \cdot c \cdot \left[10 \cdot I + \gamma\right]^2}{h \cdot 13} \quad \Leftrightarrow \quad 10 \cdot I + \gamma = 1.668 \text{ nm}$

I = 0.131 nm $\qquad$ **γ = 0.352 nm**

d) $\Delta E = E_{N+k} - E_N \qquad N = x + 5 \qquad b = 2 \cdot x + 8$

$\Rightarrow \quad \lambda = \frac{8 \cdot m \cdot c \cdot \left[(2x+8) \cdot I + \gamma\right]^2}{k \cdot h \cdot (2x+10+k)}$

x = 3 and k = 2 lead to λ = 438.4 nm, a good approximation, q.e.d.

Solution to problem 4-7

a)

m/z = **98**	$^{28}Si^{35}Cl_2$		
m/z = **99**		$^{29}Si^{35}Cl_2$	
m/z = **100**	$^{28}Si^{35}Cl^{37}Cl$		$^{30}Si^{35}Cl_2$
m/z = **101**		$^{29}Si^{35}Cl^{37}Cl$	
m/z = **102**	$^{28}Si^{37}Cl_2$		$^{30}Si^{35}Cl^{37}Cl$
m/z = **103**		$^{29}Si^{37}Cl_2$	
m/z = **104**			$^{30}Si^{37}Cl_2$

alltogehter a maximum of 7 peaks

b)

M = 49	$^{12}C^1H_2{}^{35}Cl^+$	$0.989 \cdot 0.99985^2 \cdot 0.7577$	= **0.7491**
M+1 = 50	$^{13}C^1H_2{}^{35}Cl^+$	$0.011 \cdot 0.99985^2 \cdot 0.7577$	= 0.00833
	$^{12}C^1H^2H^{35}Cl^+$	$0.989 \cdot 0.99985 \cdot 0.00015 \cdot 0.7577$	= 0.00011
	$^{12}C^2H^1H^{35}Cl^+$		= 0.00011
			= **0.00855**

c) Rel. intensity of M+1 = 50: $\quad (0.00855/0.7491) \cdot 100\%$ $\quad$ **= 1.14%**

d) Base peak $^{11}B^{35}Cl^+$ M = 46 only (B), (C), (D) fulfill this condition

because of 80.1·24.23 > 19.9 · 75.77 the peak of $^{11}B^{37}Cl$ (M+2=48) is the one with the second highest intensity,
only (C), (D) fulfill this condition,

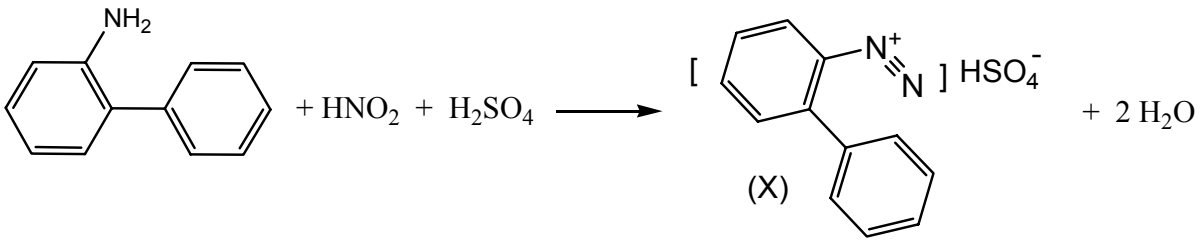
the rel. intensity for this peak is (0.801·0.2423)/(0.801·0.7577)·100% = 32% ⇨ **C**

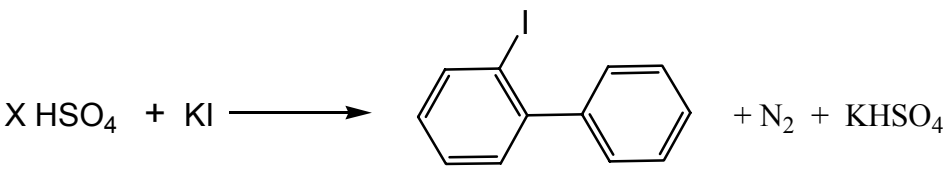
e) we search for the fragment with intentsity(M+1)/intensity(M) = 0.0115

N_2^+	M: $^{14}N_2^+$	$(0.99634)^2$	= 0.9927
	M+1: $^{14}N^{15}N^+$ und $^{15}N^{14}N^+$	$2\cdot0.99634\cdot0.00366$	= 0.007193
	M/M+1		= 0.00735
CO^+	M: $^{12}C^{16}O^+$	$0.989\cdot0.99762$	= 0.9866
	M+!1: $^{13}C^{16}O^+$ und $^{12}C^{17}O^+$	$0.011\cdot0.99762 + 0.989\cdot0.00038$	= 0.01135
	M/M+1:		= 0.0115
CH_2N^+	M: $^{12}C^1H_2{}^{14}N^+$	$0.989\cdot0.99985^2\cdot0.99634$	= 0.9851
	M+1: $^{13}C^1H_2{}^{14}N^+$. $^{12}C^1H^2H^{14}N^+$. $^{12}C^2H^1H^{14}N^+$. $^{12}C^1H_2{}^{15}N^+$		
	$0.011\cdot0.99985^2\cdot0.99634 + 2\cdot0.989\cdot0.99985\cdot0.00015\cdot0.99634 +$		
		$0.989\cdot0.99985^2\cdot0.00366$	= 0.01487
	M/M+1:		= 0.0151

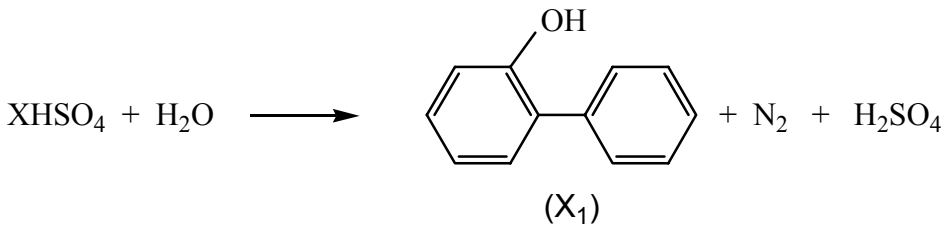
CO^+ only has to be considered.

Solution to problem 4-8

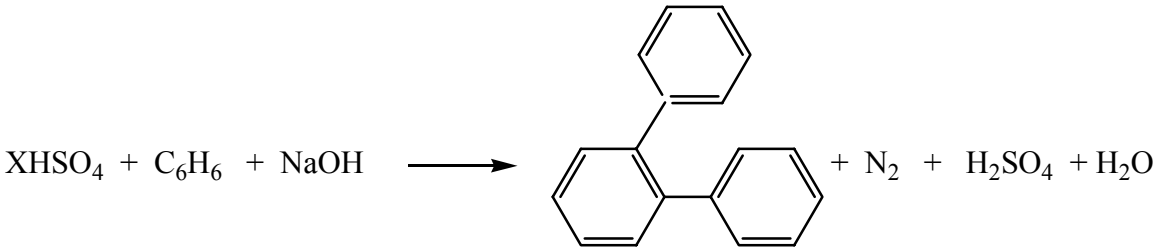




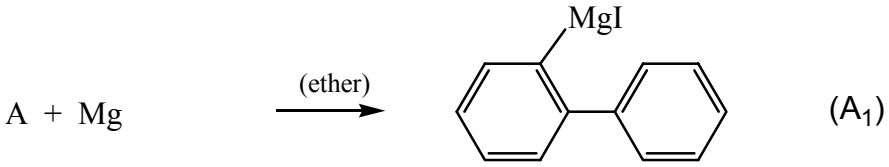
(A)


XHSO4 + H2O
OH
+ N2 + H2SO4

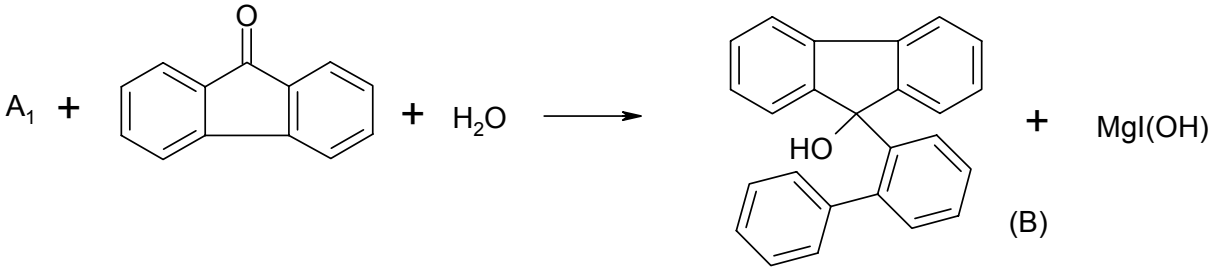
(X_1)


XHSO4 + C6H6 + NaOH
+ N2 + H2SO4 + H2O

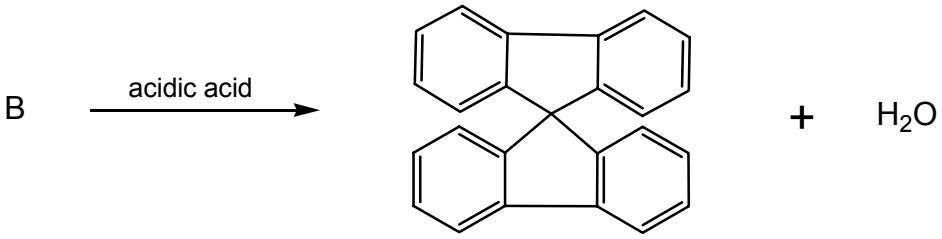
(X_2)


A + Mg
(ether)
MgI

(A_1)


A1 +
O
+ H2O
HO
+ MgI(OH)

(B)

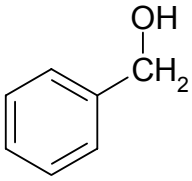

B
acidic acid
+ H2O

(C)

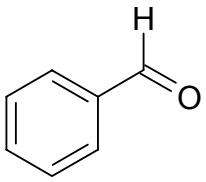
Solution to problem 4-9

a) δ = 2,05 (3 protons; CH_3 group)
δ = 3,66 (2 protons; CH_2 group)
δ = 7,17 (5 protons; 5 CH groups)

b)

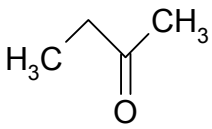


(A) Benzyl alcohol



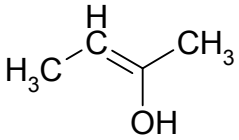
(B) Benzaldehyde

c)

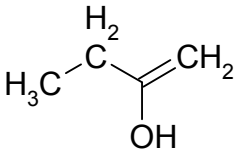


(C) 2-Butanone

d)



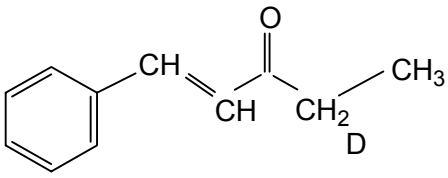
C1/C2



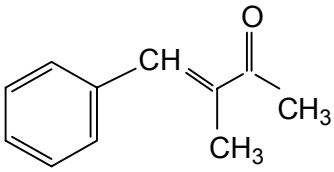
C1/C2

e)

D:



E:



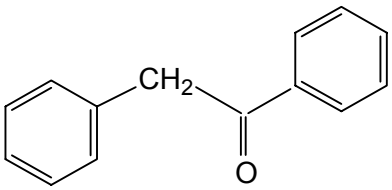
f) Spektrum IV applies to E

reasons: two isolated CH_3 groups, no CH_2 group exists.

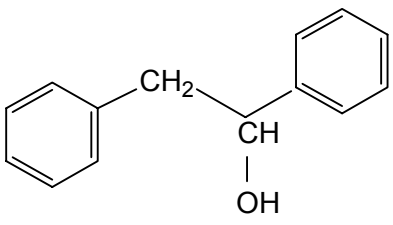
Solution to 4-10

a)

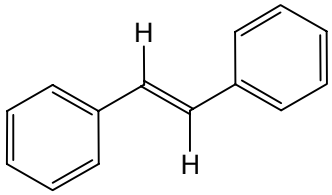
A:



B

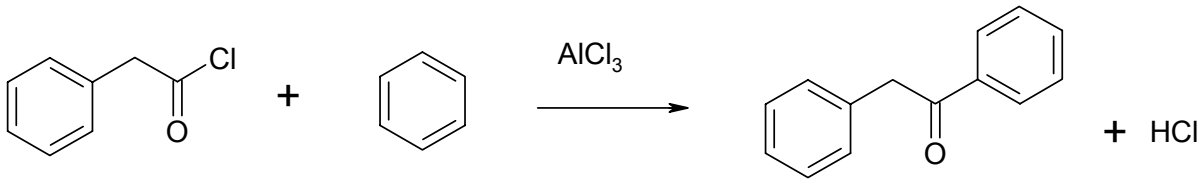


C (trans structure)



Reason for trans structure: steric hindrance of the groups in cis structure.

b)



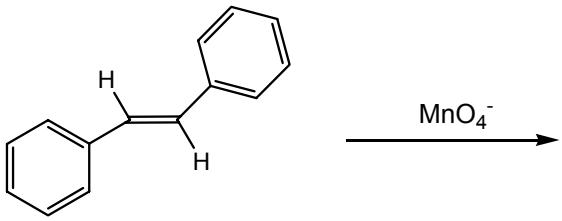
1. Step: ROCL + $AlCl_3$ ⟶ RC ≡ O^+ + $AlCl_4^-$

2. Step: ArH + RC ≡ O^+ ⟶ H-Ar^+-COR (Ar = C_6H_5)

Electrophilic aromatic substitution by RC ≡ O^+

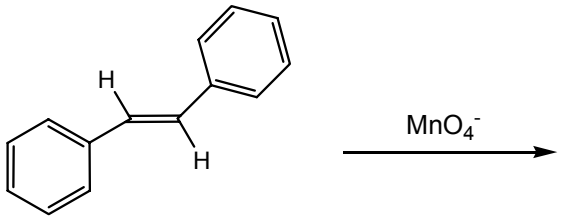
3. Step: H-Ar^+-COR + $AlCl_4^-$ ⟶ Ar-CO-CH_3 * HCl + $AlCl_3$

c) First reaction of C results in D1 and D2



attack from upside

D1

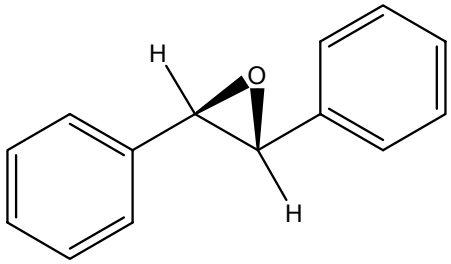


attack from downside

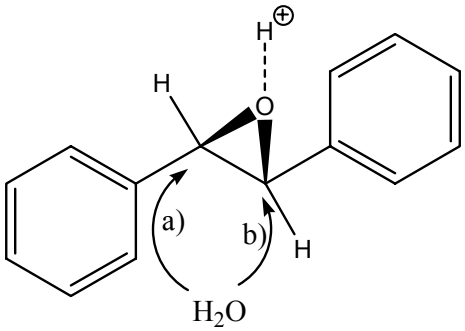
D2

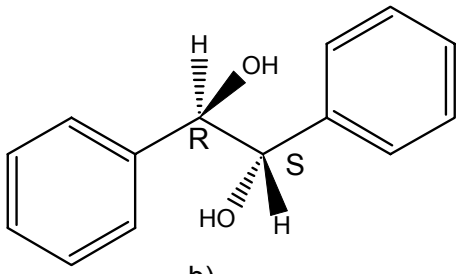
d) Enantiomerism

e) In the second reaction an epoxide forms:

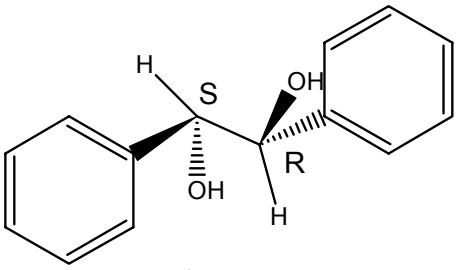


f)





b) Meso compound E1



a)

Both products are identical.

g) The meso compound E1 does not show any optical activity because of an internal mirror plane.

Part 3

榮獲錄選的2005年圖徵設計

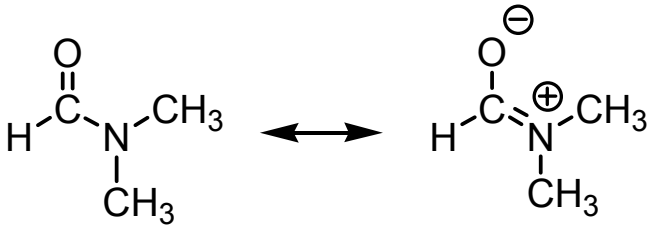
Theoretical Test **2005-07-21**

Practical Test **2005-07-19**

Theoretical Problems

Problem 1: Chemistry of Amides and Phenols

Condensation of a carboxylic acid with an amine gives an amide product. For example, condensation of formic acid with dimethylamine forms *N*,*N*-dimethylformamide (DMF), which can be described as the following resonance structures.



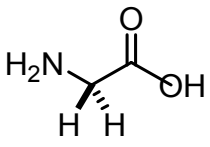
1-1 Predict the order of melting points among N,N-dimethylformamide (compound A), N-methylacetamide ($CH_3CONHCH_3$, compound B), and propionamide ($CH_3CH_2CONH_2$, compound C). Express your answer from high to low melting point as follows:

____ > ____ > ____ *(Insert compound codes A, B, C)*

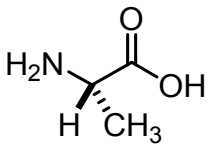
1-2 Carbonyl groups are usually identified by their characteristic strong absorptions in the infrared spectra. The position of the absorption is dependent on the strength of the C=O bond, which in turn is reflected in their bond lengths. In amides, the strength of the carbonyl groups can be shown by the resonance structure noted above. For example, cyclohexanone shows an absorption at 1715 cm^{-1} for the carbonyl group (C=O). In comparison with cyclohexanone, predict the absorption band for the carbonyl group in propionamide. Select your answer from the following choices.
(a) 1660 cm^{-1} because of the shorter carbonyl bond length
(b) 1660 cm^{-1} because of the longer carbonyl bond length
(c) 1740 cm^{-1} because of the shorter carbonyl bond length
(d) 1740 cm^{-1} because of the longer carbonyl bond length

1-3 Glycine (H_2N-CH_2-COOH) is an α-amino acid. Three glycine molecules can form a tripeptide Gly-Gly-Gly via amide linkages, accompanied by elimination of two water molecules. Draw the structural formula of this tripeptide.

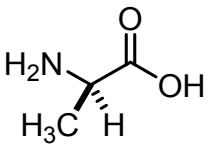
1-4 When an α-amino acid contains a substituent, there is a possibility of optical isomers. For example, L-alanine and D-alanine are two enantiomers. What is the number of all possible linear tripeptides that can be formed from the following three amino acids: glycine, L-alanine and D-alanine as the starting materials in the condensation reaction?



Glycine (Gly)



L-Alanine (L-Ala)



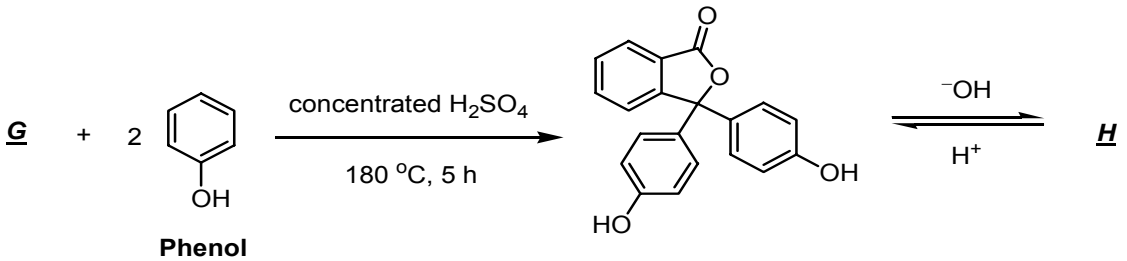
D-Alanine (D-Ala)

1-5 Among the tripeptides synthesized in 1-4, how many are optically active?

Nowadays, polyacrylamide gel associated with electrophoresis (PAGE) was widely used in analyses of proteins and nucleic acids. However, one of the first applications of polyamide gel is the separation of phenol compounds on thin-layer chromatography. The phenol compounds bearing different substituents have varied acidities. The higher acidity results in stronger binding to PAGE gel.

1-6 Predict the binding affinity of phenol (compound D), 4-methylphenol (compound E) and 4-nitrophenol (compound F) with a polyamide gel. Express your answer from high to low binding affinity as follows:
_____>_____> (Insert compound codes D, E, and F)

The absorption maximum of a molecule in its ultraviolet and visible spectrum (UV-vis spectrum) is related to the number of conjugated double bonds in a chain. A compound containing more than 5 conjugated double bonds tends to absorb visible light, and hence shows the complementary color. For example, phenolphthalein is a commonly used acid-base indicator, which is colorless in acidic and neutral solutions, but reddish pink in basic solutions (pH 8.3-10.0).

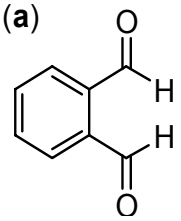


Phenol **Phenolphthalein**

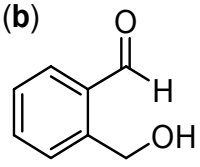
1-7 Draw the structural formula of H derived from phenolphthalein that is attributable to the reddish pink color in aqueous NaOH solution.

1-8 A simple way to prepare phenolphthalein is via condensation of compound G with 2 equivalents of phenol. What is the most effective reagent for G to accomplish this transformation? Select your answer from the following compounds.

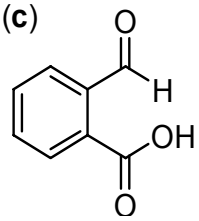
(**a**)



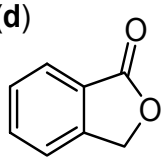
(**b**)



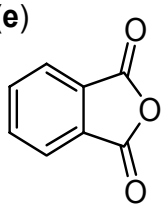
(**c**)



(**d**)

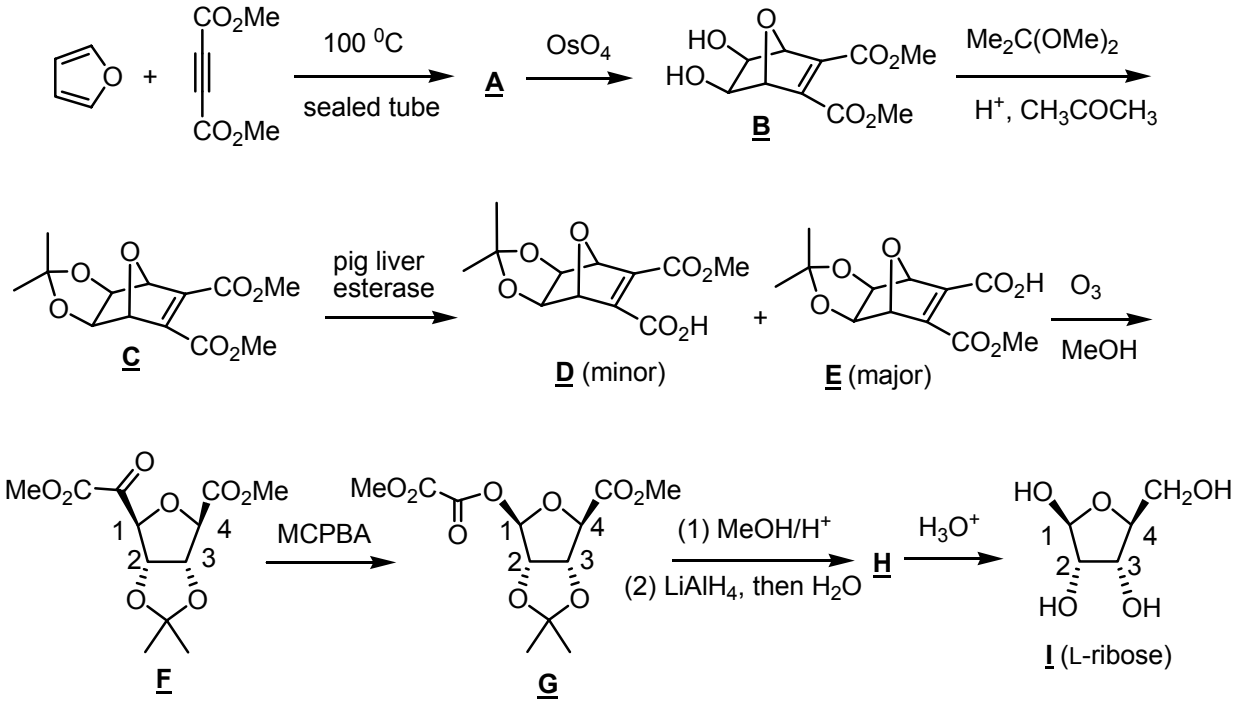


(**e**)



Problem 2: Organic Synthesis and Stereochemistry

Natural carbohydrates are generally produced by photosynthesis in plants. However, unnatural carbohydrates can be prepared by organic synthesis. The following outline is a synthetic scheme for the unnatural L-ribose (compound *I*).



2-1 *Compound A has the molecular formula of $C_{10}H_{10}O_5$. Draw the structural formula of A.*

2-2 *Given the chemistry described for reaction sequence A to C, indicate whether the following statements are true or false (Use T to represent true and F to represent false).*

___ *(a) OsO_4 is an oxidizing agent in the reaction of A to B.*

___ *(b) MeOH is generated as a by-product in the reaction of B to C.*

___ *(c) Protons act as the catalyst in the transformation of B to C.*

___ *(d) C will still be formed albeit in lower yields in the absence of $Me_2C(OMe)_2$.*

Pig liver esterase is an enzyme that can hydrolyze esters to carboxylic acids. Hydrolysis of **C** by the pig liver esterase afforded an enantiomeric mixture of **D** and **E**, in which **E** was the major component. The optical rotation of the mixture was $[\alpha]_D^{20} = -37.1^\circ$. Further purification by recrystallization gave pure **E** with the optical rotation $[\alpha]_D^{20} = -49.0^\circ$.

2-3 *What is the molar ratio of D/E in the product mixture before the recrystallization? Show your work.*

2-4 Reaction of F with meta-chloroperbenzoic acid (MCPBA) afforded G as the product. Indicate whether the following statements are true or false (Use T to represent true and F to represent false).

____ (a) The reaction was to oxidize compound F.

____ (b) The oxygen atom inserted originated from MCPBA.

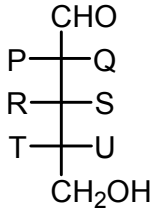
____ (c) The R/S notation of C-1 remained unchanged before and after the reaction.

The molecular formula of **H** is $C_9H_{16}O_5$. Proton NMR data of **H** are listed as follows:
^{1}H NMR ($CDCl_3$) □ 1.24 (s, 3H), 1.40 (s, 3H), 3.24 (m, 1 H), 3.35 (s, 3H), 3.58 (m, 2H), 4.33 (m, 1H); 4.50 (d, *J* = 6 Hz, 1H), 4.74 (d, *J* = 6 Hz, 1H), 4.89 (s, 1H).

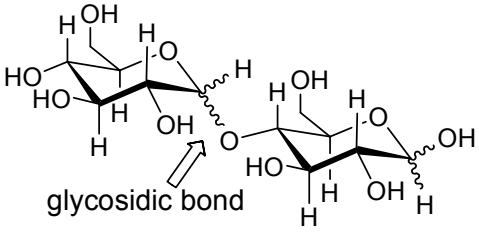
2-5 Draw the configurational formula of H.

2-6 Assign R/S notations for compound I at C-1, C-2, C-3 and C-4.
Give your answers as follows:
C-1: ____; C-2: ____; C-3: ____; C-4: ____.

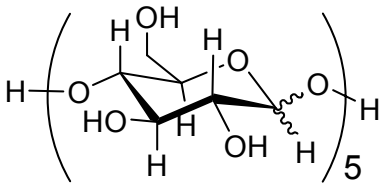
2-7 What are the identities of P, Q, R, S, T and U in the Fischer projection of compound I (L-ribose)?



Disaccharides are compounds with two monosaccharide subunits linked together by a glycosidic bond. Polysaccharides contain as few as ten, or as many as thousands, monosaccharide subunits. An example of a disaccharides is as follows:



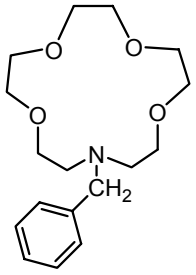
2-8 How many diastereoisomers would be obtained for pentasaccharide J, if it is derived from five units of D-glucose?



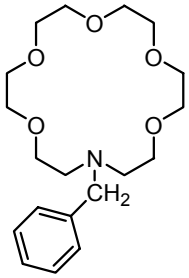
pentasaccharide **J** derived from D-glucose

Problem 3: Organic Photochemistry and Photophysics

Crown ethers show size-dependent binding capability to alkali metal ions. For example, the azacrowns **A** and **B** exhibit different binding constants for Na^+, K^+, and Cs^+.



A

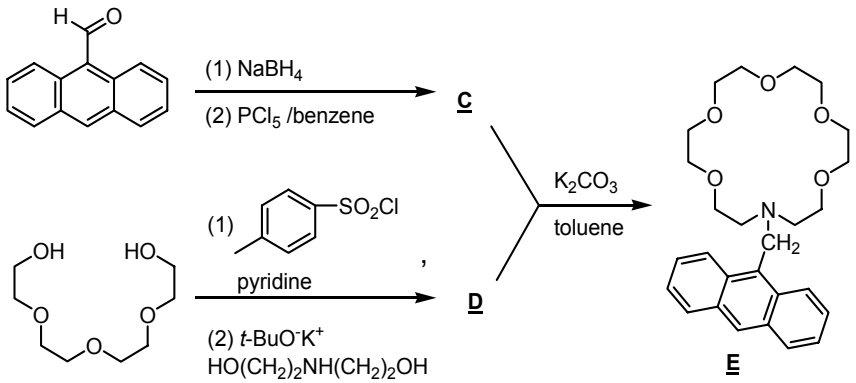


B

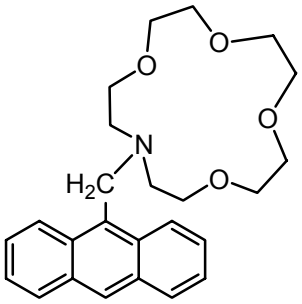
		Binding constant ($\log_{10}$ K)	
Metal ion	Radius (pm)	Compound **A**	Compound **B**
Na^+	98	2.49	3.57
K^+	133	1.83	5.00
Cs^+	165	1.37	3.39

Anthracene exhibits strong fluorescence with emission wavelength centered at 325 nm. Combining the binding selectivity of azacrowns for alkali metal ions and the highly fluorescent anthracene, a metal ion selective fluorescent sensor **E** has been developed.

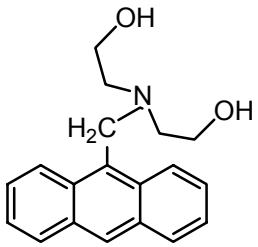
3-1 Provide the structural formula of C and D in the following synthesis.



For comparison studies, the anthracene derivatives **F** and **G** shown below were also synthesized. These compounds **E, F, and G** are almost non-fluorescent in neutral conditions due to the strong photoinduced electron transfer (PET) quenching process arising by donating nitrogen lone-pair electron to the anthracene excited-state.



F



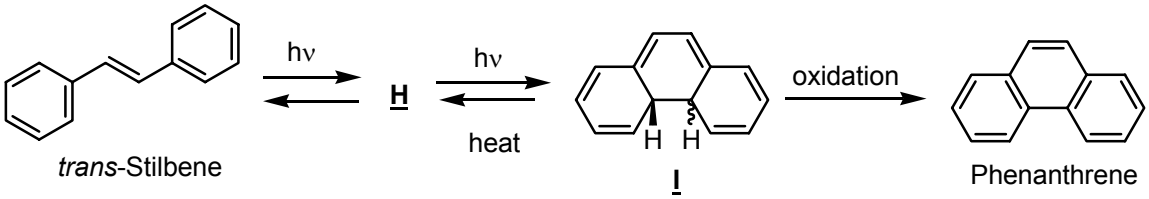
G

3-2 *Upon adding aqueous HCl, which compound will exhibit strong fluorescence? Select your answer from the following choices.*
(a) none of them (b) E and F only (c) G only (d) all of them

3-3 *By adding one equivalent of potassium acetate into a dilute solution (10^{-5} M) of E, F, and G in methanol, respectively, which compound will show the strongest fluorescence? Select your answer from the following choices.*
(a) E (b) F (c) G

3-4 *Upon adding one equivalent of metal acetate to a dilute solution of F, which metal acetate will cause the strongest fluorescence? Select your answer from the following choices.*
(a) sodium acetate (b) potassium acetate (c) cesium acetate (d) doesn't make any difference

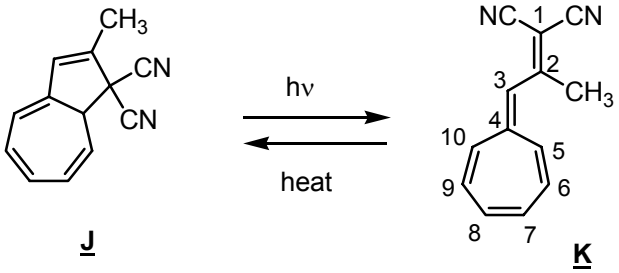
Upon irradiation with ultraviolet light, trans-stilbene is transformed into an intermediate **H**, which undergoes a photocyclization to form dihydrophenanthrene **I**. Further oxidation of **I** gives phenanthrene.



3-5 *Draw the structural formula of compound H?*

3-6 *What is the relative stereochemistry of the two H-atoms shown (cis or trans) in compound I?*

Dihydroazulene derivative **J** exhibits interesting photochromic behavior. Upon irradiation, colorless dihydroazulene **J** undergoes photoinduced rearrangement to the corresponding vinylheptafulvene **K**. The vinylheptafulvene undergoes thermal reversion to dihydroazulene.



J **K**

3-7 Which compound will absorb light with longer wavelength? Select your answer from the following choices.
(a) J (b) K

3-8 Compound K can react with one equivalent of CF_3CO_2H to generate a stable aromatic salt. Which position of K is most likely protonated? Select your answer from the following choices.
(a) C-2 (b) C-3 (c) C-4 (d) C-5

Problem 4: Gold Capital of Asia

A

Chiufen, the old mining town located within the hills in the northeast Taiwan, is a place where you can really experience Taiwan's historical legacy. It was the site of one of the largest gold mines In Asia. Accordingly, Chiufen is often referred to as the Gold Capital of Asia. The compound KCN is traditionally used to extract gold from ore. Gold dissolves in cyanide (CN^-) solutions in the presence of air to form $Au(CN)_2^-$, which is stable in aqueous solution.

$$4\ Au(s) + 8\ CN^-(aq) + O_2(g) + 2\ H_2O(l) \rightleftharpoons 4\ Au(CN)_2^-(aq) + 4\ OH^-(aq)$$

4A-1 Draw a structure for $Au(CN)_2^-$ showing the spatial arrangements of the atoms.

4A-2 How many grams of KCN are needed to extract 20 g of gold from ore? Show your work.

Aqua regia, a 3:1 mixture (by volume) of concentrated hydrochloric acid and nitric acid, was developed by the alchemists as a means to “dissolve” gold. The process is actually a redox reaction with the following simplified chemical equation:

$$Au(s) + NO_3^-(aq) + Cl^-(aq) \rightleftharpoons AuCl_4^-(aq) + NO_2(g)$$

4A-3 Write down the half reactions, and use them to obtain a balanced redox reaction for this process.

4A-4 What are the oxidizing and reducing agents for 4A-3 process?

Gold is too noble to react with nitric acid. However, gold does react with aqua regia because the complex ion $AuCl_4^-$ forms. Consider the following half-reactions:

$$Au^{3+}(aq) + 3\ e^- \longrightarrow Au(s) \qquad E^o = +1.50\ V$$

$$AuCl_4^-(aq) + 3\ e^- \longrightarrow Au(s) + 4\ Cl^-(aq) \qquad E^o = +1.00\ V$$

An electrochemical cell can be formed from these two redox couples.

4A-5 Calculate the formation constant for $AuCl_4^-$ at 25°C:

$K = [AuCl_4^-] / [Au^{3+}]\ [Cl]^4$

4A-6 The function of HCl is to provide Cl^-. What is the purpose of the Cl^- for the above reaction. Select your answer from the following choices.

(a) Cl^- is an oxidizing agent
(b) Cl^- is a reducing agent
(c) Cl^- is a complexing agent
(d) Cl^- is a catalyst

B

Gold Nanoparticles

The synthesis and characterization of gold nanoparticles is currently an active research area. The Brust-Schiffrin method for the synthesis of gold nanoparticle (AuNP) allows the facile preparation of thermally stable and air-stable AuNPs of reduced polydispersity with a controlled size distribution ranging in diameter between 1.5 and 5.2 nm. The preparative procedure is briefly described as follows. An aqueous solution of $HAuCl_4$ is mixed with a toluene solution of tetra-n-octylammonium bromide. The solution is mixed with dodecanethiol and is treated with an excess of $NaBH_4$. Formation of the AuNPs is evidenced by the immediate, pronounced darkening of the toluene phase. After ca. 24 h, the toluene solvent is removed with a rotary evaporator and the resulting solid washed on a frit with ethanol and hexane to remove excess thiol. These AuNPs can be repeatedly isolated and re-dissolved in common organic solvents without irreversible aggregation or decomposition.

4B-1 Is the methodology for this fabrication referred to a top-down or a bottom-up approach? Select your answer from the following choices.

(a) top-down approach, which entails reducing the size of the smallest structures to the nanoscale
(b) bottom-up approach, which involves manipulating individual atoms and molecules into nanostructures

4B-2 The trimethyl-n-octylammonium bromide can also be used as a phase-transfer reagent. It can carry $AuCl_4^-$ from an aqueous phase to an organic phase. Which property does trimethyl-n-octylammonium bromide possess to function as an efficient phase-transfer reagent? Select your answer from the following choices.

(a) one side of the molecule is electropositive, the other side is electronegative.
(b) one side of the molecule is hydrophilic, the other side is hydrophobic.
(c) one side of the molecule is acidic, the other side is basic.

4B-3 What is the function of $NaBH_4$ in this preparation? Select your answer from the following choices.

(a) reducing agent *(b) oxidizing agent*
(c) neutralization agent *(d) complexing agent*

4B-4 If the average diameter of a gold nanoparticle is 3 nm, what is the estimated number of Au atoms in each nanoparticle? (the atomic radius of Au is 0.144 nm). Select your answer from the following choices and show your work.

(a) 10^2 *(b) 10^3* *(c) 10^4* *(d) 10^5*

4B-5 What is the estimated percentage of Au atoms on the surface of a nanoparticle? Select your answer from the following choices and show your work.

(a) 20-30% *(b) 40-50%* *(c) 60-70%* *(d) 80-90%*

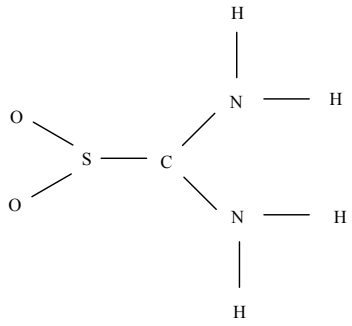
Problem 5: Lewis Structure

5-1 Draw one Lewis structure for each of the following molecules.

(a) N_2 *(b) NH_3* *(c) O_3* *(d) SO_3*

5-2 Draw the Lewis structure of carbon monoxide and assign formal charges and oxidation states to both the carbon and oxygen atoms in carbon monoxide.

Thiourea-S,S-dioxide, $O_2SC(NH_2)_2$, has the following skeletal structure



5-3 Draw the Lewis structure of thiourea-S,S-dioxide with zero formal charges on all atoms.

5-4 Based on the Valence Shell Electron Pair Repulsion (VSEPR) model, what is the geometry around the sulfur, carbon, and nitrogen according to the Lewis structure you predicted from 5-3?

<u>5-4a</u> What is the geometry around the sulfur atom? Select your answer from the following choices.

(a) trigonal pyramidal *(b) triangular planar* *(c) T-shape*

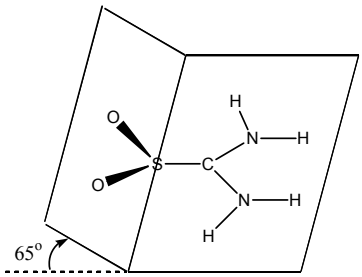
5-4b Similarly, what is the geometry around the C-atom? Select your answer from the following choices.

(a) trigonal pyramidal (b) triangular planar (c) T-shape

5-4c Finally, what is the geometry around the N-atom? Select your answer from the following choices.

(a) trigonal pyramidal (b) triangular planar (c) T-shape

Molecular structure in the solid state is usually determined by X-ray diffraction analysis. According to this method, the structure of thiourea-S,S-dioxide is shown below:



All the N, H atoms are coplanar with S, C atoms, and the dihedral angle between the OSO plane and the $SC(NH_2)_2$ plane is 65°.

5-5 Draw the Lewis structure and resonance forms that are consistent with the geometry determined.

Problem 6: Alkalinity of Water and Solubility of CO_2

The capacity of water to accept H^+ ions is called alkalinity. Alkalinity is important in water treatment and in the chemistry and biology of natural waters. Generally, the basic species responsible for alkalinity in water are HCO_3^-, CO_3^{2-}, and OH^-. At pH values below 7, H^+ in water detracts significantly from alkalinity. Therefore, the complete equation for alkalinity in a medium where HCO_3^-, CO_3^{2-}, and OH^- are the only contributors to alkalinity can be expressed as

$$\text{alkalinity} = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+]$$

The contributions made by different species to alkalinity depend upon pH. Relevant chemical equations and equilibrium constants (at 298 K) are shown below:

$CO_{2(g)}$	$\rightleftharpoons$	$CO_{2(aq)}$	$K_{CO_2} = 3.44\text{x}10^{-2}$
$CO_{2(aq)} + H_2O$	$\rightleftharpoons$	H_2CO_3	$K_{H_2CO_3} = 2.00\text{x}10^{-3}$
H_2CO_3	$\rightleftharpoons$	$HCO_3^- + H^+$	$K_{a1} = 2.23\text{x}10^{-4}$
HCO_3^-	$\rightleftharpoons$	$CO_3^{2-} + H^+$	$K_{a2} = 4.69\text{x}10^{-11}$
$CaCO_{3(s)}$	$\rightleftharpoons$	$Ca^{2+} + CO_3^{2-}$	$K_{sp} = 4.50\text{x}10^{-9}$
H_2O	$\rightleftharpoons$	$H^+ + OH^-$	$K_w = 1.00\text{x}10^{-14}$

6-1 Natural waters (river or lake water) generally contain dissolved CO_2. The ratio of $[H_2CO_3] : [HCO_3^-] : [CO_3^{2-}]$ in a water at $[H^+] = 1.00 \times 10^{-7}$ M will be: (a) : 1.00 : (b). Calculate (a) and (b).

6-2 Gaseous CO_2 in the atmosphere can be regarded as a contributor to the alkalinity of water in equilibrium with air. Calculate the concentration of $CO_{2\,(aq)}$ (mol/L) in pure water that is in equilibrium with the unpolluted air at 1.01 x 10^5 Pa and 298 K containing 0.0360% (molar ratio) CO_2. (assuming standard pressure = 1.01 x 10^5 Pa)

The solubility (S) of CO_2 in water can be defined as $S=[CO_{2(aq)}] + [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}]$. The solubility of atmospheric CO_2 in water that is in equilibrium with the unpolluted air at 298 K and 1.01 x 10^5 Pa will vary with alkalinity.

6-3 Find the solubility of atmospheric CO_2 in pure water (mol/L). Neglect dissociation of water.

6-4 Find the solubility of atmospheric CO_2 in water (mol/L) initially containing 1.00x10^{-3} mol/L NaOH.

At 298 K, 1.01 x 10^5 Pa unpolluted air is in equilibrium with natural water saturated with $CaCO_3$. The following main equilibrium may exist:

$$CaCO_{3(s)} + CO_{2\,(aq)} + H_2O \rightleftarrows Ca^{2+} + 2HCO_3^-$$

6-5 Calculate the equilibrium constant for the above equation.

6-6 Calculate the concentration of Ca^{2+} (mg/L) in $CaCO_3$-saturated natural water that is in equilibrium with atmospheric CO_2.

6-7 Find the alkalinity (mol/L) of the above solution.

6-8 In an underground lake saturated with $CaCO_3$, the water has a high content of CO_2. The concentration of Ca^{2+} in this lake was found to be as high as 100 mg/L. Assume the lake and the air above is a closed system, calculate the effective pressure of CO_2 (Pa) in air which is in equilibrium with this Ca^{2+} content.

Problem 7: Kinetic Behavior of Ozone

Ozone (O_3) is a form of oxygen. It is a natural component of the stratosphere, where it shields the earth from life-destroying ultraviolet radiation. On absorbing light in this region, ozone is converted to dioxygen molecules.
For the overall reaction of ozone decomposition, $2O_3 \rightarrow 3O_2$.

One of the proposed mechanisms is expressed as

$$O_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} O + O_2 \qquad (1)$$

$$O_3 + O \xrightarrow{k_2} 2O_2 \qquad (2)$$

where k_1, k_{-1}, and k_2 are the rate constants.

7-1 *According to the above mechanism what are the differential rate equations for the formation (or consumption) of O_3, O_2, and O at time t, assuming step 2 is irreversible.*

7-2 *Simplification in obtaining the rate law may be found by making appropriate assumptions. Assuming that the concentration of O atoms reaches equilibrium rapidly, its concentration may be given by the equilibrium constant of the reaction (1). The second step is rate determining. Under this equilibrium approximation, deduce the differential rate equation for the O_3 depletion as a function of O_2 and O_3 concentrations.*

7-3 *Another assumption frequently made is that the rates of oxygen atom production and consumption are equal (this is called steady state). Under the steady state approximation, that is d[O]/dt = 0, show that the rate equation is:*

$$-\frac{d[O_3]}{dt} = \frac{2k_1k_2[O_3]^2}{k_{-1}[O_2] + k_2[O_3]}.$$

One pathway for the destruction of ozone ($2O_3 \longrightarrow 3O_2$) in the upper atmosphere is catalyzed by Freons. For instance, when CCl_2F_2 (Freon-12) migrates to the upper atmosphere, the ultraviolet photolysis of CCl_2F_2 may give rise to Cl atoms according to the following reaction:

$$CCl_2F_2 \xrightarrow{h\nu} CF_2Cl + Cl \qquad (3)$$

7-4 *Chlorine atom can act as a catalyst for the destruction of ozone. The first slow step of a Cl-catalyzed mechanism is proposed as follows:*

$$Cl_{(g)} + O_{3(g)} \rightarrow ClO_{(g)} + O_{2(g)} \qquad (4)$$

Assuming a two-step mechanism, propose the second step in the mechanism.

7-5 *The activation energy for Cl-catalyzed destruction of ozone is 2.1 kJ/mol, while the activation energy for the reaction without the presence of catalyst is 14.0 kJ/mol. Estimate the ratio of the rate constant for the catalyzed reaction to that for the uncatalyzed reaction at 25 ^{o}C. Assume the frequency factor is the same for each reaction.*

Problem 8: Protein Folding

Most proteins exist usually only in two forms, the native form (N) and the unfolded form (U) when they are thermally or chemically denatured, without appreciable concentrations of other stable intermediates in equilibrium with the native and unfolded forms. For these proteins, the folding-unfolding equilibrium can be described by the following simple chemical equation:

$$\mathbf{N} \underset{}{\overset{K(T)}{\rightleftharpoons}} \mathbf{U}$$

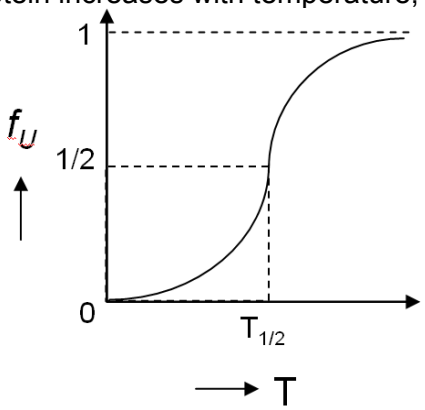
where N and U denote the folded state (native state) and the unfolded state (denatured state) of the protein, respectively. K(T) is the equilibrium constant for the process at absolute temperature T.

8-1 What is the equilibrium constant for the process when the native and denatured states are present in equal proportions at equilibrium?

8-2 What is the standard free energy change of the process ($\Delta G°(T)$) when the native and denatured states are present in equal proportions at equilibrium? Express your answer in SI units.

8-3 If $(C_N)_{eq}$ and $(C_U)_{eq}$ denote the equilibrium concentrations of N and U in solution, respectively, and C is the total concentration of the protein, the fraction of the total protein that is unfolded under the equilibrium condition is given by $f_U = (C_U)_{eq}/C$. Deduce an expression for f_U in terms of the equilibrium constant K. Show all work on the answer sheet.

When a protein is denatured by increasing the temperature of the solution, the fraction of the unfolded protein increases with temperature, as shown in the following Figure.



The mid-point of the denaturation curve is given by $f_U = ½$ and $T = T_{½}$. The latter is often referred to as the denaturation temperature. At temperatures higher than $T_{½}$, f_U increases above ½, but at temperatures lower than $T_{½}$, f_U decreases below ½.

8-4 What is the sign of $\Delta G°(T)$ at temperatures below and above $T_{½}$? Select your answer from the following choices.

(a) Negative both below and above $T_{½}$

(b) Positive both below and above $T_{½}$

(c) Positive below $T_{½}$, but negative above $T_{½}$

(d) Negative below $T_{½}$, but positive above $T_{½}$.

8-5 How does the standard Gibbs free energy change for the process vary when the temperature (i) increases above $T_{1/2}$ and (ii) decreases below $T_{½}$? Select your answer from the following choices.

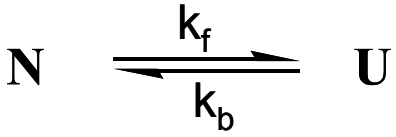
(a) Decrease in both cases.

(b) Increase in both cases.

(c) Increases above $T_{½}$, but decreases below $T_{½}$

(d) Decreases above $T_{½}$, but increases below $T_{½}$

The kinetics of unfolding and refolding of a protein has recently become an intense area of study. We could rewrite the chemical equation for the process as follows:



where k_f and k_b denote the forward and backward reaction rate constants, respectively., assuming that both the forward and reverse processes are elementary steps that follow first-order kinetics.

8-6 For the simple chemical equation and elementary kinetic steps used to describe the protein folding-unfolding process outlined above, what is the relationship between equilibrium constant K and the rate constants k_f and k_b?

8-7 Derive a rate law for the overall process, that is dC_U/dt in terms of only rate constants, C_U and $(C_U)_{eq}$.

Solutions to the Theoretical Problems

Solution to problem 1

1-1 C > B > A

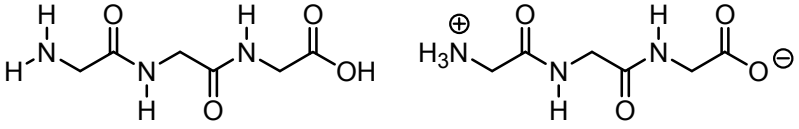
The resonance structure of amide shows a partial negative charge on oxygen and a partial positive charge on nitrogen. Primary and secondary amides also participate in strong hydrogen bondings, but not tertiary amide.

Ref. L. G. Wade, Jr., Organic Chemistry, 4th ed., p. 956.

Propionamide, mp = 79 °C; *N*-methylacetamide, mp = 28 °C; *N*,*N*-dimethylformamide, mp = - 61 °C.

1-2 (b) 1660 cm^{-1} due to a longer carbonyl bond length

1-3



Gly-Gly-Gly or **Gly-Gly-Gly**

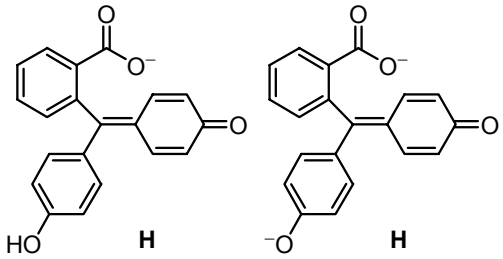
1-4 There are 27 possible tripeptides.

1-5 Among them, 26 tripeptides are optically active.

Optically inactive tripeptide: H_2N-GGG-OH

1-6 The relative binding strength with polyamide gel for phenol (compound D), 4-methylphenol (compound E) and 4-nitrophenol (compound F) is: F > D > E

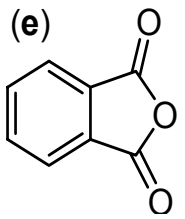
1-7



H **H**

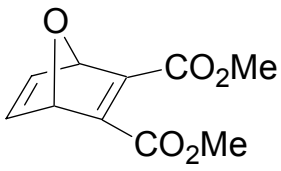
The range pH 8.3-10.0 for color change of phenolphthalein.

1-8



Solution to problem 2

2-1



2-2 T (a) OsO_4 is an oxidizing agent in the reaction of A to B.

T (b) MeOH is generated as a by-product in the reaction of B to C.

T (c) Protons act as the catalyst in the transformation of B to C.

T (d) C will still be formed albeit in lower yields in the absence of $Me_2C(OMe)_2$

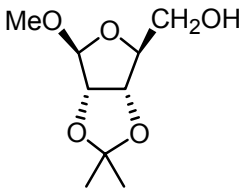
2-3 12.1 : 87.9 or 12.2 : 87.8

2-4 T (a) The reaction was to oxidize compound F.

T (b) The oxygen atom inserted originated from MCPBA.

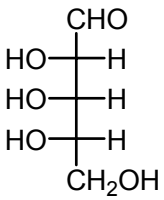
F (c) The R/S notation of C-1 remained unchanged before and after the reaction.

2-5



2-6 C-1: S ; C-2: S ; C-3: R ; C-4: S .

2-7

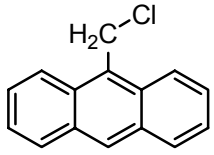


2-8 2^5

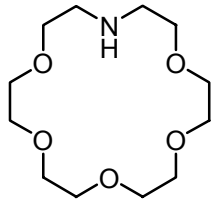
Solution to problem 3

3-1

C:

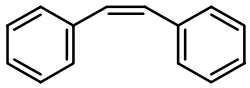


D:



3-2 (d) all of them **3-3** (a) E **3-4** (a) sodium acetate

3-5

H: 

3-6 trans **3-7** (b) K **3-8** (b) C-3

Solution to problem 4

4A-1 The structure of $Au(CN)_2^-$ is linear.

$[\ N\equiv C-\!\!-Au-\!\!-C\equiv N\ ]^-$

4A-2 13.024 g

Calculation: $4\ Au + 8\ KCN + O_2 + 2\ H_2O \rightleftarrows 4\ Kau(CN)_2 + 4\ KOH$

$20\ g \div 197\ g/mol \approx 0.10\ mol\ (Au)$

$0.10\ mol \times (8/4) \times 65.12\ g/mol = 13.024\ g\ (KCN)$

4A-3 Oxidation $Au + 4\ Cl^- \longrightarrow AuCl_4^- + 3\ e^-$

Reduction $3\ NO_3^- + 6\ H^+ + 3\ e^- \longrightarrow 3\ NO_2 + 3\ H_2O$

$Au + 3\ NO_3^- + 6\ H^+ + 4\ Cl^- \rightleftarrows AuCl_4^- + 3\ NO_2 + 3\ H_2O$

4A-4 oxidizing agent: $HN\square_3$. reducing agent: Au

4A-5 $K = 10^{25.42} = 2.6 \times 10^{25}$

Calculation: $Au^{3+} + 3\ e^- \longrightarrow Au$ $E_1° = +1.50\ V$

$AuCl_4^- + 3\ e^- \longrightarrow Au + 4\ Cl^-$ $E_2° = +1.00\ V$

$Au + Au^{3+} + 4\ Cl^- \rightleftarrows AuCl_4^-$ $E_3° = +0.50\ V$

$E = E_3^\circ - (0.059/n)\ logQ$

at equilibrium, $Q = K$ $E = 0$ $K = [AuCl\square^-] / [Au^{3+}]\ [Cl^-]^4$

$E_3^\circ = (0.059/n)\ logK$, $0.50 = (0.059/3)\ logK$, $K = 10^{25.42} = 2.6 \times 10^{25}$

4A-6 (c)

4B-1 (b) **4B-2** (b) **4B-3** (a)

4B-4 (b) 10^3 Calculation: $V_{AuNPs} = 4/3 \cdot \pi \cdot r^3_{AuNPs}$

$V_{Au} = 4/3 \cdot \pi \cdot r^3_{Au}$

$$\Rightarrow \quad N_{Au} = \frac{V_{AuNPs}}{V_{Au}} = \left(\frac{r_{AuNPs}}{r_{Au}}\right)^3 = \left(\frac{15\,\text{Å}}{1.44\,\text{Å}}\right)^3 \approx 1000$$

4B-5 (b) 40-50%

Calculation:

Method 1:

$4/3 \times \pi \times r_{AuNPs}^3 = 4/3 \times \pi \times r_{Au}^3 \times N_{Au}$ $\therefore r_{AuNPs}^3 = r_{Au}^3 \times N_{Au}$

Surface area of a gold nanoparticle: $S_{AuNPs} = 4\pi r_{AuNPs}^2$

$\Rightarrow S_{AuNPs} = 4\pi r_{Au}^2 N_{Au}^{2/3}$

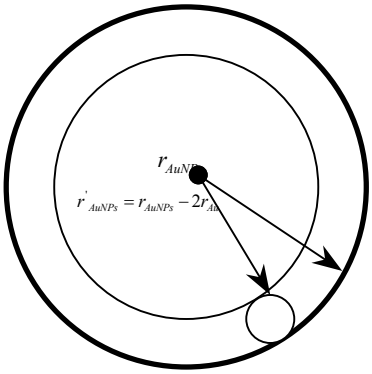
$N_S \approx S_{AuNPs} / \pi r_{Au}^2 = 4 N_{Au}^{2/3}$

$P \approx N_S / N_{Au} = 4/ N_{Au}^{1/3}$

$N_{Au} \approx 1000$

$P \approx 40\%$

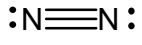
Method 2:



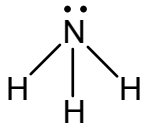
$$P\% \approx \frac{\frac{V_{AuNPs}}{V_{Au}} - \frac{V'_{AuNPs}}{V_{Au}}}{\frac{V_{AuNPs}}{V_{Au}}} \times 100\% = \frac{\left(\frac{r_{AuNPs}}{r_{Au}}\right)^3 - \left(\frac{r'_{AuNPs}}{r_{Au}}\right)^3}{\left(\frac{r_{AuNPs}}{r_{Au}}\right)^3} \times 100\% = \frac{\left(15\,\text{Å}\right)^3 - \left(12.12\,\text{Å}\right)^3}{\left(15\,\text{Å}\right)^3} \times 100\% \approx 47\%$$

Solution to problem 5

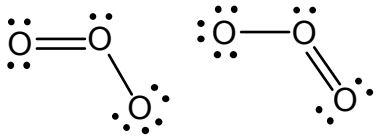
5-1 a)



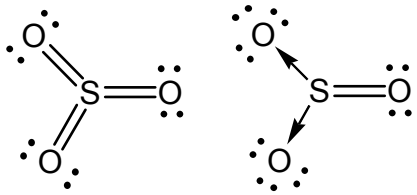
b)



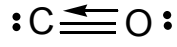
c)



d)



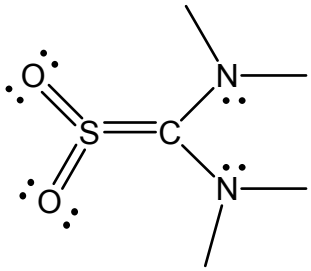
5-2



Formal charge C^{-1} ; O^{+1}

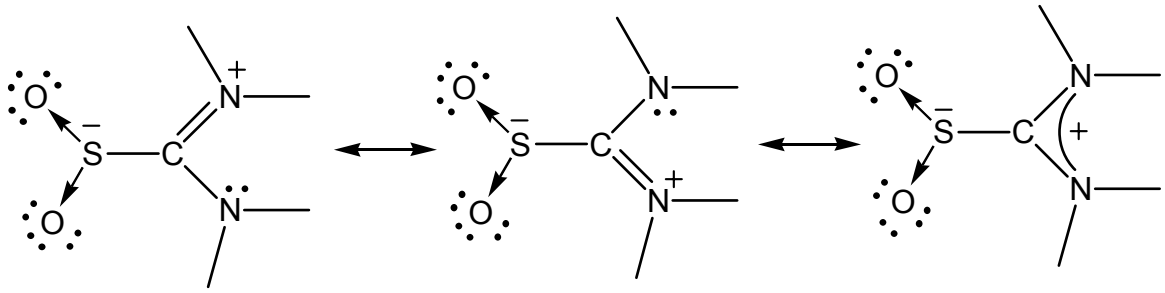
Oxidation state C^{2+} ; O^{2-}

5-3



5-4 S: (b) trigonal planar C: (b) trigonal planar N: (a) trigonal pyramidal

5-5



Solution to problem 6

6-1 $[H^+] = 1.00\times10^{-7}$ mol/L

$K_{a1} = [HCO_3^-][H^+] / [H_2CO_3] = 2.23\times10^{-4}$, $[HCO_3^-]/ [H_2CO_3] = 2.23\times10^{3}$

$K_{a2} = [CO_3^{2-}][H^+] / [HCO_3^-] = 4.69\times10^{-11}$, $[CO_3^{2-}]/ [HCO_3^-] = 4.69\times10^{-4}$

⇨ $[H_2CO_3] : [HCO_3^-] : [CO_3^{2-}] = 4.48\times10^{-4} : 1.00 : 4.69\times10^{-4}$

(a) (b)

6-2 $P_{CO_2} = (1.01\times10^5 \text{ Pa}) \times 3.60\times10^{-4} = 36.36$ Pa

$[CO_{2(aq)}] = K_{CO_2} \times P_{CO_2} = 0.0344 \times (36.36 \text{ Pa}/1.01\times10^5 \text{ Pa}) = 1.24\times10^{-5}$ mol/L

6-3 Solubility $= [CO_{2(aq)}] + [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}]$

($[H_2CO_3] = [CO_{2(aq)}] \cdot K_{H_2CO_3} = 2.48\times10^{-8}$ mol/L and

$[CO_3^{2-}] = K_{a2} / ([H^+]/[HCO_3^-]) = K_{a2} = 4.69\times10^{-11}$ mol/L,

both can be neglected)

$\approx [CO_{2(aq)}] + [HCO_3^-]$

$[H^+][HCO_3^-] / [CO_{2(aq)}] = K_{a1}K_{H_2CO_3} = (2.23\times10^{-4})\cdot(2.00\times10^{-3}) = 4.46\times10^{-7}$

From 6-2, $[CO_{2(aq)}] = 1.24\times10^{-5}$ mol/L,

$[H^+] = [HCO_3^-] = 2.35\text{x}10^{-6}$ mol/L

⇨ Solubility = $[CO_{2(aq)}] + [HCO_3^-] = 1.24\text{x}10^{-5} + 2.35\text{x}10^{-6} = 1.48\text{x}10^{-5}$ mol/L

6-4 In $1.00\text{x}10^{-3}$ mol/L NaOH solution, the solubility of CO_2 will be much higher because of the following reactions

(1) $CO_{2(aq)} + 2OH^- \square CO_3^{2-} + H_2O$ $\quad K = K_{H2CO3}\text{x}\ K_{a1}\text{x}\ K_{a2}/(1.00\text{x}10^{-14})^2 = 2.09\text{x}10^{11}$

(2) $CO_{2(aq)} + CO_3^{2-} + H_2O \square 2HCO_3^-$ $\quad K = K_{H2CO3}\ \text{x}\ K_{a1}/K_{a2} = 9.37\text{x}10^3$

Combining (1) and (2): $CO_{2(aq)} + OH^- \square HCO_3^-$ $\quad K = 4.43\text{x}10^7$

With such a large K value, all OH^- will finally be converted to HCO_3^-.

⇨ $[HCO_3^-] \square 1.00\text{x}10^{-3}$ mol/L

$[OH^-] = 1.82\text{x}10^{-6}$ mol/L $\quad [H^+] = 5.49\text{x}10^{-9}$ mol/L

$[CO_3^{2-}] = 8.54\text{x}10^{-6}$ mol/L

⇨ Solubility = $[CO_{2(aq)}] + [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}]$

≈ $[CO_{2(aq)}] + [HCO_3^-] + [CO_3^{2-}] = 1.24\text{x}10^{-5} + 1.00\text{x}10^{-3} + 8.54\text{x}10^{-6} = 1.02\text{x}10^{-3}$ mol/L

6-5 $K_{eq} = K_{sp}\cdot K_{H_2CO_3}\cdot K_{a1}/K_{a2} = (4.50\cdot10^{-9})\cdot(2.00\cdot10^{-3})\cdot(2.23\cdot10^{-4})/(4.69\cdot10^{-11}) = 4.28\cdot10^{-5}$

6-6 Mass balance $\square$ $[HCO_3^-] = 2[Ca^{2+}]$

From 6-5, $K = 4.28\text{x}10^{-5} = [Ca^{2+}][HCO_3^-]^2/[CO_{2(aq)}] = [Ca^{2+}](2[Ca^{2+}])^2 / [CO_{2(aq)}]$

From 6-2, $[CO_{2(aq)}] = 1.24\text{x}10^{-5}$ mol/L,

⇨ $[Ca^{2+}] = 0.510\text{x}10^{-3}$ mol/L = 20.5 mg/L

6-7 HCO_3^- is the major species in solution.

The pH of the solution can be estimated as pH = $(pK_{a1} + pK_{a2})/2 = (3.65 + 10.33)/2 =$ 6.99 ≈ 7.00, where K_{a1} and K_{a2} are the dissociation constants of H_2CO_3.

At pH 7.00, both $[OH^-]$ and $[H^+]$ can be neglected.

Besides, $[CO_3^{2-}] << [HCO_3^-]$ (from 6-1)

Alkalinity = $[HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+] \approx [HCO_3^-]$

From 6-6, mass balance, $[HCO_3^-] = 2[Ca^{2+}]$

Alkalinity = $1.02\text{x}10^{-3}$ mol/L

6-8 Mass balance $\square$ $[HCO_3^-] = 2[Ca^{2+}]$

$[Ca^{2+}] = 100$ mg/L = $2.50\text{x}10^{-3}$ mol/L

Inserting into $K_{eq} = 4.28\text{x}10^{-5} = [Ca^{2+}][HCO_3^-]^2 / [CO_{2(aq)}] = 4[Ca^{2+}]^3/[CO_{2(aq)}]$

$[CO_{2(aq)}] = 1.46\text{x}10^{-3}$ mol/L

$P_{CO_2} = ([CO_{2(aq)}] / K_{CO_2})\ \text{x}\ 1.01\text{x}10^5$ Pa = $4.28\text{x}10^3$ Pa

Solution to problem 7

7-1

$$-\frac{d[O_3]}{dt} = k_1[O_3] - k_{-1}[O][O_2] + k_2[O_3][O]$$

$$-\frac{d[O_2]}{dt} = -k_1[O_3] + k_{-1}[O][O_2] - 2k_2[O_3][O]$$

$$-\frac{d[O]}{dt} = -k_1[O_3] + k_{-1}[O][O_2] + k_2[O_3][O]$$

7-2

$$K = \frac{[O][O_2]}{[O_3]} = \frac{k_1}{k_{-1}} \qquad [O] = \frac{k_1[O_3]}{k_{-1}[O_2]}$$

$$-\frac{d[O_3]}{dt} = k_2[O_3][O] = \frac{k_1 k_2[O_3]^2}{k_{-1}[O_2]}$$

7-*3*

$$-\frac{d[O]}{dt} = 0$$

$$-k_1[O_3] + k_{-1}[O][O_2] + k_2[O_3][O] = 0$$

$$-\frac{d[O_3]}{dt} = 2k_2[O_3][O] = \frac{2k_1 k_2[O_3]^2}{k_{-1}[O_2] + k_2[O_3]}$$

7-4 $ClO_{(g)} + O_{3(g)} \longrightarrow Cl_{(g)} + 2O_{2(g)}$

7-5 According to equation $k = A \cdot e^{(-Ea/RT)}$,
the ratio of rate constants yields Ratio=$e^{(14.0-2.1)x1000/(8.314x298)}$ = 122.

Solution to problem 8

8-1 1 **8-*2*** 0 kJ/mol $f_U \quad \frac{C_U^{eq}}{C_N^{eq} + C_U^{eq}} = \frac{C_U^{eq}/C_N^{eq}}{1 + C_U^{eq}/C_N^{eq}} = \frac{K}{1+K}$

8-*4* (c) Positive below $T_{½}$, but negative above $T_{½}$

8-*5* (d) Decreases above $T_{½}$, but increases below $T_{½}$

8-*6* $K = k_f / k_b$

8-7 $dC_U/dt = k_f C_N - k_b C_U$

$$= k_f(C - C_U) - k_bC_U = k_fC - k_fC_U - k_bC_U = k_fC - (k_f + k_b)C_U \quad (1)$$

$K = k_f/k_b = (C_U)_{eq}/(C_N)_{eq}$

$1/K = k_b/k_f = (C_N)_{eq}/(C_U)_{eq}$

$\Rightarrow \quad k_b/k_f + 1 = (C_N)_{eq}/(C_U)_{eq} + 1$

$\Rightarrow \quad (k_b + k_f)/k_f = [(C_N)_{eq} + (C_U)_{eq}]/(C_U)_{eq}$

$\Rightarrow \quad (k_b + k_f)/k_f = C/(C_U)_{eq}$

$C = [(k_b + k_f)(C_U)_{eq}]/k_f \quad (2)$

Now substitute C obtained from eq 2 to eq 1.

$k_f\{[(k_b + k_f)(C_U)_{eq}]/k_f\} - (k_f + k_b)C_U$

$\Rightarrow \quad [(k_b + k_f)(C_U)_{eq}] - (k_f + k_b)C_U$

$\Rightarrow \quad -(k_f + k_b)[C_U - (C_U)_{eq}]$

So we get

$dC_U/dt = -(k_f + k_b)[C_U - (C_U)_{eq}] dC_u/dt = -(k_f + k_b)[C_u - (C_u)_{eq}]$

Practical Problems

Experiment 1: Organic synthesis

Equipment list

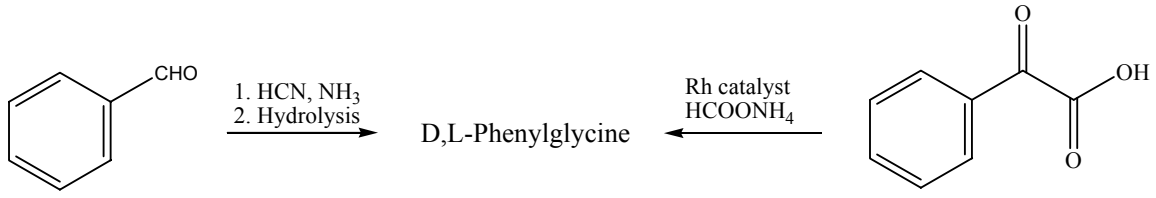
equipment	No.	equipment	No.
Hot plate/stirrer with stand	1	Weighing paper	10
Stirrer	2	Sample vial (20 mL) (blue label labelled with your student code and 1H NMR)	1
Stirrer retriever	Shared by 2 persons	Sample vial (20 mL) (pink label labelled with your student code and [□]D)	1
Filtration pump	Shared by 2 persons	Glass rod	1
Clamp with holder	3	Spatula	2
thermometer	1	Septa	2
Pasteur pipette	5	Water bath (stainless steel)	1
Pipette bulb	2	Ice bath (Styrofoam)	1
Graduated cylinder (10 mL)	1	Needle	1
Graduated cylinder(25 mL)	1	Water bottle with Deionized H_2O	1
Round bottom flask (25 mL)	1	Glove (cotton)	1 pair
Round bottom flask (50 mL)	1	Glove (latex) on central bench	
Filter, Fritted (50 mL) (labelled with your student code)	1	Flask holder	1 pc
Filter, Fritted (70 mL) (labelled with your student code)	1	Paper towel	1 roll
Filtration flask with rubber (250 mL)	1	Kimwipes	1 box
Condenser	1	Glass funnel	1
Teflon sleeve for condenser *(you can trim off 1 cm from the smaller end for a better fit)*	1	Beaker (800 mL)	1
Safety goggles	1	Beaker (400 mL)	1

Chemical list

chemicals	formula	formula weight	amount	Risk statements	Safety statements
ethanol	C_2H_5OH	46.07	50 mL	11	7-16
pre-mixed solvents ethylene glycol:ethanol (2:9)	$(CH_2OH)_2$	-	50 mL	22	-
benzoylformic acid	$C_8H_6O_3$	150.13	written on sample vial	36/37/38	26-28-36
ammonium formate	HCO_2NH_4	63.06	7.57 g	36/37/38	26-36
D,L-phenylglycine	$C_8H_9NO_2$	151.16	written on sample vial (to be provided for step 2)	-	22-24/25
Pentamethylcyclopentadienyl-rhodium(III) chloride, dimer	$[(CH_3)_5C_5RhCl_2]_2$	-	37.2 mg	20/21/22, 36/37/38	26, 36
(1*S*)-(+)-10-camphorsulfonic acid (+)-(CSA)	$C_{10}H_{16}O_4S$	232.30	1.80 g	34	26-36/37/39-45

The Synthesis of D,L-Phenylglycine and Its Enantiomeric Resolution

One of the enantiomeric forms of phenylglycine is an important raw material for the preparation of β-lactam antibiotics. Industrial production of optically active phenylglycine is prepared by the Andeno process. The starting benzaldehyde was treated with HCN/NH_3 following hydrolysis to give the racemic D,L-phenylglycine. The desired enantiomeric phenylglycine was then resolved by (+)-camphorsulfonic acid [(+)-CSA].



Benzaldehyde D,L-phenylglycine Benzoylformic acid

In this experiment, you are going to synthesize racemic D,L-phenylglycine (also referred to as R- and S- isomers, respectively) from an alternative method called reductive amination. Treatment of benzoylformic acid under Rh metal catalyzed conditions gives D,L-phenylglycine. The racemic D,L-phenylglycine is resolved by the treatment of (+)-CSA in water. The solubility of D-phenylglycine•(+)-CSA salt is 5.75 g/100g H_2O, while that of L-phenylglycine•(+)-CSA salt is >150 g/100g H_2O at 25 °C. The chemical yield and the optical purity of the diastereomeric salt will be measured.

EXPERIMENTAL PROCEDURE

Caution: You have to wear latex gloves during all operation for practical task 1.

Step 1. Preparation of D,L-phenylglycine

The following pre-weighted chemicals can be used directly without further weighing: Benzoylformic Acid; Ammonium Formate; Rh Catalyst; (+)-camphorsulfonic acid [(+)-CSA].

1. To a 50 mL round-bottomed flask is added a magnetic stirring bar, pre-weighed (approximate 1.80 g, exact mass will be on your sample bottle, write down the mass on your answer sheet and get the lab assistant to confirm the weight.) of benzoylformic acid (**NOTE: *irritant, do not contact with skin***), 7.57 g of ammonium formate (HCO_2NH_4), 37.2 mg of Rh catalyst (**NOTE: the catalyst is wrapped in a weighing paper in a plastic bag. Handle with care!**) and 22 mL of the pre-mixed solvents at ambient temperature.

2. Put a reflux condenser (use the Teflon sleeve; you can trim off 1 cm from the smaller end for a better fit) into the neck of the flask and plug the condenser with a septum. For pressure equilibration, put a needle in the septum before starting the heating. Clamp the apparatus tightly to the stand in your hot plate/stirrer. Put the flask onto a hot water bath [hot water provided by the organizer] and stir the reaction mixture gently. (**NOTE: the solvent is air cooled, so there is no tap water running through the condenser.**) The temperature of the water bath needs to be maintained in the range of 68 to 72 $^{\circ}$C by adjusting the thermostat of the hot plate/stirrer.

3. The mixture will become cloudy and the color of the solution will change from clear yellowish to dark-greenish when the product starts to precipitate (generally requiring 25 ~ 35 minutes). The hot water bath should then be removed and the solution allowed to stir in the water bath (ambient temperature) for an additional 10 minutes.

4. Add 15 mL of deionized water to the resulting mixture and stir for 10 minutes.

5. Pre-weigh the bigger fritted glass funnel (labelled with your student code), and get the lab assistant to confirm the weight. Use the stir bar retriever to remove the stir bar. Collect the product by filter suction through a fritted glass funnel under a reduced pressure (rotary aspirator apparatus). Wash the solid four times thoroughly with ethanol (10 mL each). For each washing, ***break the aspirator pressure***, use a glass rod to perturb the solid when adding ethanol, and reapply the rotary aspirator.

6. For rapid drying, you have to spread the product over the fritted glass funnel. For drying, give the fritted glass funnel to the lab assistant. The product is dried in the oven at 100 $^{\circ}$C for 1.5 hour.

During the drying period you can start working on Experiment 2 (Analytical Experiment) and you will be notified when your product is ready. Step 2 of experiment 1 will need at least 1 hour.

7. Weigh the dried product [(D,L)-phenylglycine], record the data and calculate the chemical yield (based on the starting benzoylformic acid). Get the lab assistant to confirm the weight. The purity of the product will be determined by ^{1}H NMR spectrum analysis. Turn in the product in a vial (**blue label** with ^{1}H NMR and your student code) to the lab assistant, and receive a new batch of D,L-phenylglycine for step 2.

Step 2. Enantiomeric resolution of D,L-phenylglycine by (+)-camphorsulfonic acid [(+)-CSA]

1. To a 25 mL round-bottomed flask add the pre-weighed sample of D,L-phenylglycine provided (The exact mass will be on your sample bottle, write down the mass on your answer sheet and get the lab assistant to confirm the weight). To this, add the pre-weighed (+)-camphorsulfonic acid [(+)-CSA] (1.80 g). Clamp the apparatus tightly to a stand in a magnetic stirrer. Add deionized water (4 mL) and place the flask in a hot water bath and heat it to a temperature in the range of 90 ~ 100 $^\circ$C. Keep the mixture at this temperature for 10 minutes until it turns clear.

2. Remove the hot water bath and allow the mixture to cool down to ambient temperature for 10~15 minutes. With the flask plugged with a septum, cool the flask in ice bath (Styroform) for 15 minutes. Crystals should appear in about 20 minutes, if not, you may ask for seed crystals to induce the crystallization.

3. Pre-weigh the smaller fritted glass funnel (labelled with your student code), and get the lab assistant to confirm the weight. Collect the product by filtering the solution through a fritted glass funnel under a reduced pressure. Wash the solid thoroughly two times with ice cooled distilled water (5 mL each).

4. For drying, give the fritted glass funnel to the lab assistant. The product will be dried over in oven at 100 $^\circ$C for 20 min. You will be notified when your product is ready. Weigh the product, and get the lab assistant to confirm the weight. Record the data and calculate the chemical yield (based on starting D,L-phenylglycine).

5. The optical purity of the diastereomeric salt will be measured using an accurate polarimeter apparatus by the examination committee. Transfer the dried product to a sample vial (**pink label** labelled with $[\alpha]_D$ and your student code) and give the sample vial to the lab assistant**.** The organization committee will weigh an appropriate amount of the product (0.055 ~ 0.065g) for measurement of optical purity.

The organization committee will weigh the resolved product (from the fritted glass funnel) for students who fail to finish the procedure in time. However, 15 penalty points will be taken.

Experiment 2 Identification of Unknown Inorganic Samples

Note

(1) This practical exercise is a kind of “spot test”. You can do it on the pallet or on a sheet of black film (for white precipitate).

(2) Please check all items written in the equipment and reagent list.

(3) Please check carefully the code number of the unknown sample with the Check List accompanied with your unknown samples.

(4) The volume of each unknown solution is about 1.5 mL (about 30 drops). No more reagents or samples will be provided.

(5) Be sure to confirm your results before writing your answers in the blanks of the Answer Sheet.

(6) Make sure the switch on the battery box is closed.

(7) You will get 8 points for each correct identification.

Introduction

There are 12 unknown samples in your plastic bag□9 unknown solutions are in droppers and 3 unknown solids are in vials. All unknown samples are numbered with a 3 digit code. Please check the number with the **List of Unknown Inorganic Samples** carefully, then write your student code, and name on the list. (The list is accompanied with your unknown samples) Each vial contains about 20 mg of crystals or powder of one pure compound. Each dropper contains about 1.5 mL solution of one pure compound dissolved in distilled water. The concentration of unknown solutions is in the range of 0.05 to 0.5 M (mol/L).

The unknown samples are as follows:

HCl	H_2O_2	H_2SO_4	$ZnCl_2$	NH_4SCN
NaOH	Na_2CO_3	Na_2SO_3	$BaCl_2$	$K_4Fe(CN)_6$

Note

(1) Two unknown samples are duplicates.

(2) The hydrated H_2O of crystal is omitted in the formulas listed above.

On your lab bench, there is a plastic basket which contains the equipments, unknown samples, and reagents to be used in this task.

Equipment list

equipment	No.	equipment	No.
Pt wire electrode	1	Au wire electrode	1
Battery case	1	Battery	2
Pallet	1	Black film (round)	1
Scissors	1	Dropper (1 mL)	5
Coffee stirrer	2		

Reagent list

Reagent	Conc.	Reagent	Conc.
KI	0.1M	pp (phenolphthalein)	0.01
$FeCl_3$	0.1M	Starch solution	0.01

2-1 Use the four reagents provided and mutual reactions among the unknown samples, and the simple electrolysis apparatus to identify each unknown sample, and write your answer (3 digit code) in the blanks of your answer sheet.

Note

After you have finished your work, please put the two electrodes (Pt and Au wires) and two batteries back in their original plastic bags, respectively, then return all equipment and reagents (include unknown samples) to the original places (in the plastic basket).

2-2 In this practical work, you have performed a series of tests to identify (or confirm) the unknowns. Show the reactions involved by way of chemical equations.

A. Write the electrolysis equation that would help you confirm that an unknown sample is $ZnCl_2$.

B. Write one equation that shows how to clean the deposit of Zn on the electrode (limited to the items provided in this task).

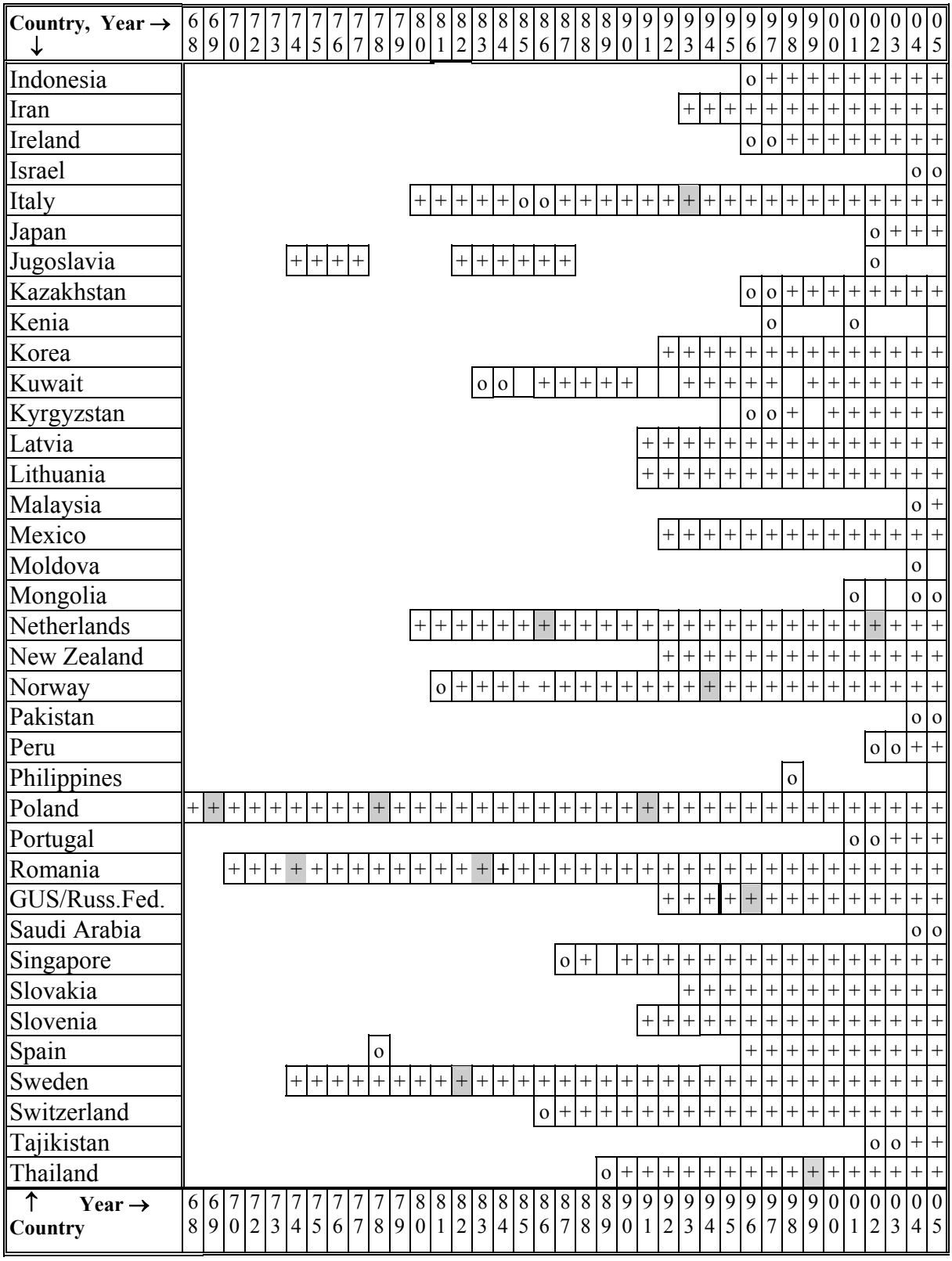
About the History of the International Chemistry-Olympiads (IChO)

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 participating countries of the following years are shown in the table.

Participating Delegations

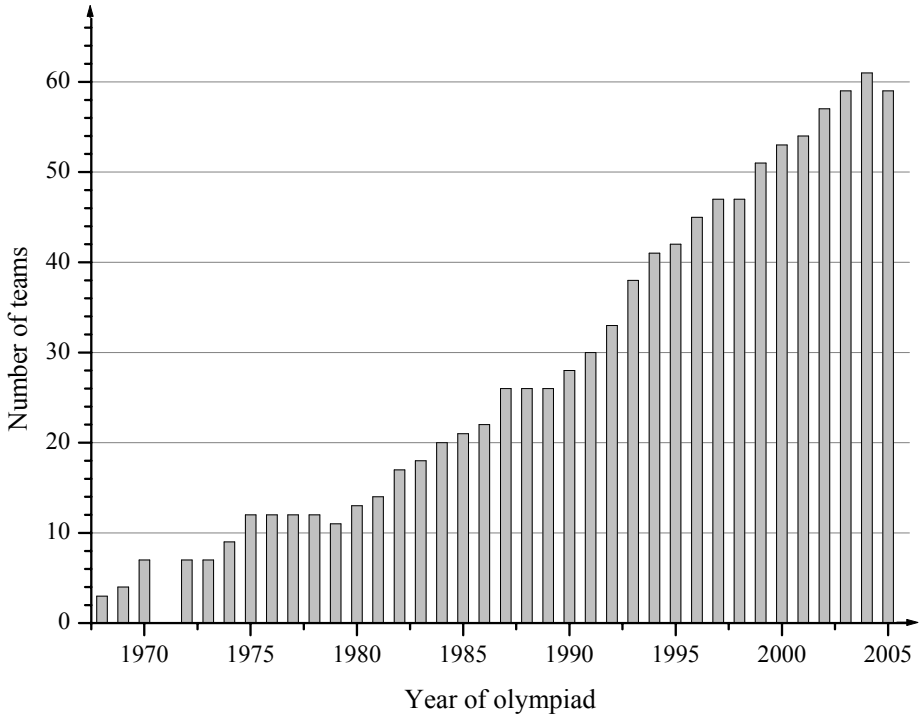
(in the alphabetical order of the German names)
(+ = host, + = participant, o = observer)

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
Argentina																											+	+	+	+	+	+	+	+	+	+	+	+
Armenia																																				o	o
Australien																			o	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Austria							+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Azerbaijan																													o	o		+	+	+	+	+	+
Belarus																												+	+	+	+	+	+	+	+	+	+
Belgium							+	+	+			+				+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Brasil																													o	o	+	+	+	+	+	+	+
Bulgaria		+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Canada																o	o	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
China																			+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+		
Chinese Taipei																								+	+	+	+	+	+	+	+	+	+	+	+	+	+
Croatia																														o	o	+	+	+	+	+	+
Cuba																	+	o	+	+	+	+		+	+	+	+	+		+		+	+	+	+	+	+
Cyprus																						o	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Czech Rep.																								+	+	+	+	+	+	+	+	+	+	+	+	+	+
Czechoslovakia	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+											
Denmark															+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
DDR		o	+	+	+	+	+	+	+	+	+	+	+	+	+		+	+	+	+	+	+															
Egypt																																o	o	+	+	+	+
Estonia																											+	+	+	+	+	+	+	+	+	+	+
Finland								o	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
France												o	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Germany							o	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Greece																+	+	+	+		+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Hungary	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Iceland																																o	o	+	+	+	+
India																													o	o	+	+	+	+	+	+	+
↑ 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


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
Indonesia
Iran
Ireland
Israel
Italy
Japan
Jugoslavia
Kazakhstan
Kenia
Korea
Kuwait
Kyrgyzstan
Latvia
Lithuania
Malaysia
Mexico
Moldova
Mongolia
Netherlands
New Zealand
Norway
Pakistan
Peru
Philippines
Poland
Portugal
Romania
GUS/Russ.Fed.
Saudi Arabia
Singapore
Slovakia
Slovenia
Spain
Sweden
Switzerland
Tajikistan
Thailand
↑ Year →
Country

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
Turkey									o	+															o	+	+	+	+	+	+	+	+	+	+	+	+	+
Turkmenistan																															o	o	o	+	+	+	
UdSSR			+	+	+	+	+	+	+	+	+		+	+	+	+	+	+	+	+	+		+														
Ukraine																										+	+	+	+	+	+	+	+	+	+	+	+	+
United Kingdom												o		o	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
United States													o		o	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Uruguay																													o	o	+	+	+	+	+	+	+
Venezuela														o		o									+	+	+	+	+	+	+	+	+	+	+	+	+	+
Vietnam																												+	+	+	+	+	+	+	+	+	+
↑ 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
Number of teams	3	4	7	7	7	9	12	12	12	12	11	13	14	17	18	20	21	22	26	26	28	30	33	38	41	42	45	47	47	51	53	54	57	59	61	59	

Number of teams attending the IChO



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	KW	C	DK
													T		
.													YU	B	C
.														YU	S
.														CDN	B
25														CH	CH
.														KW	KW
														T	T

(List of abbreviations see page 123)

	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 123)

	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012
IChO held in	**IND**	**NL**	**GR**	**D**	**TPE**	**ROK**	**RUS**					
1	RC	RC	RC	RC	ROK							
.	ROK	T	IR	ROK	VN							
.	USA	TPE	ROK	RUS	IR							
.	RUS	ROK	T	UA	RUS							
5	IR	A	BY	D	AZ							
.	TR	UA	RUS	PL	TPE							
.	IND	USA	IND	TPE	T							
.	AUS	PL	SGP	H	RA							
.	TPE	IND	D	TR	D							
10	T	D	TPE	VN	IND							
.	SGP	IR	UA	IND	A							
.	PL	H	PL	IR	CZ							
.	RO	RUS	CDN	RO	UA							
.	F	CDN	CZ	LT	PL							
15	SK	TR	RO	CZ	AUS							
.	H	AUS	KZ	USA	TR							
.	VN	GB	VN	SGP	H							
.	CZ	SGP	EST	CDN	SK							
.	RA	E	GB	AZ	USA							
20	BY	SK	AUS	AUS	GB							
.	C	BY	H	KZ	RO							
.	D	VN	SK	GB	BY							
.	GB	FIN	USA	J	SGP							
.	UA	F	YV	A	J							
25	A	LT	IND	BY	RI							
.	MEX	CZ	F	SK	LV							
.	DK	KZ	A	T	BG							
.	CDN	LV	I	RA	HR							
.	EST	NL	TR	EST	MEX							
30	RI	RO	AZ	F	KZ							
.	HR	RA	MEX	NZ	LT							
.	I	EST	LT	SLO	F							
.	N	HR	NL	HR	EST							
.	BG	BG	FIN	LV	CDN							
35	CY	NZ	HR	NL	I							
.	KZ	I	J	I	DK							
.	B	DK	DK	CH	SLO							
.	LT	SLO	RA	FIN	FIN							
.	NZ	N	GR	RI	NL							
40	CH	YV	LT	S	IRL							
.	E	MEX	E	BG	GR							
.	FIN	BR	TM	KS	NZ							
.	SLO	S	BR	E	KS							
.	NL	RI	BG	GR	S							
45	LV	TM	CH	BR	B							
.	BR	B	NZ	TM	BR							
.	S	IRL	IS	CY	CH							
.	YV	CH	IRL	YVA	P							
.	IRL	C	CY	IRL	IS							
50	GR	CY	KS	IS	N							

(List of abbreviations see page 123)

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
IND	India
IR	Iran
IRL	Ireland
IS	Iceland
J	Japan
KS	Kyrgistan
KWT	Kuwait
KZ	Kasakhstan
LV	Latvia
LT	Lithuania
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