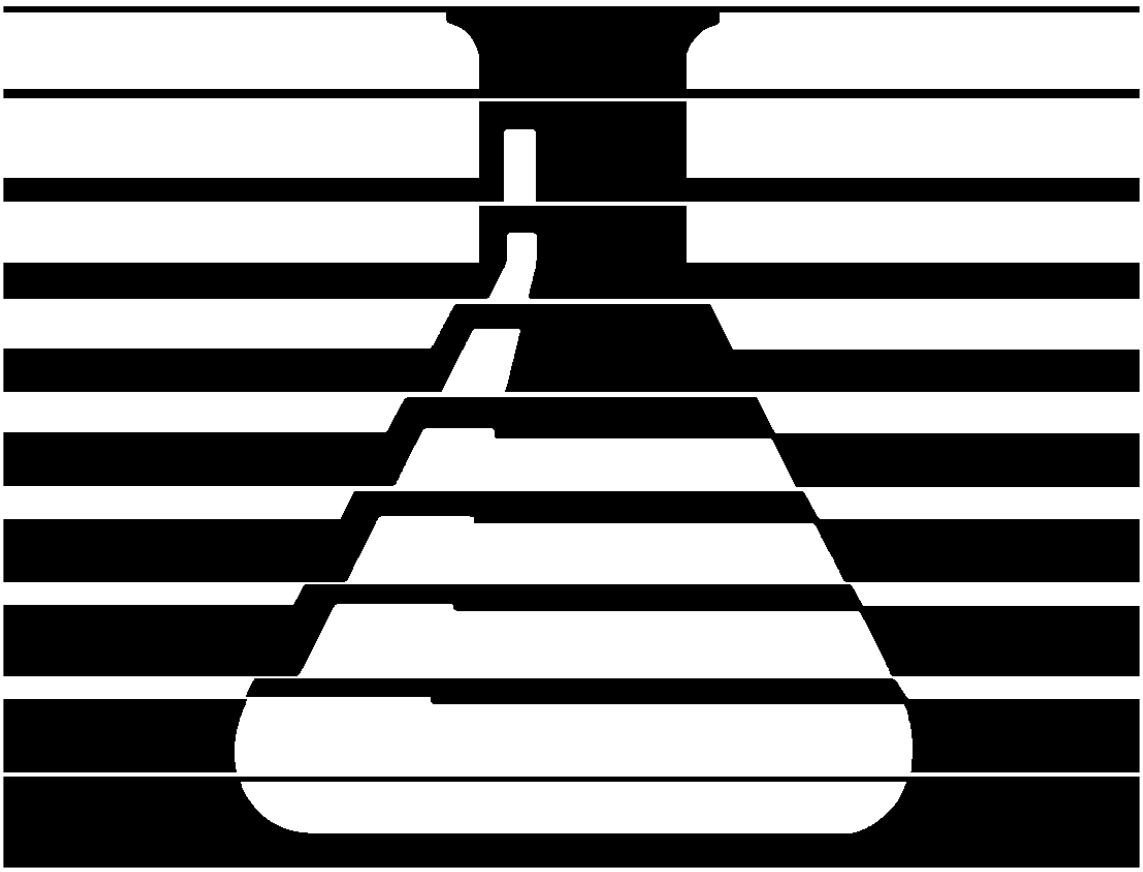
National German competition

for the IChO in 2003

Volume 9



Preface

In order to become a member of the German team for the IChO, students have to pass four successive rounds of examination. The problems to be solved in the 1st round of the competition are sent to all high schools nationwide. To solve these problems, students may use all available resources (e.g. textbooks, etc.).
Students who score 70% or higher in the first round receive the problems of the 2nd round, which are to be solved in the same way as mentioned above. These problems are generally the most difficult ones in the whole competition.
The top 60 participants of the 2nd round will be invited to the 3rd round, a one-week chemistry camp. There, students attend lectures, participate in excursions to chemical production plants or universities, and attend cultural events. In addition, two five-hour written theoretical exams are to be completed.
The top 15 students of the 3rd round advance to the 4th round, a one-week practical training that includes two five-hour exams. These exams, one theoretical and one practical, are taken under the same conditions that students will encounter at the IChO. The 4th round is also where the final German team for the IChO is elected.

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Part 1

The problem set of the four rounds

First round (homework)

Problem 1-1

Burnt lime (CaO) can be produced industrially by heating calcium corbonate at 900–1000 °C.

a) Give the chemical equation for this reaction.

The equilibrium constant K has the value K = 1.34 at 920° C. The reaction is carried out in a vessel with a constant pressure of $1.50 \cdot 10^5$ Pa .

b) Calculate the partial pressure of carbon dioxide in equilibrium with both solids at 920 °C.

Burnt lime reacts with water to give calcium hydroxide.

c) Give the chemical equation for this reaction.

Calcium hydroxide is partly soluble in water, with a solubility of L = 1.26 g/L at 20 °C.

d) Calculate the concentration of calcium ions and the pH of a saturated solution of calcium hydroxide at 20 °C.

When passing carbon dioxide through a solution of calcium hydroxide, a precipitate is formed initially.

e) Write equations for all reactions involved in this process.

When passing carbon dioxide through a solution of calcium chloride, however, no precipitate can be detected.

f) Explain this observation.

Problem 1-2

0.490 mol NO_2 are added to a vessel containing 0.720 mol SO_2 and 0.710 mol SO_3. The following equilibrium is established

$$SO_{2(g)} + NO_{2(g)} \rightleftarrows SO_{3(g)} + NO_{(g)} .$$

At equilibrium the vessel contains 0.390 mol $NO_{(g)}$.

a) Calculate the equilibrium constant at the prevailing temperature.

At the same temperature 1.000 mol $SO_{2(g)}$ is added.

b) Calculate the amount of each of the four gases present in the vessel after a state of equilibrium has been reached.

Problem 1-3

oxygen	nitrogen	argon
21.0	78.1	0.90

In a caravan there are eight candles made of stearic acid weighing 58 g each. The caravan contains 19.0 m^3 of air. The table shows the initial percentage composition (V/V) of the air in the caravan. The initial temperature is 21° C, the pressure 98.0 kPa.
The candles are burnt in the caravan without gas exchange with the surroundings.

a) Write a balanced reatin equation for the complete combustion of the candles made of stearic acid.

b) Calculate the percentage by volume (V/V) of oxygen and carbon dioxide after combustion. The initial amount of carbon dioxide is to be neglected.

Problem 1-4

An organic compound A contains three types of atoms, hydrogen, carbon and oxygen.
Burning 0.749 g of A gives 1.124 g of carbon dioxide and 0.306 g of water.
In the mass spectrum of A the peak with the highest m/z ratio occurs at m/z = 176.1.

a) Determine the empirical formula, the molar mass and the molecular formula of A.

Special tests including spectroscopic methods lead to the following conclusions:

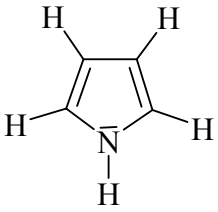
- Compound A contains a five-membered ring.
- There is an oxygen bridge between two carbon atoms in the ring.
- Between the two other carbon atoms of the ring there is a double bond.
- One oxygen atom has a double bond to a carbon atom of the ring.
- Compound A contains four hydroxyl groups each bond to a carbon atom.
- The only two hydroxyl groups bond directly to the ring are connected with the carbon atoms of the double bond.
- Outside the ring there are two carbon atoms bond to each other.

b) Sketch the structure of A.

c) What kind of isomerism is possible?

Problem 1-5

Pyrrole is a heterocyclic compound with the structure indicated.
In the presence of acetic anhydride it reacts with nitric acid to give product X in high yield.

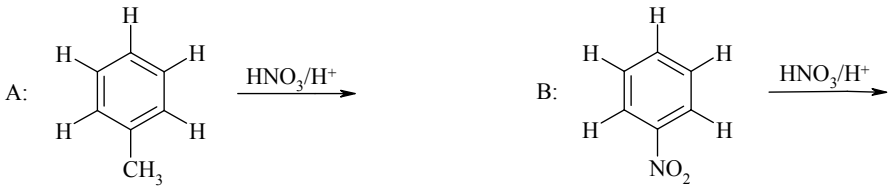


a) Identify X. Give a balanced equation for the reaction to give X.

b) Of which type is this reaction? Give the reasons for your answer by using the electronic structure of pyrrole.

c) Where is the site of attack to start this reaction? Give the reasons for your answer by sketching the intermediates and explaining their stability.

Compare the reaction of pyrrole given above with the two following reactions A and B:

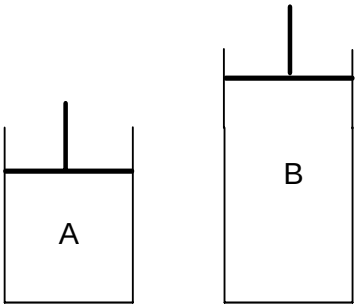


d) Which of these two reactions is most similar to the reaction of pyrrole? Explain your decision.

Second round (homework)

Problem 2-1

Preparing an experiment a student takes two vessels A und B which are closed by pistons.



Vessel A contents a mixture of CO_2 and H_2 with a 1:1 molar ratio of the components. Vessel B contains propane.
Both vessels are heated to 527°C at constant pressure.
The equilibrium systems are represented by

(A) $CO_2 + H_2 \rightleftarrows CO + H_2O$ $\quad K_1 = 2{,}50 \cdot 10^{-1}$

(B) $C_3H_8 \rightleftarrows C_3H_6 + H_2$ $\quad K_2 = 1{,}30 \cdot 10^{-3}$ mol/L

The equilibrium constants apply to concentrations at 527°C.

The student notices that the equilibrium pressure in both vessels is identical at 527 °C. The percentage of propane in vessel B is 80% (V/V).

a) Calculate the equilibrium concentrations of the components in vessel B as well as the total equilibrium pressure.

b) Calculate the equilibrium concentrations of the components in vessel A.

In the second part of the experiment the student uses the pistons to reduce the volume of each vessel to half of the initial volume at constant temperature.

c) Calculate the total equilibrium pressure in each of the vessels.

Problem 2-2

An electrolyzer filled with a solution of NaOH (pH = 14) and a second one are put in an electrical circuit. The second electrolyzer is filled with sulfuric acid (pH = 0). (T = 298 K)
The voltage of the electricity source can be controlled.
If you increase the voltage slowly you find that a gas is emitted in both electrolyzers starting at the same voltage.

a) *Give equations for all reactions taking place in the electrolytes and combine them to a total reaction for each electrolyte. Disregard the formation of H_2O_2 and. $H_2S_2O_8$.*

b) *Give the reasons for the identical decomposition potential in both electrolytes. Disregard overvoltage. Which is the value of the decomposition potential?*

c) The pH of the given solution of NaOH shall be lowered to pH = 11.
Can you accomplish this with ammonium chloride? If not give other appropriate chemicals.
In any case give the equation of the reaction causing the change of pH.
Calculate the mass of ammonium chloride or the chosen chemical to lower the pH of 1 L solution of NaOH from 14 to 11 ($pK_B(NH_3) = 4{,}75$).

d) *Explain whether or not the decomposition voltage of the solution of NaOH changes when the pH is lowered to 11. If it changes what is the extent of the alteration ?*

e) The solution of NaOH (pH = 14) and the solution of sulfuric acid (pH = 0) are used as half-cells connected by a salt bridge.
Calculate the decomposition voltage.

f) *Does the decomposition voltage change if you exchange the poles? If yes calculate the new decomposition voltage.*

If you need more data for this problem look them up in text books.

Problem 2-3

A solution containing 160.0 g water and 100.0 g calcium nitrate is electrolysed between graphite electrodes for 12 hours with a currrent of 5.00 A. At the end of the electrolysis the mass of the solution has decreased by 41.9 g.

a) *Calculate the amount of cristalline calcium nitrate tetrahydrate ($Ca(NO_3)_2 \cdot 4H_2O$) that can be dissolved in 100.0 g of water at this temperature.*

b) The solubility of poorly soluble salts may be influenced by two imporant factors, the pH and the presence of complex-forming reagents.
Silver oxalate is such a salt with the solubility $S = 2.06 \cdot 10^{-4}$ mol/L. The solubility is influenced by the pH as well as by a complex-forming agent, e.g. ammonia.

Explain, why the pH influences the solubility of silver oxalate.

c) *Calculate the solubility of silver oxalate in a solution with pH = 5.*

(The equilibrium constants of oxalic acid at 25 °C are $K_{a1} = 5.9 \cdot 10^{-2}$ mol/L and $K_{a2} = 6.4 \cdot 10^{-5}$ mol/L)

In the presence of ammonia silver ions form two types of complexes, $Ag(NH_3)^+$ and $Ag(NH_3)_2^+$. The stability constants for the stepwise formation of these complexes are $K_3 = 2.09 \cdot 10^3$ mol/L and $K_4 = 8.32 \cdot 10^3$ mol/L, respectively.

d) *Calculate the solubility of silver oxalate in a saturated solution with pH = 10.8 and $c(NH_3) = 0.02$ mol/L .*

Problem 2-4

Two moles of benzaldehyde react to give one mole of compound **A** using cyanide ions as a catalyst. **A** exists as a pair of enantiomers.

Compound A reacts with sodium borohydride to give compound B. B exists in three stereomeric configurations.

a) Give the mechanism of the reaction leading to A and the chemical equation for the reaction leading to B.
Give the structural formulas of A and B.

b) Draw tetrahedral representations of A and B. Assign R, S configurations (according to Cahn-Ingold-Prelog rules) to each of them.
Which kind of steroisomerism exists in particular?

In contact with Al_2O_3 compound B reacts by elemination of water to give C_1 and C_2. C_1 and C_2 are in equilibrium with C_3. The IR-spectrum of C_1 and C_2 shows absorption around 1600 cm^{-1}, and both C_1 and C_2 decolour bromine water.
If B is treated with conc. sulfuric acid in order to eliminate water a total different reaction occurs. A compound D is formed with a strong absorption band around 1700 cm^{-1}. Furthermore, compound D reacts with semicarbazide (H_2N-NH-CO-NH_2) to give a sparsely soluble compound.

c) Write the chemical equations leading to the compounds C_1, C_2, C_3 and D.
Give the structural formulas of C_1, C_2, C_3 and D.
Write the mechanism of the reaction to give D.

Compound D is reduced to compound E.

d) Give the structural formula of E.

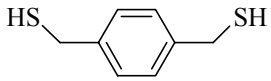
If E is treated with strong acids elimination of water takes place to give compound F. Ozonolysis of F and further treatment with an oxidizing reagent leads to product G ($C_{13}H_{10}O$).

e) Write the structural formulas of F and G.

f) Give the name of G.

Problem 2-5

This question is about the synthesis of compound X:
Toluene (A) reacts with nitrating acid (HNO_3/H_2SO_4) to yield a mixture of isomers B_x. From this mixture the para compound (B) is seperated. Half of the amount of B reacts with an equivalent amount of sulfuryl chloride and a small amount of azoisobutyric nitrile (AIBN) as a radical starter to give compound C with a molecular mass of 171.6 u. C is transformed with triphenyl phosphine to the phosphonium salt D. Next D reacts with n-butyl lithium to give ylide E.
The second half of B is converted with two equivalents of sulfuryl chloride and a small amount of azoisobutyric nitrile (AIBN) to compound F with a molecular mass of 206.0 u. With strong acids F gives compound G and a pungent smelling gas is released. Compound G can be oxidized by Tollens reagent.
E and G react in a Wittig reaction to give H, under conditions that favor the formation of the cis isomer. This isomer is irradiated intensively and undergoes an oxidative cylisation reaction to yield I (empirical formula of I : $C_{14}H_8N_2O_4$).
I is reduced by Fe in HCl to give J. At 5°C J is treated with $NaNO_2$ in an acid solution. A diazonium salt is formed. In the following, CuCl is added and compound K is formed. Compound K is converted with Mg in ether to give L. Compound L reacts with formaldehyde to give M. Compound M reacts in a strongly acidic surrounding (H_2SO_4) with HBr to give compound N. N has the empirical formula $C_{16}H_{12}Br_2$. In a basic surrounding N reacts with O to give P and two molecules of HBr.



(O)

P is converted with an excess of H_2O_2 to Q. Q is submitted to pyrolysis at high temperatures in a vacuum releasing SO_2. Compound X is formed. X contains only C and H atoms.
The molecular mass of X is 308.5 u.

1. *Draw the structural formulas of the compounds A to X.*
2. *What is the name of the reaction $J \rightarrow K$?*
   Write the reaction mechanism.

Third round EXAM 1

(5 hours exam, use of the attached collection of formulas and the provided periodic table is permitted)

Problem 3-1 (multiple choice, some questions may have more than one correct answer)

a) Which of the following chemical bonds has the highest positive partial charge on C?

A) C – Si	B) C – Al	C) C – Mg	D) C – F	E) C – O

b) Which of the following compounds has two isomers?

A) C_3H_8	B) C_2H_6	C) C_3H_7Br	D) C_2H_5Br	E) CH_4O

c) Which of the following formulas represents an optical active substance?

A) C_4H_9OH	B) CCl_2BrF	C) C_3H_7Br	D) C_4H_{10}	E) C_2H_5Br

d) Which of the following molecules have a dipole moment?

A) $H_2C=C=CH_2$	B) SO_2	C) $CHCl_3$	D) CO_2	E) para $C_6H_4Cl_2$

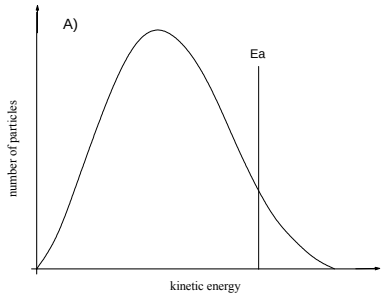
e) An element with the electron configuration [Xe] $4f^{14}\ 5d^7\ 6s^2$ is a (an)

A) inert gas	B) transition element	C) alkaline earth element	D) rare earth metal

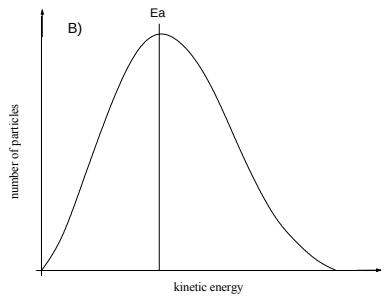
f) What products are formed during the electrolysis of a concentrated aqueous solution of sodium chloride? I $Cl_2(g)$, II NaOH(aq) , III $H_2(g)$

A) I only	B) I and II only	C) I and III only	D) I, II and III

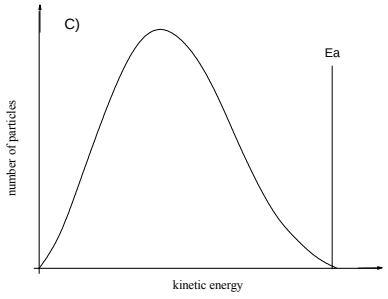
g) A)



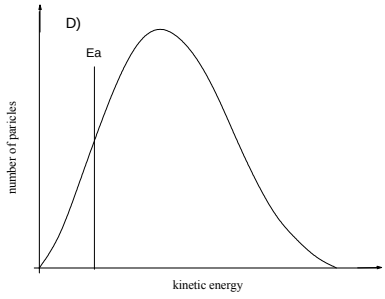
B)



C)



D)



The four pictures show the same distribution of energy. At the same temperature four reactions are possible. Their activation energy Ea is marked.
Which of these four reactions is likely to have the highest reaction rate? Explain your decision!

Proplem 3-2

When H_2S is dissolved in water the solution is saturated at a concentration close to 0.1 mol/L. Three species containing sulfur (H_2S, HS^-, S^{2-}) exist in this solution, and their ratio is depends on the acidity of the solution. The equilibrium constants are as follows:

$H_2S + H_2O \rightleftarrows H_3O^+ + HS^-$ $\quad K_{a1} = 1.0 \cdot 10^{-7}$ mol/L

$HS^- + H_2O \rightleftarrows H_3O^+ + S^{2-}$ $\quad K_{a2} = 1.3 \cdot 10^{-13}$ mol/L.

a) Calculate the concentration of sulfide ion in a saturated 0.100 M solution of H_2S where the pH is adjusted at 2 by HCl.

A solution contains the cations Mn^{2+}, Co^{2+}, Ag^+ at an initial concentration of 0.010 mol/L each. The following solubility products are given:

$K_{sp}(MnS) = 2.5 \cdot 10^{-10}(mol/L)^2$, $K_{sp}(CoS) = 4.0 \cdot 10^{-21}(mol/L)^2$, $K_{sp}(Ag_2S) = 6.3 \cdot 10^{-50}(mol/L)^3$.

b) Which of these ions will precipitate, if the solution is saturated with H_2S and the pH adjusted to pH = 2. Explain your answer.

The following solubility products are given:

$K_{sp}(PbSO_4) = 1.6 \cdot 10^{-8}(mol/L)^2$, $K_{sp}(PbS) = 2.5 \cdot 10^{-27}(mol/L)^2$.

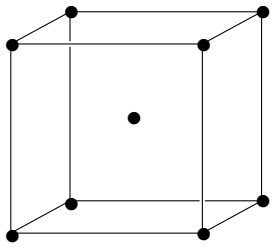
c) How many grams of lead(II) sulfide will precipitate from 1.00 L of a saturated solution of lead(II)-sulfate, if the concentration of sulfide ions is adjusted to give a concentration of $1.00 \cdot 10^{-17}$ M?

Problem 3-3

a) Calculate the lattice energy $\Delta H_{lattice}$ of potassium fluoride from the following data

sublimation energy of potassium	ΔH_{Subl} = 90 kJ/mol
bond dissociation energy of fluorine	ΔH_D = 158 kJ/mol
ionization energy of potassium	$\Delta H_{I(K)}$ = 419 kJ/mol
electron affinity of fluorine	$E_{A(F)}$ = - 333 kJ/mol
heat of formation of potassium fluoride	ΔH^0_f = - 567 kJ/mol

Tungstan crystallizes in a body–centered cubic lattice. The edge of a unit cell has a length of 300 pm.



b) Calculate the radius of a tungsten atom.

Silver crystallizes in a face-centered cubic lattice. The edges of the unit cell have a length of 409 pm.

c) Calculate the density of silver. How much (%) of the space of the unit cell is filled by silver?

Problem 3-4

The thermal decomposition of nitrogen(V)oxide takes place according to the equation

$$2\ N_2O_5 \longrightarrow 4\ NO_2 + O_2\ .$$

The concentration of N_2O_5 **in liquid bromine** varied with time as follows (T>298 K):

time in s	0	200	400	600	1000
$c(N_2O_5)$ in mol/L	0.110	0.073	0.048	0.032	0.014

a) Confirm that this reaction is of first order by drawing a diagram .

b) Calculate the rate constant k_1 for the reaction under these conditions.

The rate constant for the first order decomposition of N_2O_5 **in the gas phase** has the value of $4.8 \cdot 10^{-4}\ s^{-1}$.

c) Calculate the half-life of the reaction.

N_2O_5 with the initial pressure of 66.75 kPa decomposes in a closed vessel of constant volume.

d) Calculate the total pressure after 10 minutes.
Calculate the final pressure.

e) Derive a relationship linking the total pressure p_t with the initial pressure of N_2O_5 (p_0) and time.

The rate constant for the gas decomposition of N_2O_5 at 298 K is $3.38 \cdot 10^{-5}\ s^{-1}$, whereas the rate constant for the decompostion in liquid bromine has a value of $4.47 \cdot 10^{-5}\ s^{-1}$ at the same temperature.

f) Comment on this difference.

Problem 3-5

When Co^{3+}-ions are added to an aqueous solution of ammonia the following reaction takes place

$$Co^{3+}(aq) + 6\ NH_3(aq) \longrightarrow [Co(NH_3)_6]^{3+}(aq)$$

K is the overall constant for the formation of the complex, $K = 4.5 \cdot 10^{33}\ (mol/L)^{-6}$.

In a solution the equilibrium concentration of ammonia is $c(NH_3(aq)) = 0.1$ mol/L and the sum of the equlibrium concentrations of $Co^{3+}(aq)$ and $[Co(NH_3)_6]^{3+}(aq)$ is 1 mol/L.

a) Calculate the concentration of $Co^{3+}(aq)$ in this solution.

The overall formation constant K for $[Co(NH_3)_6]^{2+}(aq)$ is much lower, $K = 2.5 \cdot 10^{4}\ (mol/L)^{-6}$.

b) Determine the ratio $c(Co^{2+}(aq)/\ c([Co(NH_3)_6]^{2+}(aq))$ in a solution for which the equilibrium concentration of ammonia is $c(NH_3(aq)) = 0.1$ mol/L.

c) Calculate the concentration of $Co^{2+}(aq)$ in a solution if the total concentration of all Co^{2+}-species is 1 mol/L .

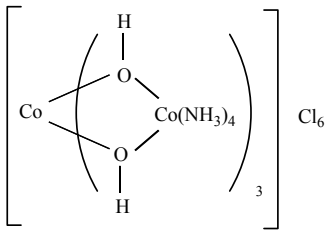
d) $Co^{3+}(aq)$ reacts with water to liberate a gas. What is the gas? Give reasons for your answer.

e) Why is there no liberation of gas in the solution of a)?

In a solution containing $Co^{2+}(aq)$, $Co^{3+}(aq)$ and NH_3 the overall concentration of all Co^{2+}-species and the overall concentration of all Co^{3+}-species is 1 mol/L each and the equilibrium concentration of NH_3 is 0.1 mol/L.

f) Calculate the potential of the $Co^{3+}(aq)/Co^{2+}(aq)$ couple in this solution.

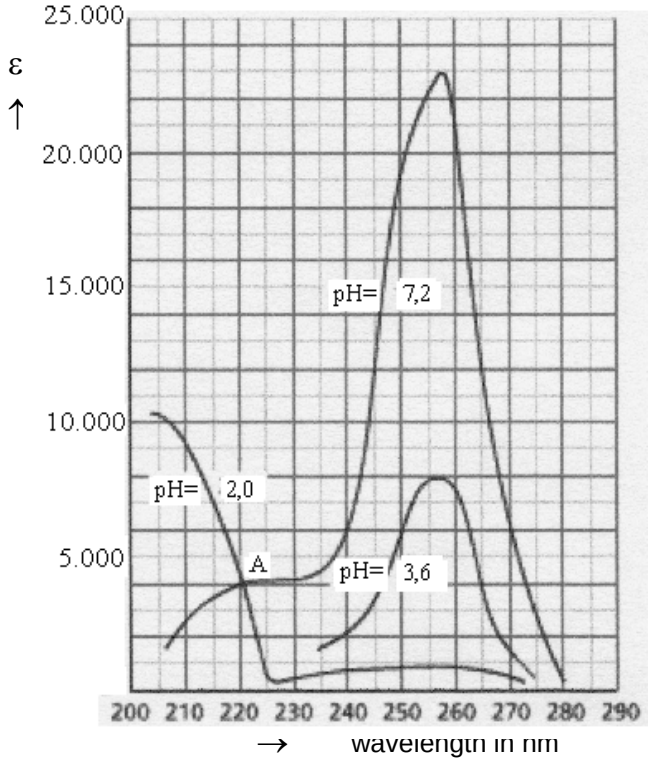
It was thought only carbon compounds could exist as enantiomers until the Swiss chemist Werner prepared the compound of the following structure:
This can be viewed as a complex with the bidentate ligand $[Co(NH_3)_4(OH)_2]^+$.
Already this ligand exists as isomers.



g) Draw these isomers. Mark the isomer which is suitable for the complex prepared by Werner. Of what type are these isomers?

h) Draw the two enantiomers of the complex prepared by Werner. You need not show the geometry of the "outer" cobalts, they can simply be written as $Co(NH_3)_4$.

Problem 3-6 (from problem of the month, the Netherlands)



Barbituric acid is a monoprotic acid, in this problem indicated as HA. pK_a-Wert ≈ 4.

The value of K_a can be determined more exactly by using UV-spectroscopy.
Both HA und A^- absorb UV-light with a maximum of absorbance at different wavelengths.
Barbituric acid is dissolved in three buffer solutions at pH = 2.0 , pH = 3.6 and pH = 7.2 .
The absorbance of the three solutions is measured at wave-
lgths between 200 and 280 nm.
The results of the measurements have been used to derive the molar absorption coefficient of the solutions for each wavelength.
These results are given in the diagram.

The graph of pH = 3.60 is incomplete. At the intersection A the wavelength is 221 nm.

a) Explain whether the graph of pH = 3.6 also intersects with point A or not.

b) Calculate K_a for barbituric acid.

Problem 3-7

During respiration an exchange of gases takes place in the lungs. At rest an adult normally breathes in 500 mL air (78% nitrogen, 21% oxygen, 1% noble gases) with a frequency of 15 breaths per minute.

a) Calculate the mass of oxygen which reaches the lungs in one minute (p = 1.000 bar, δ = 37 °C) considering air as an ideal gas.

b) What assumptions do you make when you speak of an ideal gas?

One hemoglobin molecule may transport up to four oxygen molecules.
According to Hill the dissociation of Hb follows the equation:

$Hb(O_2)_n \leftrightarrows Hb + n\ O_2$ $\qquad K_D = \frac{[Hb]\cdot[O_2]^n}{[Hb(O_2)_n]} = 8.15\times10^{-5}$

In the case of hemoglobin the Hill coefficient has the value 2.80.
The saturation degree α shows the part of the centres occupied by oxygen. It is defined as

$$\alpha = \frac{(p_{O_2}/1{,}000\text{bar})^n}{(p_{O_2}/1{,}000\text{bar})^n + K_D}$$

In the blood of the veins (before entering the lung) $p(O_2) = 0.0533$ bar, in the blood of the arteries after leaving the lung $p(O_2) = 0.133$ bar.

c) Calculate the degree of saturation of hemoglobin in the blood of the arteries and of the veins.

One litre of blood contains 150 g of hemoglobin. Hemoglobin has a molar mass of 64500 g/mol.

d) Using the degree of saturation (α) calculate the volume of O_2, which may be stored in one litre of blood in the arteries (body temperature 37°C and 1 bar pressure).

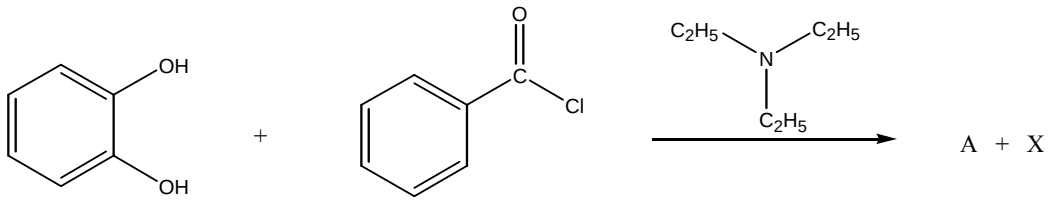
e) Calculate the percentage of the oxygen released in the body.

An adult person needs approximately 8000 kJ energy per day. In the biological oxidation of fat 400 kJ of energy are released per mol of oxygen.

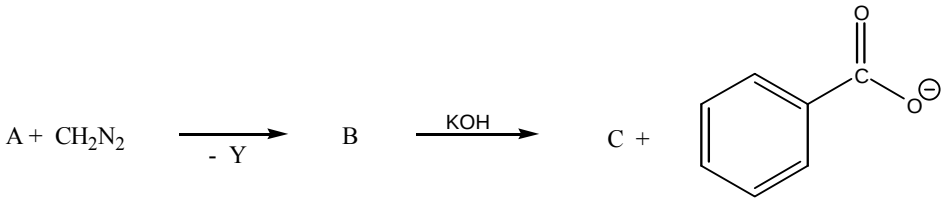
f) Calculate the amount of blood pumped by the heart in litres per minute assuming that the total energy is gained from the oxidation of fat, and assuming that the blood in the arteries and in the veins have the composition calculated above.

Problem 3-8

o-Dihydroxibenzene reacts with the same amount of benzoyl chloride:



A reacts with diazomethane to give B. In a solution of potassium hydroxide in water B is converted to give C and benzoic acid:



a) Identify A, B, C and X, Y. Write the reaction equations.

b) What is the reason for using benzoyl chloride in this reaction sequence?

Problems 3-9

A very precisely performed elementary analysis of a compound A which contains only carbon, hydrogen and oxygen gives a mass balance of 70.97 % C and 10.12 % H.

a) Determine the stoichiometric formula of A.

The mass spectrum von A shows the peak with the highest m/z-ratio at 340.

b) Determine the empirical formula of A.

In order to identify the structure of A several reactions are performed:

1. A reacts with acids to give an ester.
2. A can be hydrogenated (Pd catalyst) to give a compound X. X also reacts with acids to give an ester.
3. Potassium permanganate cleaves X. CO_2 and a long-chain terminal dicaboxylic acid are formed.

c) These reactions do not allow to determine the structure unambiguously. Find a possible structure for X and A. Your proposal should show symmetrical molecules. Give the reasons for your proposal by writing the appropriate reaction equations (c1 to c3).

Problem 3-10

2-Methyl-2-butene reacts with hydrochloric acid to give 2-chloro-2-methylbutane.

a) Write the reaction equation..

b) Give the mechanism of this reaction.
The formation of another product is possible in principle. Which one is it and why is it not formed as the main product?

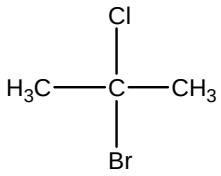
c) Draw a reaction energy diagram for the overall process including intermediates.

d) Identify the compounds X and Y in the following reaction

3-Methyl-1-butene reacts with hydrochloric acid to give 2-chloro-3-methylbutane and 2-chloro-2- methylbutane.

e) Explain the formation of these two derivates by writing the reaction mechanism.

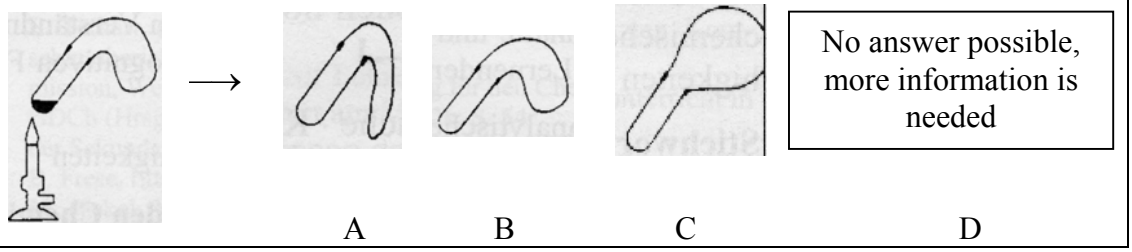
f) Show how to carry out the formation of the compound shown below starting with an unsaturated hydrocarbon.



EXAM 2

Problem 3-11 (multiple choice, some questions may have more than one correct answer)

a) A test tube with 0.10 g carbon in it is filled up with oxygen and then closed with a balloon filled with oxygen too. The test tube is heated until all carbon disappears. Which of the shown results is expected after cooling down?



b) Someone has accidently spilled battery acid on his skin. The first aid treatment is to apply plenty of

A) salt solution	B) water	C) vinegar	D) baking soda solution	E) washing soda solution

c) Which of the following substances, when dissolved in water, gives the solution with the lowest pH?

A) Li_2O	B) Na_2O_2	C) KO_2	D) H_2S	E) HI

d) Which of the following statements is correct?

A) In an electrolytic cell oxidation takes place at a positive anode
B) In an electrolytic cell oxidation takes place at a negative anode
C) In an electrochemical cell reduction takes place at a positive anode
D) In an electrochemical cell oxidation takes place at a positive anode
E) In an electrochemical cell reduction takes place at a negative anode

e) Monocalcium phosphate ($CaHPO_4$) is used as an acid in baking powders. Solutions of $CaHPO_4$ in water may contain a variety of species. Which of the following is the conjugated base of the HPO_4^{2-}-ion?

A) Ca^{2+}	B) OH^-	C) H_2O	D) PO_4^{3-}	E) $H_2PO_4^-$

f) Some students have been measuring the rate of reaction between 5.0 g of zinc granules and 100 mL of hydrochloric acid (c = 1.0 mol/L) at room temperature. Which of the following changes in the procedure will probably **not** increase the rate of reaction?

A) Warming the HCl before adding the zinc
B) Using zinc powder instead of zinc granules
C) Using 200 mL of HCl (c = 1,0 mol/L) instead of 100 mL of 1 M hydrochloric acid
D) Using 50 mL of HCl (c = 2,0 mol/L) instead of 100 mL of 1 M hydrochloric acid
E) Using 100 mL of H_2SO_4 (c = 1,0 mol/L) instead of 100 mL of 1 M hydrochloric acid

Problem 3-12

This task is about compounds of fluorine.

A is a colourless, neutral gas. 250 cm^3 of it weigh 1.31 g at s.t.p. (1.000 bar, 298 K).
When 0.651 g of A reacts with 0.380 g of fluorine at 400 °C the only product is a white cristalline solid B.
1.036 g of B reacts with dioxygen difluoride at -78°C to give 124 cm^3 of oxygen at s.t.p. and 1.23 g of a white solid C.
D can be made by irradiating a mixture of A with fluorine at 25 °C.
1 mole of D reacts with hydrogen at 400 °C. If the products are dissolved in water (as much as possible) 2 moles of sodium hydroxide are required to neutralise the resulting solution.

a) Identify A, B, C and D. Give the equations for the reactions mentioned

b) What is the shape (gemetry) of the compound B?

c) What happens when fluorine is irradiated by UV-light?

Problem 3-13

In basic solutions hydrogen peroxide, H_2O_2, is an oxidizing agent, e.g. oxidizing Mn^{2+} to MnO_2 .

a) Give a balanced equation for this reaction.

In an acidic solution H_2O_2 can react as reducing agent, for example reducing permanganate ions to Mn^{2+} .

b) Give a balanced equation for this reaction.

20.00 cm^3 of an acidic solution of H_2O_2 are titrated with a solution of potassium permanganate (c = 0.018 mol/L): 13.30 cm^3 are needed.

c) Calculate the concentration of H_2O_2.

The following standard redox potentials are given:

$$Fe^{3+} + e^- \rightleftarrows Fe^{2+} \quad E^o = 0{,}77\ V$$
$$Ce^{4+} + e^- \rightleftarrows Ce^{3+} \quad E^o = 1{,}61\ V$$

d) Determine the reaction constant for $Fe^{2+} + Ce^{4+} \rightleftarrows Fe^{3+} + Ce^{3+}$.

A solution of iron(II) sulfate is titrated with a solution of cerium(IV) sulfate at standard conditions.

e) Determine the ratio $\frac{c(Fe^{3+})}{c(Fe^{2+})}$ *at the equivalence point.*

Calculate the redox potential of the solution at the equivalence point.

Problem 3-14

The element uranium is found in nature as a mixture of isotopes.
The mixture contains 99.28 % ^{238}U (half life $t_{½} = 4.5 \cdot 10^9$ years) und 0.72 % ^{235}U ($t_{½} = 7.0 \cdot 10^8$ years).
Assume the earth is $4.5 \cdot 10^9$ years old.

a) What was the original percentage of ^{235}U in natural uranium?

^{238}U decays by a series of steps to an isotope of lead. Overall 8 α particles are emitted during the process.

b) How many β particles are also emitted? Which isotope of lead is formed?

Uranium has the electron configuration Rn $5f^3$ $6d^1$ $7s^2$.

c) How many unpaired electrons does an atom of uranium possess?
What is its maximum oxidation state likely to be?

Before uranium can be used for nuclear fission, the content of ^{235}U must be increased to about 2.5 %.. UF_6 is an important compound used during the seperation of the isotopes of uranium, which is formed as a very volatile liquid is formed by passing ClF_3 over heated crystalline
UF_4.

d) Give a balanced equation for this reaction. Sketch the structures of UF_6 and ClF_3.

At a given temperature, the rate at which a gas passes through a membrane is inversely proportional to the square root of its relative molar mass.
The natural mixture of uranium is enriched from 0.7 % to 2.5 % ^{235}U.

e) How many membranes must the mixture pass through to achieve this enrichment?

Fission of ^{235}U produces a variety of products and 2 or 3 neutrons. One product of the fission is ^{95}Kr.

f) Write a balanced nuclear equation for this fission process assuming that 2 neutrons are also emitted.

Listed below are some standard redox potentials for uranium at various oxidation states:

$UO_2^{2+} + 4\,H^+ + 2\,e^-$	$\longrightarrow U^{4+} + 2\,H_2O$	$E^0 = +\,0.32$ V
$UO_2^{2+} + e^-$	$\longrightarrow UO_2^{+}$	$E^0 = +\,0.06$ V
$UO_2^{+} + 4\,H^+ + e^-$	$\longrightarrow U^{4+} + 2\,H_2O$	$E^0 = +\,0.58$ V
$U^{4+} + e^-$	$\longrightarrow U^{3+}$	$E^0 = -\,0.63$ V
$H^+ + e^-$	$\longrightarrow$ ½ H_2 at pH = 7	$E^0 = -\,0.42$ V

g) Give balanced reaction equations to explain why aqueous solutions of UO_2^{+}- und U^{3+} ions are unstable.

Problem 3-15

This task is about the complex ion $[CoCl(NH_3)_5]^{2+}$.

a) What is the name of the complex ion? What is the oxidation state of Co in the complex ion?

b) Draw the structure of this complex ion.

When two molecules of NH_3 are replaced by two chloride ions another complex is obtained.

c) Write its formula. How many isomers exist? Draw their structures. What kind of isomers are they?

A solution of the complex ion $[CoCl(NH_3)_5]^{2+}$ (c = 0.0200 mol/L) is red. The transmission in a 1 cm cuvette at 520 nm has the value T = 7.50 %.

d) Calculate the molar absorption coefficient of this complex.

In an acidified solution Fe^{2+} reduces $[CoCl(NH_3)_5]^{2+}$ to produce Co^{2+}.

e) Write a balanced equation for this reaction.

This reaction is of second order with the rate law

$$-\frac{d(c[CoCl(NH_3)]^{2+})}{dt} = k_2 \cdot c([CoCl(NH_3)_5]^{2+}) \cdot (c[Fe(H_2O)_6]^{2+}).$$

In order to determine the rate constant a concentration of $[Fe(H_2O)_6]^{2+}$ is chosen, which is many times higher than that of $[CoCl(NH_3)_5]^{2+}$.

f) Give the formula of the new rate law. What is its order?

10,0 mL of a solution of $[CoCl(NH_3)_5]^{2+}$ are mixed with 10,0 mL of a solution of $[Fe(H_2O)_6]^{2+}$ (c = 0,300 mol/L, high excess). The absorbance A is measured as follows:

t /min	10	20	40	60	∞
A	1.15	0.875	0.558	0.410	0.283

The concentration $[CoCl(NH_3)_5]^{2+}$ is proportional to $(E - E_\infty)$.

g) Show by calculation that your predicted order k in f) is correct. Calculate this rate law constant. Calculate the rate law constant k_2 .

Problem 3-16

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

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

b) Give a balanced equation for the reaction.

Copper sulfate ($CuSO_4$) is white, the hydrate of copper sulfate ($CuSO_4 \cdot 5\ H_2O$) is blue. Copper sulfate exposed to air slowly takes up water and the colour changes to blue.
5.49 g of a sample of copper sulfate, which was exposed to air for a long time is dissolved in a volumetric flask, and 20 cm^3 of concentrated sulfuric acid are added. Then the volumetric flask filled up with water to 100 cm^3 .
2 g potassium iodide are added to 10 cm^3 of this solution which is then diluted using approximately 100 cm^3 and titrated with sodium thiosulfate (c = 0.100 mol/L), using starch solution as an indicator. The average volume of sodium thiosulfate needed: V = 29.40 mL.

c) Give a balanced equation for the reaction.

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

Problem 3-17

In the human body, the pH of blood has to be kept constant at appoximately 7.4. Changes in this value are dangerous and may cause death.
In order to keep the pH constant the buffer system of carbonic acid plays an important role based on the reaction

$$CO_2(aq) + H_2O \rightleftarrows HCO_3^-(aq) + H^+(aq).$$

Under physiological conditions (37 °C) the acidity constant for CO_2 is $pK_a = 6.1$.

a) Given this data calculate the ratio (concentration of carbon dioxide) /(concentration of hydrogencarbonate) in human blood at pH = 7.4

b) Is this a better buffer system against acids or against bases? Explain your answer.

The result of a) gives the ratio of the concentrations but no value of the absolute concentrations of $CO_2(aq)$ and $HCO_3^-(aq)$. In order to determine these absolute concentrations a sample of blood is exposed to various pressures of CO_2 until equilibrium is reached. Then the pH is measured:

$p(CO_2)$ in kPa	x	9.5	7.5	3.0	1.0
pH-Wert	7.4	7.2	7.3	7.5	7.6

c) Determine $p(CO_2)$ at pH = 7.4 .

d) Calculate the concentration of carbon dioxide dissolved in blood at pH = 7.4.

Under these conditions the Henry Law constant is $K_H = 2.25 \cdot 10^{-4}$ mol/(L· kPa)

e) Calculate the concentration of HCO_3^- in the sample at pH = 7.4.

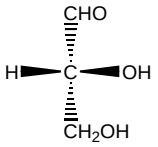
In everyday life people often talk of super-acidification of blood by lactic acid ($pK_a = 3.86$).

f) Calculate the pH of an aqueous (unbuffered) solution of lactic acid (c = 0.001 mol/L).

g) Under the conditions of blood mentioned above, show by calculation that lactic acid is mainly present as lactate, the anion of lactic acid.

Problem 3-18

Since all carbohydrates have chiral carbon atoms it was recognized long ago that a standard method of representation was needed. One method often used is the Fischer projection which refers to naturally occuring glyceraldehyde as a standard for the notation of the stereogenic center.



D-Glyceraldehyde

The horizontal lines represent bonds coming out of the page, the vertical lines represent bonds going into the page.

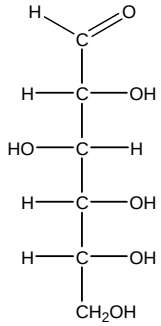
Sugars with the same stereochemical configuration as D-glyceraldehyde at the chiral carbon atom furthest from the carbonyl group (hydroxyl group at the lowest chiral atom pointing to the right) are called D sugars. In contrast to D sugars L sugars have the hydroxyl group at the lowest chiral atom on the left in the Fischer projection.

a) Using the rules of Cahn, Ingold, Prelog determine whether D-glyceraldehyde has R or S configuration.

b) Draw Fischer projections of all stereoisomers of 2,3,4-trihydroxypentane. Which of them are enantiomers, which are diastereomers, which of them show optical activity?

The picture shows the Fischer projektion of D-glucose.

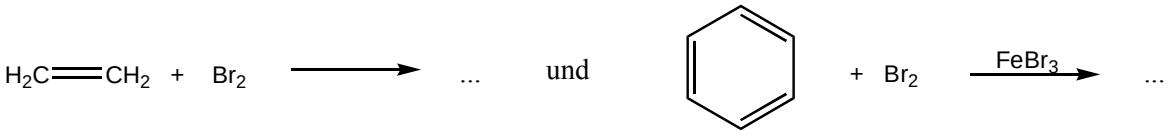
c) Give the systematical name of D-glucose using the rules of Cahn, Ingold, Prelog.



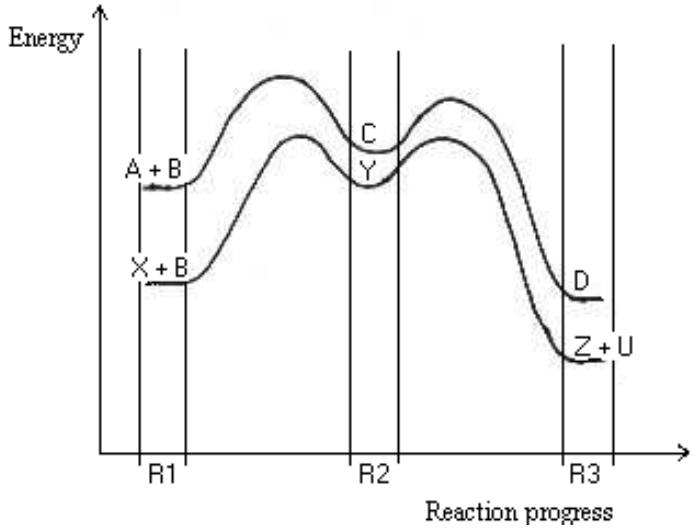
D-Glucose

Problem 3-19

Given are the two following reactions:



and the following energy diagram



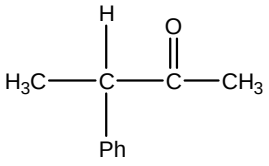
a) Assign structural formulas to the letters A, B, C, D, X, Y, Z, U.

b) Compare both reactions.

Problem 3-20

(3S)-Phenyl-2-butanone (A) is reduced by lithium aluminium hydride (in ether). Two products are formed.

A:



Ph ≡ Phenyl

Write the reaction equation.

Draw the Fischer projection of the two products and assign systematical names to them

.

Round 4 (theoretical)

Problem 4-1: Mass spectrometry (from prep.prop. Australia '98)

A sample of an isomer of dichloropropadiene is analysed in a mass spectrometer. A strong signal is observed at a mass-to-charge ratio (m/z) of 75, and another at m/z = 77.
Under certain operating conditions, these are the only two signals seen in the mass spectrum. Under different conditions the same sample gives rise to a number of different signals, including m/z = 82 (but not 83) and m/z = 28 (but not 27). Regardless of the operating conditions, it is found that the signal at m/z = 77 is always 60% of the intensity of the peak at m/z = 75.

You can assume the following:

- observed ions are all single charged and arise directly by dissociative ionisation of the dichloropropadiene, without any rearranging occuring during fragmentation.
- The dichloropropadiene has been prepared from elemental carbon, hydrogen , and chlorine in some unspecified fashion. The elemental feedstocks used are known to contain isotopic abundance ratios different from those conventionally observed for carbon, hydrogen and chlorine, but contain only stable isotopes. Furthermore, no efforts have been made to label specific atoms within the molecule with any particular isotope.

a) Which isotopes of H, C and Cl respectively are possible?

b) What are the chemical formulas of the ions detected at m/z = 75 and m/z = 77. Explain your decisions.

c) Which isotopes existed in the feedstocks dichloropropadiene has been prepared from? If there were more than one isotope calculate the molar ratio (n/n).
Which is the isotopic distribution in the dichloropropadiene sample. Calculate the percentage of each isotopomer in % (n/n).
(Isotopomeres are molecules which have identical chemical structures but which differ in the constituent isotopes)

d) Identify the isomer of dichloropropadiene studied here.
Draw the structure and indicate the positions of fracture which lead to the fragments observed.

Problem 4-2: Crystals

The mineral „wuestit", Fe_xO, crystallizes in a NaCl lattice (Na^+ ions form a cubic face centered lattice octahedrally surrounded by 6 Cl^- ions).
In the crystal examined the value of x is $x < 1$ due to lattice defects. The reason for such defects is that there are some iron ions with the charge +3 and therefore the number of iron ions needed for charge balance has decreased.

The density of the examined crystal is $\rho = 5.71$ g/cm^3.
An X-ray analysis was done. The reflection angle ϑ for the reflection at the (2 0 0) plane was found at $\vartheta = 9.56°$ using Mo K_α radiation ($\lambda = 71.07$ pm).
(Remark: In a unit cell with axes a,b,c a plane is denominated by its reciprocal intercepts of the axes in the order *reciprocal intercept on the a-axis/ reciprocal intercept on the b-axis/ reciprocal intercept on the c-axis*. Hence „0“ for example means that the plain is parallel to the axis refered to.)

a) Sketch the unit cell of the NaCl lattice.

b) Calculate the length of the edge of the unit cell.

c) Determine x.

d) Determine the molare ratio of Fe^{2+} and Fe^{3+} with reference to the total content of iron.

e) Give a formula of „wuestit“ considering the different charges of the iron ions.

f) Mn, Co, Ni form similar compounds. In which of them has x the highest, in which the lowest value. Explain your answer.

Problem 4-3: Acids, buffers and so on

a) The pH of a solution of acetic acid ($pK_a = 4.76$; $K_a = 1.74 \cdot 10^{-5}$) is 4.50.
Calculate the concentration c_0 of the acid and the degree of protolysis $\alpha = c(A^-)/c_0$.

b) A buffer solution with the same pH as in a) (4.5) shall be prepared by mixing acetic acid (c = 0.10 mol/L) and sodium hydroxide solution (c = 0.15 mol/L).
Which volume of sodium hydroxide solution must be added to 1.4 L acetic acid?

c) 100 mL of a sodium hydroxide solution (c = 0.010 mol/L) are added to 1.4 L acetic acid with the concentration calculated in a).
Calculate the pH value.

d) 100 mL of sodium hydroxide solution (c = 0.010 mol/L) are added likewise to 1.4 L of the buffer solution prepared in b).
Calculate the pH value.

e) A buffer solution was prepared from 1 L of acetic acid (c = 0.10 mol/L) and 1 L of sodium acetate (c = 0.10 mol/L).
Calculate the pH of the buffer solution (pH_{buffer}).

f) The buffer solution prepared in e) shall guarantee the range

$$pH_{Puffer} - 0.2 < pH < pH_{Puffer} + 0.2.$$

Which is the maximum amount of H^+ or OH^- respectively that may be added?

g) A buffer solution is to be prepared in the same way as in e) by mixing 1 L of acetic acid and 1 L of sodium acetate solution both of the same concentration. If you add 0.5 L of

hydrochloric acid (c = 0.35 mol/L) to this buffer solution it shall guarantee the range $pH_{Puffer} - 0.2 < pH < pH_{Puffer} + 0.2$.
Calculate the concentration of acetic acid.

h) *Calculate and draw the titration curve obtained from adding sodium hydroxide solution (c = 0.10 mol/L) to 10 mL of a diprotic organic acid.*
(H_2B; c = 0.10 mol/L; $K_{a\,1} = 6.6 \cdot 10^{-5}$ mol/L , $K_{a\,2} = 1.0 \cdot 10^{-10}$ mol/L).
Consider only the range 0 to 15 mL NaOH solution.

i) The calculation of the pH of the first equivalence point in h) can be done by $pH = ½ \cdot (pK_{a\,1} + pK_{a\,2})$. This in an approximate formula.
Explain why.
Give the equations which lead to an exact calculation of the pH of the first equivalence point. ***Don't carry out*** *this calculation.*

Problem 4-4: States

The vapor pressure of liquid SO_2 is given by the empirical equation

$$\lg \frac{p}{Pa} = - \frac{1425.7K}{T} + 10.4435,$$

that of solid SO_2 by

$$\lg \frac{p}{Pa} = - \frac{1871.2K}{T} + 12.7165 .$$

a) Calculate the coordinates (p, T) of the triple point where gaseous, fluid and solid SO_2 are at equilibrium.

b) Calculate the boiling temperature at the pressure of $p = 1.013 \cdot 10^5$ Pa.

c) Calculate the pressure at the equilibrium

(i) $SO_2(s) \rightleftarrows SO_2(g)$

(ii) $SO_2(\ell) \rightleftarrows SO_2(g)$ *at room temperature (20°C)?*

d) Sketch a phase diagram of SO_2 due to your calculations.

e) Which phase of SO_2 is stable at room temperature and standard pressure due to your sketch?

f) Determine from your sketch whether SO_2 is able to sublimize when the temperature is higher than –50 °C.

Problem 4-5: Solutions and solubility

Calcium carbonate and calcium oxalate have the solubility products

$K_L(CaCO_3) = 1{,}2 \cdot 10^{-8}$ (mol/L)^2 $K_L(CaC_2O_4) = 2 \cdot 10^{-9}$ (mol/L)^2 respectively.

a) *Calculate the concentration of calcium ions in a saturated solution of $CaCO_3$.*

b) *Calculate the concentration of calcium ions in a solution saturated with both $CaCO_3$ and CaC_2O_4.*

c) In a thermally insulated vessel 25 mL of an aqueous solution of potassium hydroxide are placed. 5 mL portions of nitric acid (c = 2,00 mol/L) were added sucesssively. After each addition the temperature was measured:

mL nitric acid	0	5	10	15	20	25	30	35	40	45
temperature in °C	18.0	20.5	22.6	24.4	26.2	27.7	29.0	29.5	29.1	28.7

What was the mass in the initial sample?

d) *Explain why there is no linear increase in temperature.*

Aufgabe 4-6: Extraction

The distribution of a weak acid (HA) between two inmiscible solvents, such as water (w) and ether (e) follows the Nernst distribution law

$$(1) \qquad \frac{c(HA)_e}{c(HA)_w} = K_D \ .$$

K_D depends on the temperature and the character of both the solvents and the solute.
In this case K_D has the value $K_D = 5.4$.

a) *Calculate the molar percentage of the acid HA which can be extracted from1 L of dilute acid with 500 mL ether by*

i) using the whole amount of ether for one extraction,

ii) five sucessive extractions with 100 mL ether each

Use equation (1)!

b) The result of a), the extraction of HA, is valid only under certain conditions. *What are these conditions and how can you make sure that these conditions are established?*

c) 100 mL of a buffer solution (pH = 3,5) contains among other substances an acid HA, with $pK_a = 4{,}25$. A fraction of the acid is extracted by 100 mL ether.
The amount of extracted acid in the ether portion is 0.0864 mole HA.
Determine the total concentration of HA which was in the initial buffer solution.
(Assumption: The pH value does not change during the extraction)

d) The distribution coefficient K_D for a substance A between two inmiscible solvents S_1 and S_2 (equation (1)) refers to the species A present in both solvents. If there is any ionisation,

dimerisation or complexation of A, the distribution ratio D better describes the extraction efficiency

$$D = \frac{\text{total concentration of all species of A in } S_2}{\text{total concentration of all species of A in } S_1}$$

i) For the acid HA calculate D under the conditions of part c) ($pK_a = 4.25$; $K_D = 5.4$; pH = 3.5) with the solvents water and ether. In ether there exists only HA.

ii) Derive a formula for D containing only K_a, K_D and $c(H^+)$.

Problem 4-7

Air is sucked through an aqueous solution of cobalt(II) chloride, ammonium chloride and ammonia for several hours at room temperature. A crystalline compound A is formed.
Properties of A:

- A contains: 22.03 % Co; 6.78 % H; 39.76 % Cl; 31.43 % N.
- A reacts with a solution of silver nitrate to give silver chloride and a mononuclear compound of cobalt.
- In aqueous solution A dissociates in four types of ions.

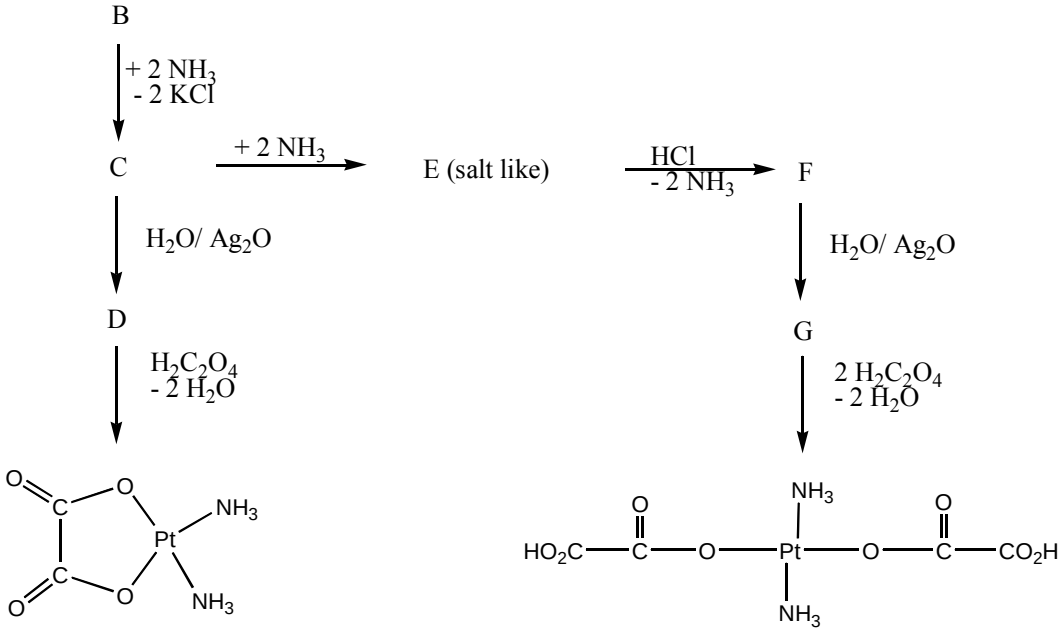
a) Which is the empirical formula of A?

b) Draw the constitutional formula.

c) A is diamagnetic. Predict the electron configuration of the 3d, 4s and 4p subshells.

Treating the compound dipotassium-tetrachloroplatinate(II) (B) with ammonia gives C.

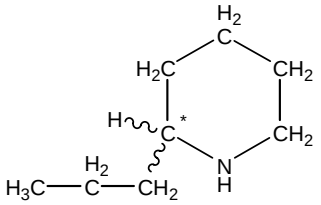
d) Using the scheme below derive the formulas of C and D as well as of the salt-like compound E and of the compounds F and G.

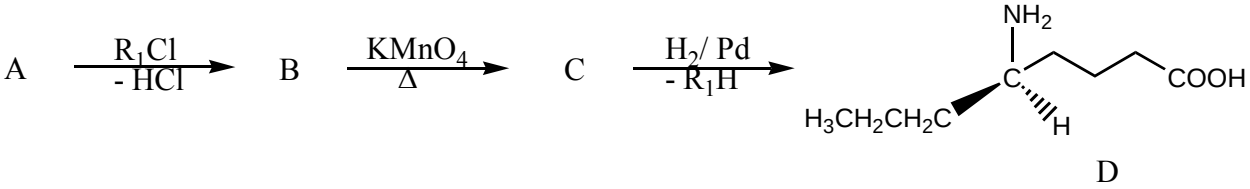


Problem 4-8

In order to find the configuration of the compound A the following reactions were performed :

A =





D

$KMnO_4$ leads to an oxidative cleavage of a C-C bond in the ring to get C among other compounds.

a) Identify the compounds B and C.

b) Write the full name of D, denote with R or S notation.

c) Denote the stereogenic center in A with R or S.

Problem 4-9

Cis-2-butene and *trans*-2-butene react with bromine.

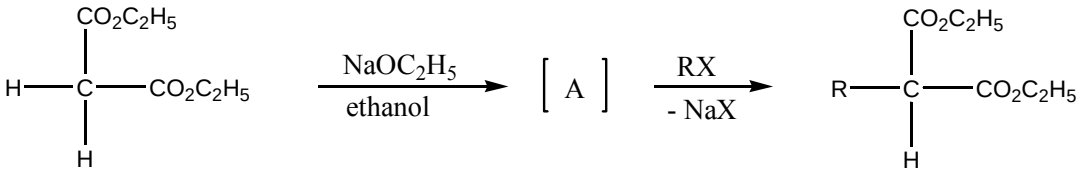
a) Write the full names of all products formed (no intermediates).

b) Draw the Fischer projections of all products.
Write the structural formulas for the reaction intermediates (X and Y respectively).

c) Which of the products formed are enantiomers, which are diastereomers, which of them show optical activity?

Aufgabe 4-10

Malonic ester syntheses are an excellent method to prepare substituted carboxylic acids. The syntheses follow the scheme shown below:

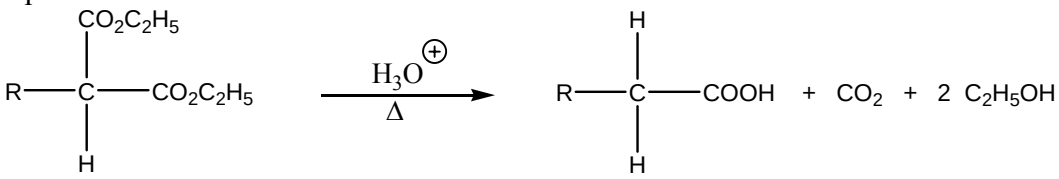


diethyl malonic ester

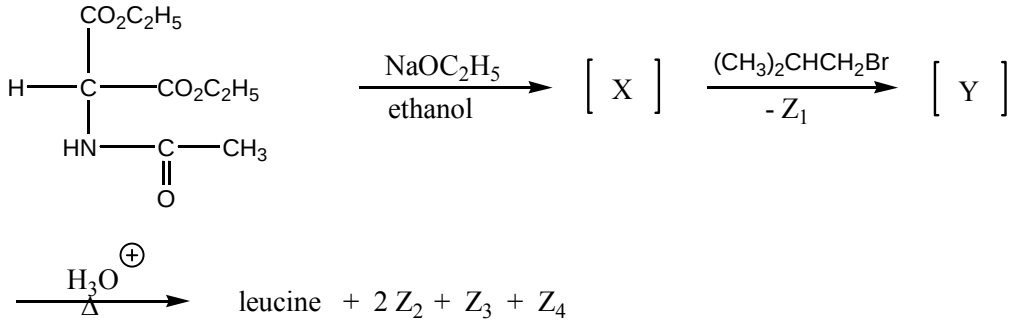
RX = Alkylhalide

Draw the structure of A and explain the course of the reaction.

The alkylated malonic esters can be hydrolyzed and decarboxylated when heated with aqueous acid:

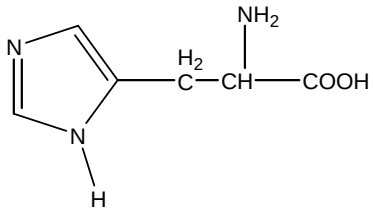


a) The synthesis of leucine is carried out by malonic ester synthesis as shown in the following scheme. Give the formulas of X and Y, Z_2, Z_3 and Z_4.



b) Does the solution of leucine synthesized in this way show a rotation of plane–polarized light?

The structure of histidine is



c) Suggest the starting reagents to synthesize histidine by malonic ester synthesis.

d) Amino acids react with each other to give peptides.
Give the structure of H-Leu-His-OH and H-His-Leu-OH respectively.

Round 4 (practical)

Practical Problem 4-11

Determination of magnesium, calcium und chloride ions in a water sample

1. Determination of the sum of calcium and magnesium ions

Fill up the 250 ml volumetric flask on your table.
Add 5 mL buffer solution and some water to a 25 mL aliquot. Before starting the titration add a spatula-tipfull of a powdered indicator (m(ErioT)/m(NaCl) = 1: 100) .
Titrate this sample with a solution of EDTA (c = 0.1 mol/l) to a clear blue end point.
Repeat this procedure twice.

a) Explain the principles of complexometric titration.

b) Calculate the concentration of the sum of Ca^{2+} and Mg^{2+} ions (mol/l).

2. Determination of calcium ions by precipitation with oxalate followed by titration with permanganate.

Transfer a 25 mL-aliquot into a beaker, add 6 ml diluted HCl and about 100 ml of water. Add NH_3 solution until the solution is slightly alkaline. Heat until the solution is very hot and add small portions of ammonium oxalate solution until no more precipitate is formed. After 15 minutes of boiling the precipitate is collected on a filter.
The preciptiate is washed carefully five times with a small amount of a solution of ammonium oxalate.
The precipitate is dissolved in warm sulfuric acid ($V(H_2O)$: V(conc. H_2SO_4) = 3 : 1. 50 mL water are added, the solution heated to about 80° C and titrated with a solution of potassium permanganate (c = 0.02 mol/l).

c) Write the reaction equation of the titration with potassium permanganate.

d) Determine the amount of calcium ions in mol/l.

3. Determination of chloride ions (Mohr)

   Add 2 ml of a solution of potassium chromate (5%) to a 25 mL aliquot with pH about 7. Titrate with a solution of silver nitrate (c = 0.1 mol/l) to a red end point (stable for 1 minute).
   Repeat the procedure twice.

e) Using a reaction equation explain how the indicator works.

f) Calculate the concentration of the chloride ions in mol/l.

Practical Problem 4-12

Synthesis of an organic compound

There are 1.9 g aniline (20 mmol) in a round-bottomed flask (with reflux condenser). 2.3 g of 2,5-hexanedione (20 mmol), 5 cm^3 of methanol (solvent) and 10 drops of concentrated HCl are added. The solution is heated to reflux for 15 minutes. Then add the reaction mixture to 50 cm^3 of hydrochloric acid (0.5 mol/l) which is kept cool in an ice bath.

The crystals formed are collected by suction filtration and recrystallized from an ethanol/water mixture (9:1) . The isolated recrystallized product is washed with about 20 cm^3 of the same ethanol/water mixture (9:1) and pressed dry on a filter.

The dry product is weighed.

A small amount (3 – 5 mg) of the product is dissolved in a few drops (ca. 5) of acetone.

Using of a capillary tube, a drop of this solution is placed on a TLC plate. A similarly prepared sample of the starting material (aniline) is applied next to the product as a reference.
The TLC plate is developed with a (1:3) mixture of ethyl acetate / hexane.
Using UV light you can see the spots on the TLC plate.

a) *Calculate the theoretical yield and the obtained yield as a percentage of the theoretical. (molar mass of the product $M \approx 171$ g/mol)*

b) *Determine the melting point of the product.*

c) *Calculate the Rf value of the product.*

d) *Suggest a structure of the product.*

Part 2

Answers

Answers round 1

Problem 1-1

a) $CaCO_{3\,(s)} \longrightarrow CaO_{(s)} + CO_{2\,(g)}$

b) $K = p(CO_2)/p_o$ where $p_o = 1.00 \cdot 10^5$ Pa (1 bar) $\Leftarrow p(CO_2) = 1.34 \cdot 10^5$ Pa

c) $CaO_{(s)} + H_2O_{(l)} \longrightarrow Ca(OH)_{2(s)}$

d) $c(Ca^{2+}) = 1.70 \cdot 10^{-2}$ mol/L $c(OH^-) = 3.4 \cdot 10^{-2}$ mol/L pH = 12.5

e) $CO_{2\,(g)} \rightleftarrows CO_{2\,(aq)}$
$CO_{2\,(aq)} + 2\,H_2O_{(l)} \rightleftarrows HCO_3^-{}_{(aq)} + H_3O^+{}_{(aq)}$
$HCO_3^-{}_{(aq)} + H_2O_{(l)} \rightleftarrows CO_3^{2-}{}_{(aq)} + H_3O^+{}_{(aq)}$
$CO_3^{2-}{}_{(aq)} + Ca^{2+}{}_{(aq)} \rightleftarrows CaCO_{3\,(s)}$.

f) The solution of calcium hydroxide is alkaline. Thus the third equilibrium mentioned in e) is shifted towards the formation of $CO_3^{2-}{}_{(aq)}$. The concentration of $CO_3^{2-}{}_{(aq)}$ then is sufficient for the precipitation of $CaCO_3$.
A solution of calcium chloride is neutral, the concentration of $CO_3^{2-}{}_{(aq)}$ is considerable smaller than in a solution of calcium hydroxide. Therefore, the solubility product will not be exceeded.

Problem 1-2

a)

	$SO_{2(g)}$	+	$NO_{2(g)}$	$\rightleftarrows$	$SO_{3(g)}$	+	$NO_{(g)}$
Initial amount (/mol)	0.720		0.490		0.710		0
at equilibrium (/mol)	0.720-0.390		0.490-0.390		0.710+0.390		0.390

$$K = \frac{c(SO_3) \cdot c(NO)}{c(SO_2) \cdot c(NO_2)} \qquad K = \frac{1{,}100 \cdot 0{,}390}{0{,}330 \cdot 0.100}$$

K = 13.0

b)

	$SO_{2(g)}$	+	$NO_{2(g)}$	$\rightleftarrows$	$SO_{3(g)}$	+	$NO_{(g)}$
initial amount (/mol)	1.330		0.100		1.100		0.390
at new equilibrium (/mol)	1.330-x		0.100-x		1.100+x		0.390+x

$$K = \frac{c(SO_3) \cdot c(NO)}{c(SO_2) \cdot c(NO_2)} \qquad 13 = \frac{(1.10 + x) \cdot (0.39 + x)}{(1.33 - x) \cdot (0.10 - x)}$$

$x^2 + 1.49x + 0.429 = 13x^2 - 18.59x + 1.729$
$(x_1 = 1.6)$ $x_2 = 0.067$

$\Leftarrow$	$SO_{2(g)}$	+	$NO_{2(g)}$	$\rightleftarrows$	$SO_{3(g)}$	+	$NO_{(g)}$
	1.263 mol		**0.033 mol**		**1.167 mol**		**0.457 mol**

Problem 1-3

a) $C_{17}H_{35}COOH_{(s)} + 26\,O_{2(g)} \longrightarrow 18\,CO_{2(g)} + 18\,H_2O_{(l)}$.

b)

oxygen	nitrogen	argon
V = 3.99 m^3 n = 160.0 mol	V =14.84 m^3 n = 594.9 mol	V =0.17 m^3 n = 6.9 mol

After combustion:

oxygen	carbon dioxide	nitrogen	argon
n = 117.6 mol	n = 29.3 mol	n = 594.9 mol	n = 6.9 mol

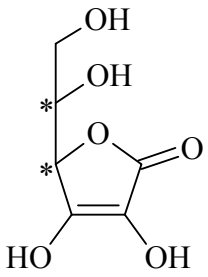
oxygen	carbon dioxide	nitrogen	argon
15.7 Vol%	**3.9 Vol%**	**79.5 Vol%**	**0.9 Vol%**

Problem 1-4

a) n(C) = 25.5 mmol n(H) = 34.0 mmol n(O) = 25.5 mmol

n(C) : n(H) : n(O) = 3 : 4 : 3 ; M = 176 g/mol ⇐ $C_6H_8O_6$

b)



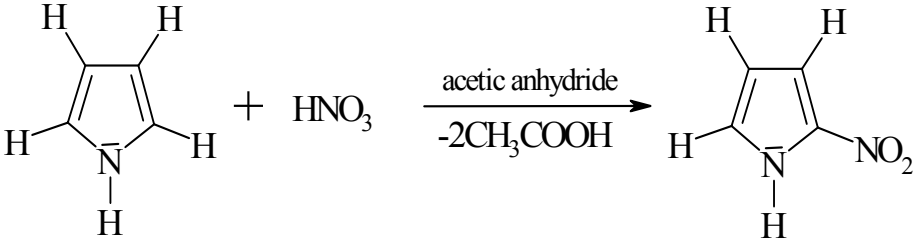
ascorbic acid

c) There are two stereogenic centers marked with *. Therefore you find two diastereomeric pairs of enantiomers:

diastereo-mers { R,R-compund A ⟷ (enantiomers) S,S-compound A
R,S-compound A ⟷ (enantiomers) S,R-compound A } diastereo-mers

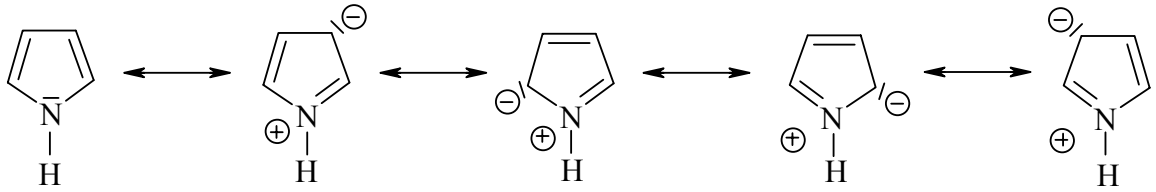
Problem 1-5

a)

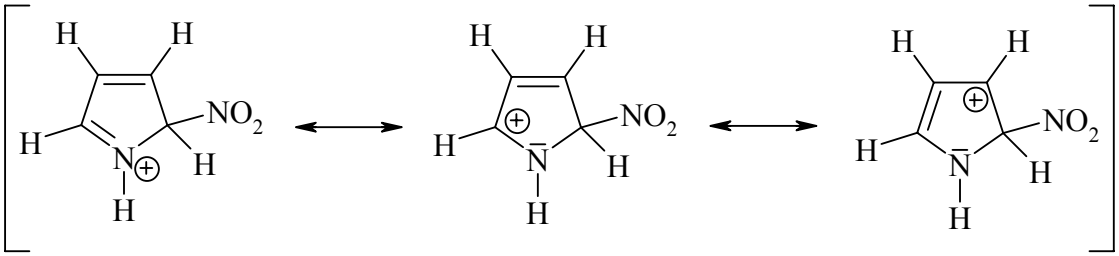


b) Type: elektrophilic aromatic substitution.

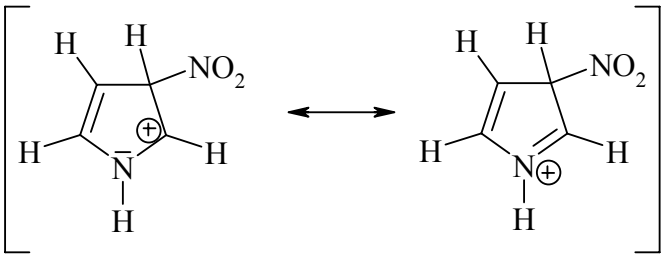
Pyrrole is an electron-rich aromatic compound. There are six π-elektrons distributed to five atoms of the ring, while in benzene six atoms share six π-elektrons.
Pyrrole fulfills the Hückel rule having 4n+2 (n = 1) π-elektrons. Therefore pyrrole is an aromatic compound. The lone electron pair on the nitrogen atom is part of the aromatic system and increases the electron density in the ring compared to benzene.
Electrophilic substitutions are therefore made easier. This is shown in the following picture of resonance structures:



c) The elektrophilic substitution takes place at the ortho positon (ortho to the nitrogen atom). This can be explained by analyzing the stabilities of the carbocation intermediates.
An attack on the C2-atom leads to three mesomeric structures:



On the other hand an attack on the C3-Atom leads to only two mesomeric structures:



Therefore, the carbenium ion resulting from attack on C2 is more stable than that resulting from attack on C3. Substitution in ortho positon is thus favoured by kinetics.

d) Because the nitrogen lone pair is a part of the aromatic sextet, the carbon atoms of pyrrole are more electron-rich than those of benzene. In general, pyrrole is more reactive toward electrophiles than benzene rings are.
Reactions A and B are electrophile substitutions.
You can compare pyrrole with a benzene ring that has an activating substituent. One such ortho-directing activator is CH_3 (reaction A) while NO_2 is deactivating and meta-directing.
Nitration of pyrrole is similar to reaction A.

Answers round 2

Problem 2-1

a) C_3H_8 80.0% $\Leftarrow$ C_3H_6 10.0% und H_2 10.0 % .
Let c_B = total concentration of all species in equilibrium:

$c(C_3H_8) = 0.80 \cdot c_B$. $c(C_3H_6) = 0.10 \cdot c_B$ und $c(H_2) = 0.10 \cdot c_B$.

$$1.30 \cdot 10^{-3}\,\text{mol/L} = \frac{(0{,}100 \cdot c_B)^2}{0{,}800 \cdot c_B} \Leftarrow \quad c_B = 0.104\ \text{mol/L}.$$

⇨ $c(C_3H_8) = 0.0832$ mol/L, $c(C_3H_6) = c(H_2) = 0.0104$ mol/L, $p_B = 692$ kPa

b) If $p_A = p_B$ then $c_A = c_B$. At equilibrium $c(CO_2) = c(H_2) = x$

$$c(CO) = c(H_2O) = \frac{0.104\text{mol/L} - 2x}{2} = 0.052\ \text{mol/L} - x.$$

$$0.25 = \frac{(0.052\text{mol/L} - x)^2}{x^2} \quad \Leftarrow \quad x = 3.47 \cdot 10^{-2}\text{mol/L}$$

⇨ $c(CO_2) = c(H_2) = 3.47 \cdot 10^{-2}$ mol/L $c(CO) = c(H_2O) = 1.73 \cdot 10^{-2}$ mol/L

c) Vessel A $p'_A = 2 \cdot p_A$ **$p'_A = 1384$ kPa**

vessel B $C_3H_8 \rightleftarrows C_3H_6 + H_2$

initial concentration / mol/L	$2 \cdot 0.0832$	$2 \cdot 0.0104$	$2 \cdot 0.0104$
equilbrium concentr./ mol/L	$0.1664 + y$	$0.0208 - y$	$0.0208 - y$

$$1.30 \cdot 10^{-3}\,\text{mol/L} = \frac{(0.0208\text{mol/L} - y)^2}{(0.1664\text{mol/L} + y)} \quad \Leftarrow \quad y = 5.84 \cdot 10^{-3}\ \text{mol/L}.$$

$c'_B = 2 \cdot c_B - y$. $c'_B = 0.2022$ mol/L $p'_B = c'_B \cdot R \cdot T$ **$p'_B = 1345$ kPa**

Problem 2-2

a)

Electrolyte: NaOH solution

anode: $2\ OH^- \longrightarrow H_2O + ½\ O_2 + 2\ e^-$
cathode: $2\ H_3O^+ + 2\ e^- \longrightarrow H_2 + 2\ H_2O$
or $2\ H_2O + 2\ e^- \longrightarrow H_2 + 2\ OH^-$
everywhere $4\ H_2O \longrightarrow 2\ H_3O^+ + 2\ OH^-$
in total $H_2O \longrightarrow H_2 + ½\ O_2$

Electrolyte: H_2SO_4 solution

anode: $2\ HSO_4^- + H_2O \longrightarrow ½\ O_2 + 2\ H_2SO_4 + 2\ e^-$
$2\ H_2SO_4 + H_2O \longrightarrow 2\ HSO_4^- + 2\ H_3O^+$
or $3\ H_2O \longrightarrow ½\ O_2 + 2\ H_3O^+ + 2\ e^-$
cathode: $2\ H_3O^+ + 2\ e^- \longrightarrow H_2 + 2\ H_2O$
in total $H_2O \longrightarrow H_2 + ½\ O_2$

b) In both cells water is electrolyzed. Thus the decomposition voltage is the same in bothe cells.

Decomposition voltage $U_z = \Delta_R G^0/z \cdot F$. $\Delta_R G^0 = -\Delta G^0_f(H_2O) = \Delta H^0 - T \cdot \Delta S^0$.

With

	ΔH^0_f in kJ/mol	S^0 in J/(K·mol)
$H_2(g)$	0.00	130.8
$O_2(g)$	0.00	205.3
$H_2O(l)$	- 286.3	70.1

you get

$\Delta_R G^0 = -\Delta G^0_f(H_2O) = 237.6$ kJ/mol (z = 2; F = 96487 A·s/mol) **U_z = 1.23 V**

Or

Electrolyte: NaOH solution

anode $E_A = 0.40$ V (standard conditions)

cathode $E_K = 0\ V + \frac{0{,}059}{2} V \cdot \lg (10^{-14})^2$. $E_K = -0.83$ V

$U_z = E_A - E_K$ **U_z = 1.23 V**

Electrolyte : H_2SO_4 solution

anode $E_A = 1.23$ V (standard conditions)

kathode $E_K = 0$ V (standard conditions)

$U_z = E_A - E_K$ **U_z = 1.23 V**

c) Any ammonium salt will do: **$NH_4^+ + OH^- \rightarrow NH_3 + H_2O$**

In a solution with OH^-, NH_3 und NH_4^+ : $pOH = pK_B + \lg [c(NH_4^+)/c(NH_3)]$.

$3 = 4.75 + \lg c(NH_4^+)/c(NH_3)$ $\lg c(NH_4^+)/c(NH_3) = -1.75$

$\Leftarrow c(NH_4^+)/c(NH_3) = 0.0178$ $c(NH_4^+) = 0.0178 \cdot c(NH_3)$

$c(OH^-)$ is to be lowered to 1/1000 of the initial value, $c(OH^-) = 1 \cdot 10^{-3}$ mol/L.

Thus $(1 - 1 \cdot 10^{-3})$ mol = 0.999 mol OH^- have to vanish, the same amount of ammonia is formed.

$n(NH_3) = 0.9990$ mol $n(NH_4^+) = 0.0178 \cdot n(NH_3)$ $\Leftarrow n(NH_4^+) = 0.0178$ mol

$n_0(NH_4Cl) = n(NH_4^+) + n(NH_3)$ $n_0(NH_4Cl) = 1.0168$ mol

$m = n \cdot M$ $M(NH_4Cl) = 53.45$ g/mol $\Leftarrow$ **$m(NH_4Cl) = 54.35$ g**

d) The decomposition voltage does not change because the total reaction does not change. The change of the pH by 3 changes the potential of the half cells by $\approx 3 \cdot 59$ mV each, but in a way that these effects compensate each other in the calculation of the decompositon voltage.

e) Standard conditions at both electrodes.

E^0(cathode) = $E^0(H_3O^+/H_2) = 0$ V

E^0 (Anode) = E^0 $(O_2/OH^-) = 0.40$ V **U_z = 0.40 V**

f) Cathode: pH = 14 $\Leftarrow c(H_3O^+) = 1.00 \cdot 10^{-14}$mol/L $E_K = 0V + 0.059V \cdot \lg 10^{-14}$

anode: pH = 0 $\Leftarrow c(OH^-) = 1.00 \cdot 10^{-14}$mol/L $E_A = 0.40V + 0.059V \cdot \lg(1/10^{-14})$

decomposition voltage $U_z = E_A - E_K = 0.40V + 2 \cdot 0.059V \cdot \lg 10^{14}$ **U_z= 2.05 V**

Problem 2-3

a) The decrease of mass is caused by electrolysis and crystallization of calciumnitrate-tetrahydrate ($Ca(NO_3)_2 \cdot 4\ H_2O$). When the electrolysis is over there is a saturated solution.

$Q = I \cdot t$ $\quad Q = 12 \cdot 60 \cdot 60 \cdot 5$ As $\quad Q = 216{,}000$ As

formed mass of hydrogen $= \frac{216{,}000}{96487} \cdot 1\text{g} = 2.24$ g hydrogen

formed mass of oxygen $= \frac{216{,}000}{2 \cdot 96487} \cdot 16\text{g} = 17.91$ g oxygen

Decrease of mass by electrolysis $= 20.15$ g water

Decrease of mass by crystallisation = 41.9 g – 20.15 g = 21.75 g $Ca(NO_3)_2 \cdot 4H_2O$.

[$M(Ca(NO_3)_2 \cdot 4\ H_2O) = 236.1$ g/mol] $\quad$ 0.09 mol $Ca(NO_3)_2 \cdot 4\ H_2O$.

In solution before electrolysis:

H_2O: 160 g

$Ca(NO_3)_2$: 100 g, which corresponds to 100/164.1 mol = 0.61 mol.

In solution after electrolysis:

H_2O: (160 - 20.15 – 0.09·4·18) g = 133.37g

$Ca(NO_3)_2$: (0.61- 0.09) mol = 0.52 mol.

To produce such a (saturated) solution you need x g of water and 0.52 mol $Ca(NO_3)_2 \cdot 4H_2O$ which give additional water.

133.7 g = x + 0.52·4·18g $\quad$ x = 95.93 g H_2O .

Thus in 100 g of water you can dissolve a maximum of $\frac{100}{95{,}93} \cdot 0.52 = 0.54$ mol

$Ca(NO_3)_2 \cdot 4H_2O$, that are **127.5 g $Ca(NO_3)_2 \cdot 4H_2O$.**

b) Dissolving silver oxalate in water produces oxalate ions. According to the pH they react with H_3O^+. The lower the pH, the more oxalate ions react to give $HC_2O_4^-$ and $H_2C_2O_4$, respectively, the more silver oxalate will dissolve in water. Thus the solubility of silver oxalate depends on the pH.

c) $Ag_2C_2O_{4(s)} \rightleftarrows 2\ Ag^+_{(aq)} + C_2O_4^{2-}{}_{(aq)}$

Solubility product $K_L = c^2(Ag^+) \cdot c(C_2O_4^{2-})$ (1) where $c(Ag^+) = 2 \cdot S$.
(S = solubility of silver oxalate in water in mol/L)

$c_{Ox} = c(C_2O_4^{2-}) + c(HC_2O_4^-) + c(H_2C_2O_4)$ (2) where $c_{Ox} = S$.

$$K_{a1} = \frac{c(HC_2O_4^-) \cdot c(H_3O^+)}{c(H_2C_2O_4)} \quad \text{and} \quad K_{a2} = \frac{c(C_2O_4^{2-}) \cdot c(H_3O^+)}{c(HC_2O_4^-)}$$

$$S = c(C_2O_4^{2-}) \cdot \frac{K_{a1} \cdot K_{a2} + K_{a1} \cdot c(H_3O^+) + c(H_3O^+)^2}{K_{a1} \cdot K_{a2}},$$

$S = c(C_2O_4^{2-}) \cdot u$ where $u = \frac{K_{a1} \cdot K_{a2} + K_{a1} \cdot c(H_3O^+) + c(H_3O^+)^2}{K_{a1} \cdot K_{a2}}$

$c(C_2O_4^{2-}) = S/u.$

(1) $K_L = (2 \cdot S)^2 \cdot (S/u).$ (3)

pH = 7 $\Leftarrow$ 1/u = 0.998 ≈ 1 thus $K_L = 4 \cdot S^3$; $K_L = 3.5 \cdot 10^{-11}$ $(mol/L)^3$.

pH = 5 $\Leftarrow$ 1/u = 0.865 and following (3) $S = \sqrt[3]{\frac{K_L \cdot 0.865}{4}}$. **$S = 2.16 \cdot 10^{-4}$ mol/L**

d) pH = 10,8 $\Leftarrow$ u = 1 and $c_{Ox} = c(C_2O_4^{2-}) = S$.
The total concentration of silver in the solution c_{Ag} is
$c_{Ag} = c(Ag^+) + c(Ag(NH_3)^+) + c(Ag(NH_3)_2^+)$ (4) where $c_{Ag} = 2 \cdot S$.

$K_3 = \frac{c(Ag(NH_3)^+)}{c(Ag^+) \cdot c(NH_3)}$ und $K_4 = \frac{c(Ag(NH_3)_2^+)}{c(Ag^+) \cdot c(Ag(NH_3)^+)}$.

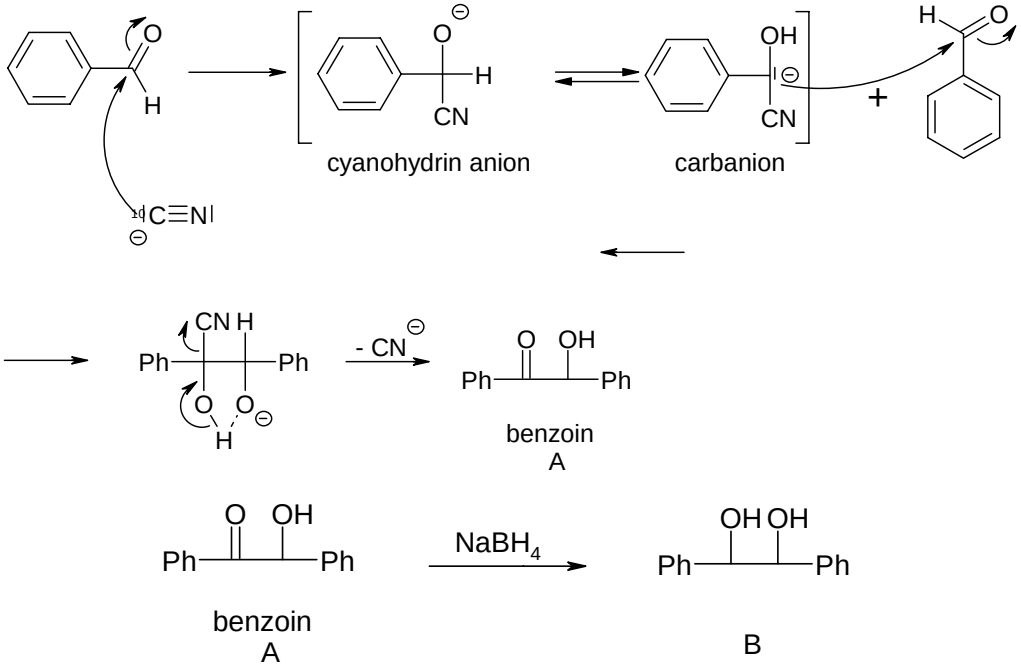
$2 \cdot S = c(Ag^+) \cdot (1 + K_3 \cdot c(NH_3) + K_3 \cdot K_4 \cdot c(NH_3)^2)$
$2 \cdot S = c(Ag^+) \cdot v$ where $v = 1 + K_3 \cdot c(NH_3) + K_3 \cdot K_4 \cdot c(NH_3)^2$
$\Leftarrow c(Ag^+) = 2 \cdot S/v.$
v = 6998.

$K_L = c^2(Ag^+) \cdot c(C_2O_4^{2-})$ where $K_L = 3{,}5 \cdot 10^{-11} (mol/L)^3$

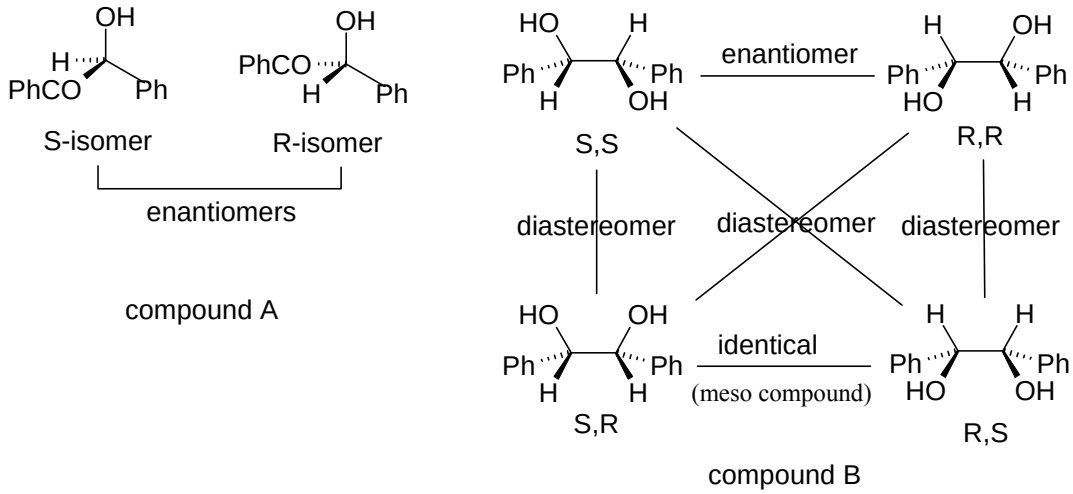
$K_L = (2 \cdot S/v)^2 \cdot S$ $S = \sqrt[3]{\frac{K_L \cdot 6998^2}{4}}$ **$S = 7.54 \cdot 10^{-2}$ mol/L**

Problem 2-4

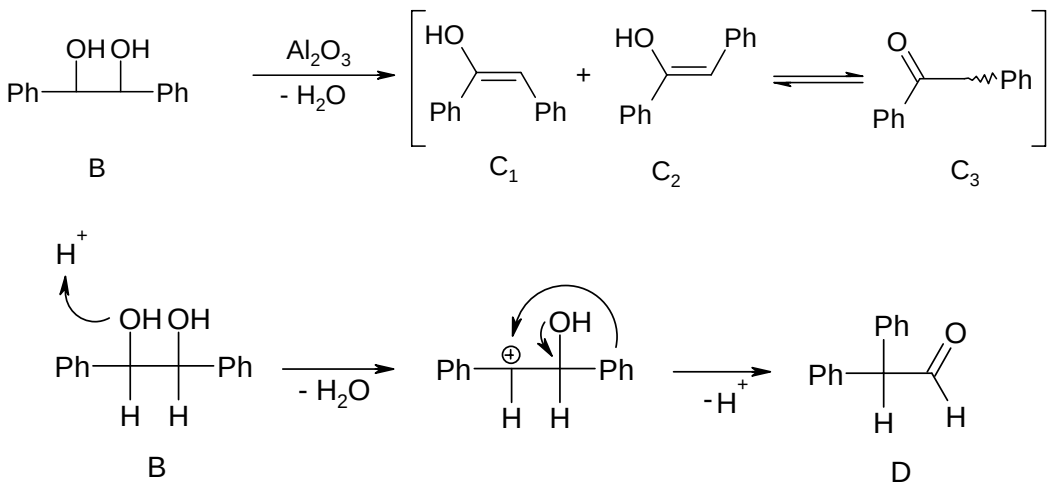
a)



b)

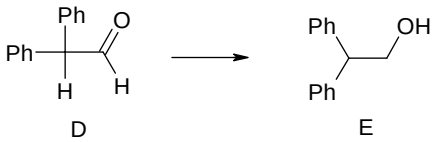


c)



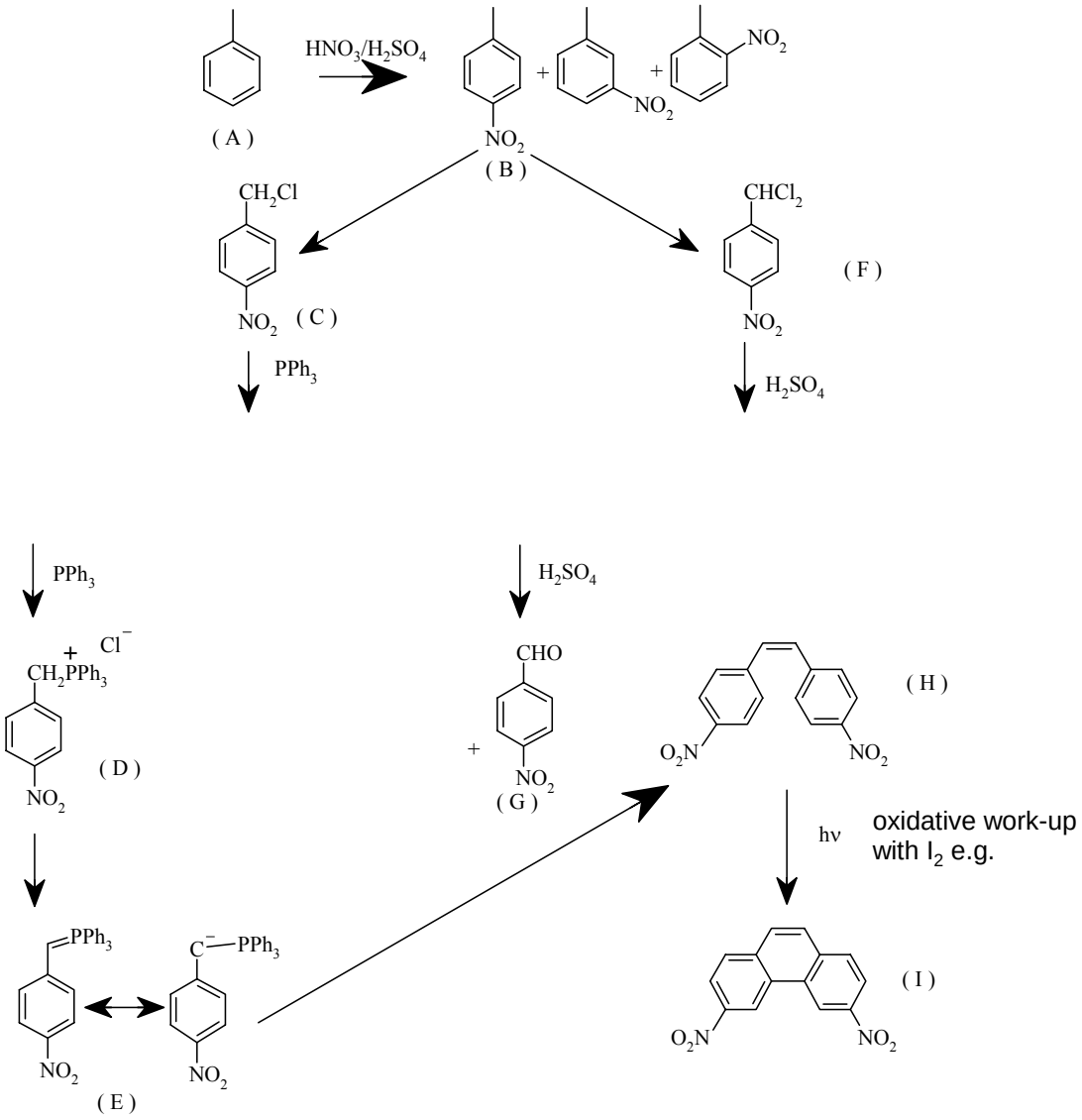
D is an aldehyde and shows a characteristic IR absorption at about 1700 cm^{-1}. It forms a sparsely soluble semicarbazone.

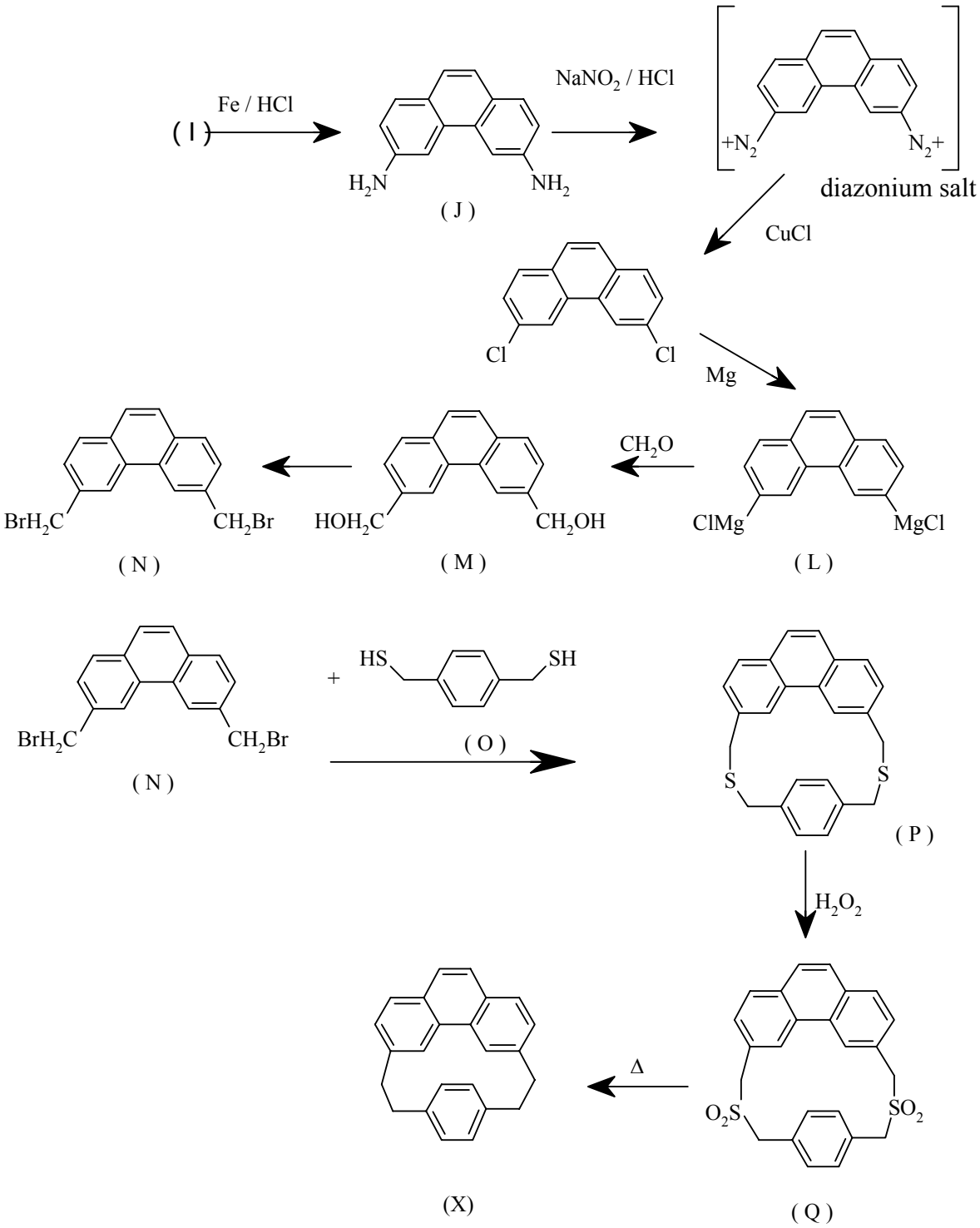
d)



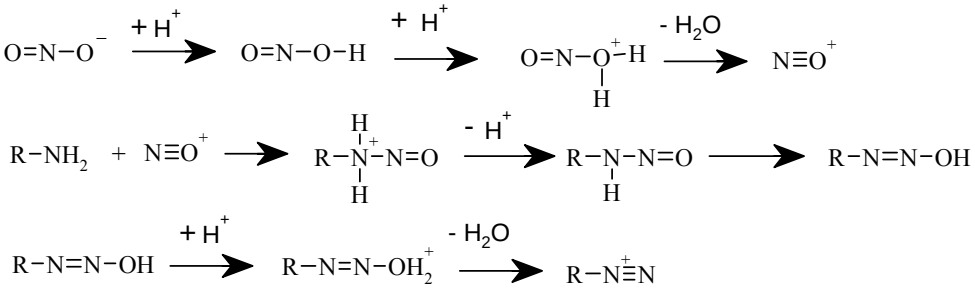
e) , f)

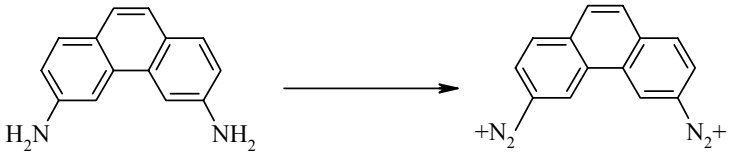
Problem 2-5

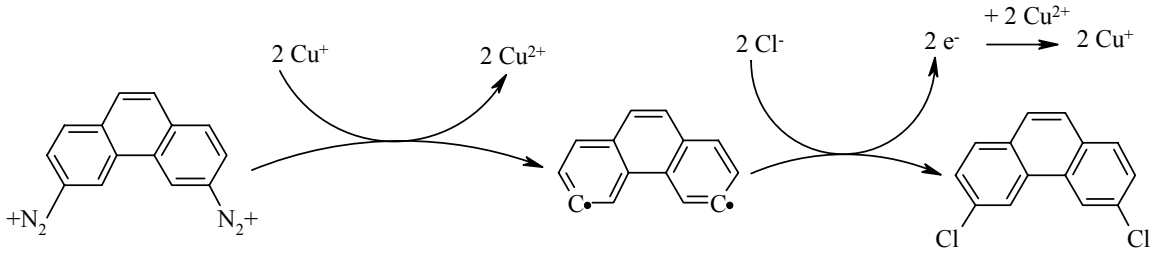

HNO3/H2SO4
(A)
NO2
(B)
CH2Cl
NO2
(C)
PPh3
CHCl2
NO2
(F)
H2SO4
PPh3
Cl−
CH2PPh3
NO2
(D)
H2SO4
CHO
NO2
(G)
(H)
O2N
NO2
hν
oxidative work-up
with I2 e.g.
PPh3
C−
PPh3
NO2
NO2
(E)
(I)
O2N
NO2


(I)
Fe / HCl
(J)
NaNO2 / HCl
diazonium salt
CuCl
Mg
CH2O
(L)
(M)
(N)
(N)
(O)
(P)
H2O2
(Q)
Δ
(X)

b) Sandmeyer reaction:







Answers round 3 exam 1

Problem 3-1

a) D b) C c) A d) B and C e) B f) D
g) D, the kinetic energy of most of the particles is higher than Ea

Problem 3-2

a) $c(S^{2-}) = 1{,}3 \cdot 10^{-17}$ mol/L.
b) MnS: $1{,}3 \cdot 10^{-17} \cdot 0{,}010 = 1{,}3 \cdot 10^{-19} < 2{,}5 \cdot 10^{-10}$ ⇐ no precipitate
CoS: $1{,}3 \cdot 10^{-17} \cdot 0{,}010 = 1{,}3 \cdot 10^{-19} > 4{,}0 \cdot 10^{-21}$ ⇐ precipitate
Ag_2S: $1{,}3 \cdot 10^{-17} \cdot 0{,}010^2 = 1{,}3 \cdot 10^{-19} > 6{,}3 \cdot 10^{-50}$ ⇐ precipitate
c) m = 0,030 g

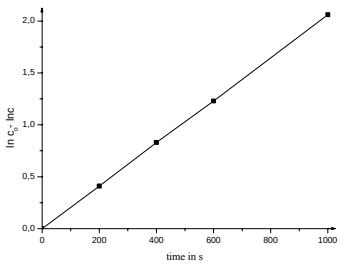
Problem 3-3

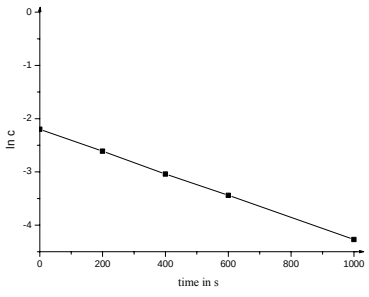
a) $\Delta H_{lattice} = - \Delta H_{I(K)} - E_{A(F)} - \Delta H_{Subl} - ½ \cdot \Delta H_D + \Delta H^0_f$
$\Delta H_{lattice} = -822$ kJ/mol
b) r = 130 pm.
c) $\rho = 10.5$ g/cm^3 74 %

Problem 3-4

a)

time/s s	0	200	400	600	1000
$c(N_2O_5)$ in mol/L	0.110	0.073	0.048	0.032	0.014
$\ln c_o - \ln c$	0	0.41	0.83	1.23	2.06
$\ln c$	-2.20	-2.61	-3.04	-3.44	-4.27





straight line,
thus first order

b) $k_1 = 2.06 \cdot 10^{-3}$ s^{-1}

c) $t_{1/2} = 1444$ s d) $p_{total} = 91.81$ kPa $p_\infty = 166.9$ kPa

e) $p_{total} = (2.5 - 1.5\, e^{-4.8 \cdot 10^{-4} s^{-1} \cdot t}) \cdot p_0$

f) The activation energy will differ for the different reactions

Problem 3-5

a) $c(Co^{3+}) = 2.2 \cdot 10^{-28}$ mol/L

b) $\frac{c[Co(NH_3)_6^{2+}]}{c(Co^{2+})} = 2.5 \cdot 10^{10}$

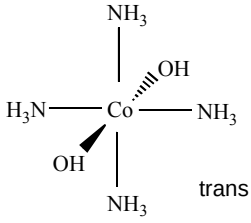
c) $c(Co^{2+}) = 4.0 \cdot 10^{-11}$ mol/L

d) Oxygen

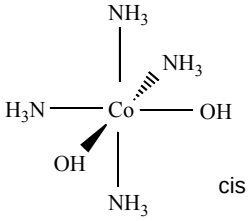
e) The concentration of Co^{3+} is so small (see a)) that the potential is lower than that of $2\ H_2O/O_2 + 4H^+$ and no oxidation will occur.

f) E = 0.80 V

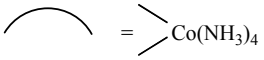
g) Stereoisomerism, diastereomers (cis-trans-isomers),
only the cis-isomer is suitable because of spatial reasons

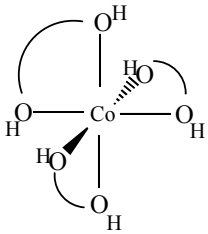


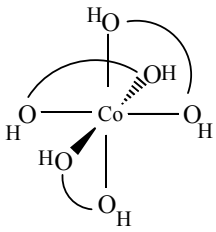
trans



cis







Problem 3-6

a) yes, same ε.

b) $\alpha = c(HA)$, $\beta = c(A^-)$ at 257 nm: $\varepsilon(HA) = 1 \cdot 10^3$, $\varepsilon(A^-) = 23 \cdot 10^3$, $\varepsilon(pH=3{,}60) = 8 \cdot 10^3$

$\alpha + \beta = 1$ and $1 \cdot \alpha + 23 \cdot \beta = 8$ $\Leftarrow$ $\alpha = \frac{15}{22}$, $\beta = \frac{7}{22}$, $K_a = \frac{\beta \cdot 10^{-3,6}}{\alpha}$ mol/L

$K_a = 1{,}17 \cdot 10^{-4}$ mol/L

Problem 3-7

a) $n = 61.1 \cdot 10^{-3}$ mol m = 1.96 g O_2 .

b) 1. particles without volume 2. no intermolecular forces

c) $\alpha_{ven} = 0.770$ $\alpha_{art} = 0.977$

d) $c_{Hb} = 2.33 \cdot 10^{-3}$ mol/L_{blood}

$c_{O_2}^{art} = c_{Hb} \cdot 4 \cdot \alpha_{art}$ $c_{O_2}^{art} = 9.09 \cdot 10^{-3}$ mol/L_{blood} $V_{O_2}^{art} = 0.234$ L/L_{blood}

e) $c_{O_2}^{ven} = c_{Hb} \cdot 4 \cdot \alpha_{ven} = 7.18 \cdot 10^{-3}$ mol/L_{blood}

$$x = \frac{c_{O_2}^{art} - c_{O_2}^{ven}}{c_{O_2}^{art}} \cdot 100\,\% \qquad x = 21.0\,\%$$

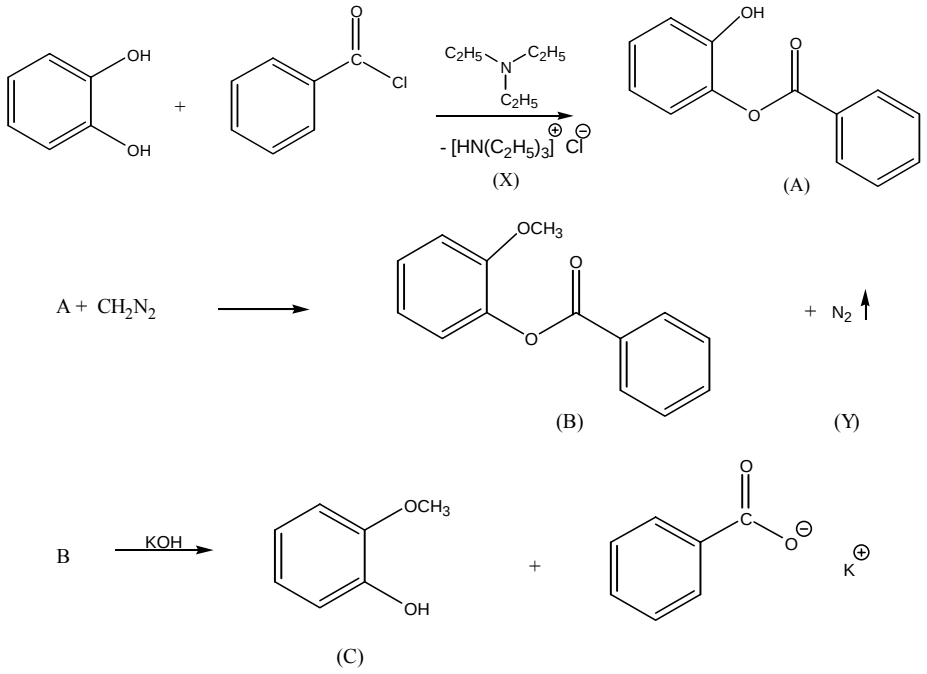
f) consumption (O_2) = 20 mol/day

$$\text{amount of blood} = \frac{20\text{mol/day}}{c_{O_2}^{art} - c_{O_2}^{ven}}$$

amount of blood = 7.27 L/min

Problem 3-8

a)



b) Benzoyl chloride is a protective group for the OH - group.

Problem 3-9

a) $C_{10}H_{17}O_2$

b) $C_{20}H_{34}O_4$

c) 1.) Substance A and substance X contain an OH group (formation of esters).

2.) A contains an unsaturated C-C-bond (hydrogenation).

3.) The oxidation points to an α,β-diol. As carbon dioxide and a terminal dicarboxylic acid are formed, both OH groups are bond to the ends of an unsaturated (compound A) and a saturated (compound X) hydrocarbon.

Proposal:

A: $HOCH_2—CH(OH)—C_{16}H_{24}—CH(OH)—CH_2OH$

X: $HOCH_2—CH(OH)—C_{16}H_{32}—CH(OH)—CH_2OH$

c1) Esterification of A:

$HOCH_2—CH(OH)—C_{16}H_{24}—CH(OH)—CH_2OH$

$\xrightarrow{\text{acetic acid}}$ $(CH_3COO)CH_2—CH(OOCCH_3)—C_{16}H_{24}—CH(OOCCH_3)—CH_2(OOCCH_3)$

c2) Hydrogenation of A to give X:

$HOCH_2—CH(OH)—C_{16}H_{24}—CH(OH)—CH_2OH$

$\xrightarrow{H_2\ (Pd)}$ $HOCH_2—CH(OH)—C_{16}H_{32}—CH(OH)—CH_2(OH)$ (compound X)

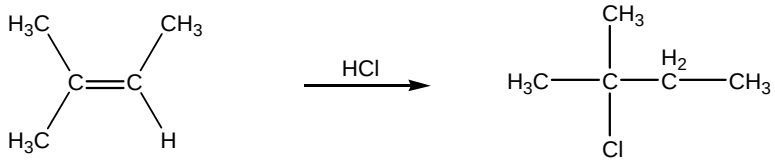
c3) Oxidation:

$HOCH_2—CH(OH)—C_{16}H_{32}—CH(OH)—CH_2OH$

$\xrightarrow{KMnO_4}$ $HOOC—(CH_2)_{16}—COOH + CO_2$

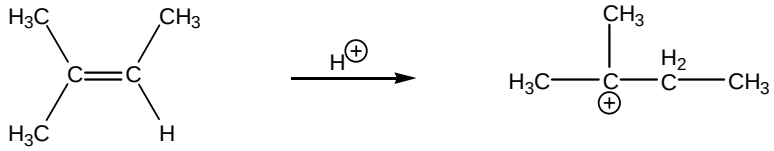
Problem 3-10

a)



b) Two possibilities for the reaction to proceed:

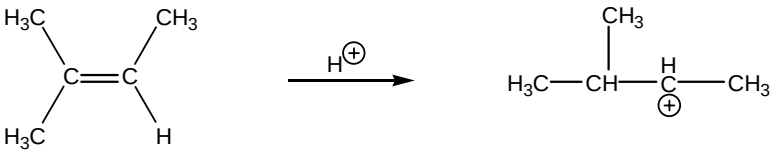
i)



1. step: slowly — carbocation I

rate-limiting — more stable than carbocation II

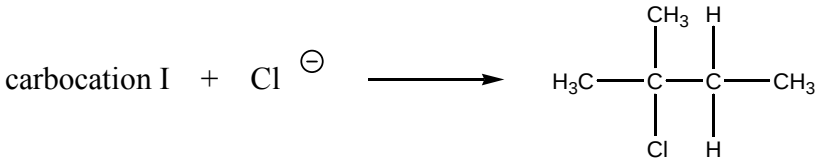
ii)



1. step: slowly — carbocation II

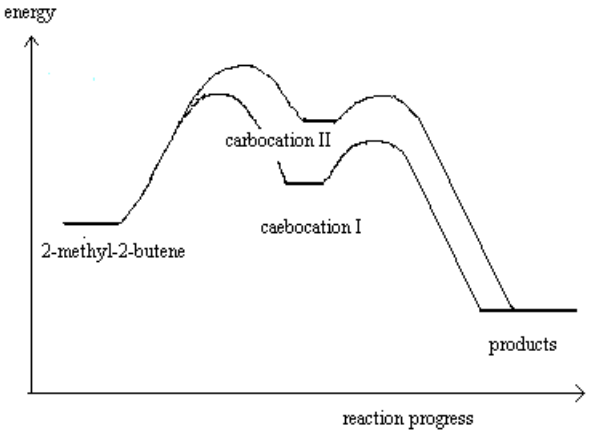
rate-limiting — less stable than carbocation I

The more stable cation is formed faster than the less stable one. Therefore, the following main product is obtained:

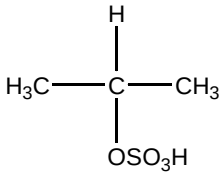


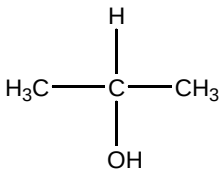
2. step: fast 2-chloro-2-methylbutane
(main product)

c) Energy diagram:



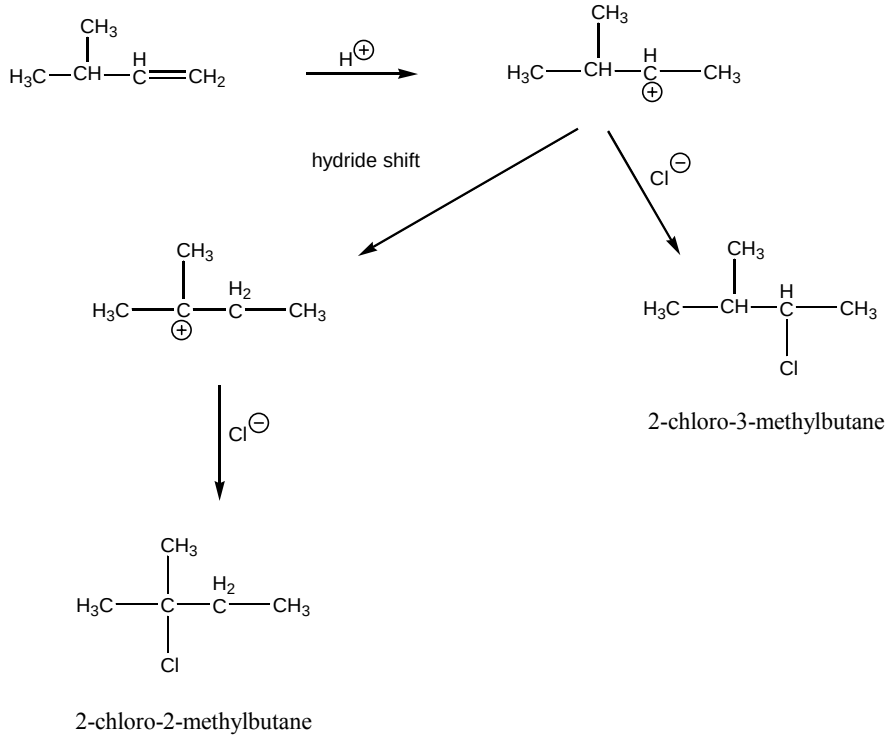
d) Compounds X and Y:

X: 

Y: 

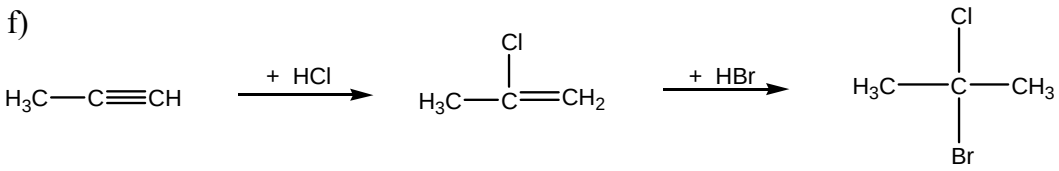
isopropanol

e) Reaction mechanism:



The secondary carbocation intermediate rearranges to a more stable tertiary carbocation by hydride shift. This tertiary carbocation leads to the formation of 2-chloro-2-methylbutane.

f)



Answers round 3 exam 2

Problem 3-11

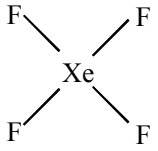
a) B b) B c) E d) A e) D f) C

Problem 3-12

a) **A = Xe**
B = XeF_4 (M = 207 g/mol)
C = XeF_6
D = X_eF_2

$Xe + 2\,F_2 \longrightarrow XeF_4$
$XeF_6 + O_2F_2 \longrightarrow XeF_6 + O_2$
$XeF_2 + H_2 \longrightarrow 2\,HF + Xe$

b) XeF_4 is square planar



c) Fluorine free radicals, F·

Problem 3-13

a) $H_2O_2 + Mn^{2+} + 2\,OH^- \longrightarrow MnO_2(s) + 2\,H_2O$

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

c) $c(H_2O_2) = 0.030$ mol/L d) $K_c = 1.61 \cdot 10^{14}$ e) E = 1.19 V.

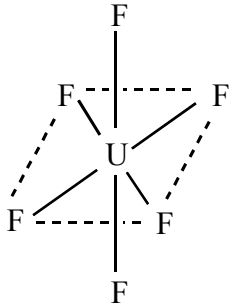
Problem 3-14

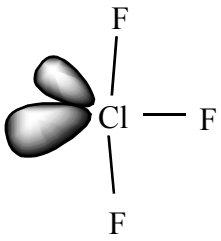
a) 23.8 %

b) 6 β-particles, isotope of lead $^{206}_{82}Pb$

c) 4 unpaired electrons, max. oxidation state + 6

d) $2\,ClF_3 + 3\,UF_4 \rightleftarrows 3\,UF_6 + Cl_2$





e) $M(^{238}UF_6) = 352$ g/mol , $M(^{235}UF_6) = 349$ g/mol $\Leftarrow$ $\sqrt{\frac{352}{349}}^{n} = \frac{2.5}{0.7}$ **n = 298**

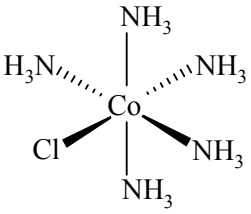
f) $^{235}_{92}U \longrightarrow {}^{95}_{36}Kr + {}^{138}_{56}Ba + 2\,{}^{1}_{0}n$

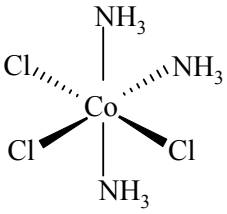
g) $2\,UO_2^+ + 4\,H^+ \longrightarrow U^{4+} + UO_2^{2+} + 2\,H_2O$
$U^{3+} + H^+ \longrightarrow U^{4+} + ½\,H_2$

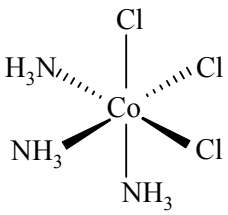
Problem 3-15

a) Chloro pentammine cobalt(III) oxidation state: +3

b) c) $[CoCl_3(NH_3)_3]$, 2 isomeres, diastereomers







d) $E = \lg (I_0/I)$, $T = 100\% \cdot (I/I_0) \Leftarrow E = \lg(100\%/T)$ $E = 1.125$

$E = \varepsilon \cdot c \cdot d \Leftarrow \varepsilon = E/(c \cdot d)$ $\varepsilon = 56.3$ L/(mol·cm)

e) $[CoCl(NH_3)_5]^{2+} + Fe^{2+} + 5\ H^+ \longrightarrow Co^{2+} + Fe^{3+} + Cl^- + 5\ NH_4^+$

f) $-\frac{d(c[CoCl(NH_3)]^{2+})}{dt} = k \cdot c([CoCl(NH_3)_5]^{2+})$ mit $k = k_2 \cdot (c[Fe(H_2O)_6]^{2+})$.

Pseudo first order

g) $k = \frac{1}{\Delta t} \cdot \ln \frac{c_{t_1}}{c_{t_2}} = \frac{1}{\Delta t} \cdot \ln \frac{E_{t_1} - E_\infty}{E_{t_2} - E_\infty}$

time interval	10-20	10-40	10-60	20-60	40-60
k in s^{-1}	$6.36 \cdot 10^{-4}$	$6.38 \cdot 10^{-4}$	$6.40 \cdot 10^{-4}$	$6.41 \cdot 10^{-4}$	$6.44 \cdot 10^{-4}$

$k = 6.40 \cdot 10^{-4}\ s^{-1}$ (constant). $k_2 = 4.27 \cdot 10^{-3}$ L/(mol·s).

Problem 3-16

a) Yellow brownish solution: I_2 or I_3^-, precipitate: CuI.

b) $2\ Cu^{2+} + 4\ I^- \longrightarrow 2\ CuI\downarrow + I_2$

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

d) $m(H_2O) = 0.80$ g $n(CuSO_4) : n(H_2O) = 2.94 \cdot 10^{-2} : (0.80/18) = 1 : 1.51$

Problem 3-17

a) $pH = pK_a + \lg \frac{c(HCO_3^-)}{c(CO_2)}$ $\Leftarrow \lg \frac{c(HCO_3^-)}{c(CO_2)} = 1{,}3$, $\frac{c(HCO_3^-)}{c(CO_2)} = 10^{1,3} \approx 20$

b) In the buffer is $c(HCO_3^-) >> c(CO_2)$, ⇐ better suitable to buffer acids

c) $p(CO_2) = 5{,}3$ kPa.

d) $K_H = \frac{c(A(aq))}{p(A(g))}$, $2{,}25 \cdot 10^{-4}$ mol/(L·kPa) $= \frac{c(CO_2(aq))}{5{,}3\text{kPa}} = 1{,}1925$ mol/L

$c(CO_2) = 1{,}19 \cdot 10^{-3}$ mol/L

e) Using a) $\frac{c(HCO_3^-)}{c(CO_2)} = 10^{1.3}$ and c) $c(CO_2) = 1.19 \cdot 10^{-3}$ mol/L: $c(HCO_3^-) = 23.8$ mol/L.

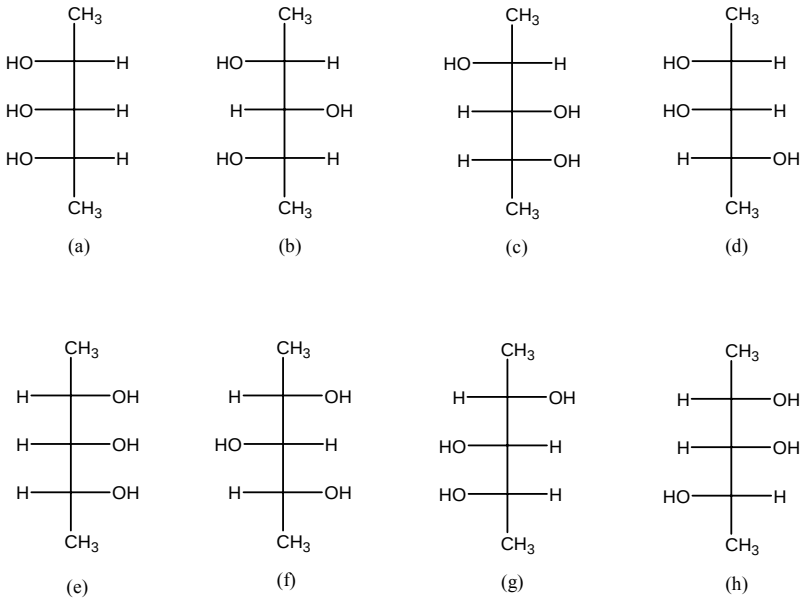
f) pH = 3.5.

g) $\frac{c(Lac^-)}{c(HLac)} = 10^{7.4-3.86} \Leftarrow c(Lac^-) = 3467 \cdot c(HLac)$ mainly Lac^- is present.

Problem 3-18

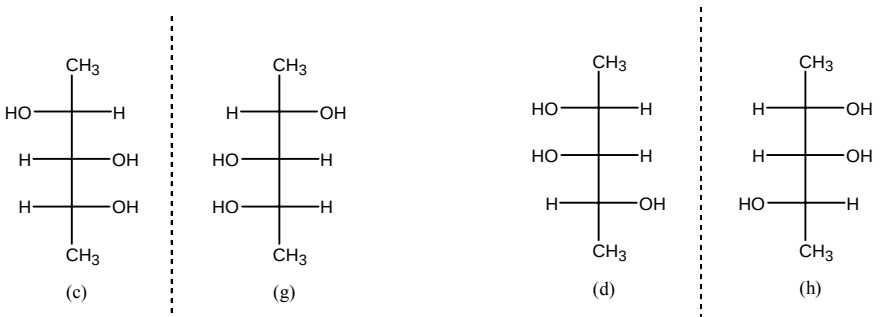
a) Systematical name of D glyceraldehyde: (2R)-2,3-dihydroxypropanal.

b) Stereoisomers of 2,3,4-trihydroxypentane:



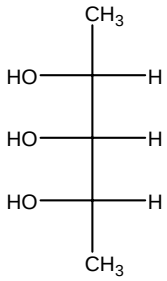
Identical structures: a = e, b = f, g = h, c = d

Enantiomers:



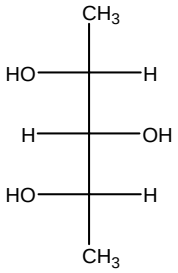
optically active optically active

Diastereomers:



(a = e)

meso form (optically not active) diastereomer towards (c/d), (g/h) and (b/f)



(b = f)

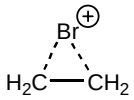
meso form (optically not active) diastereomer towards (c/d), (g/h) and (a/e)

Analogical solutions for compounds (c/d) und (g/h).

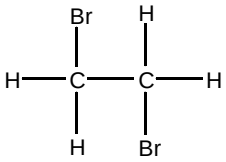
c) Systematical name of D glucose: (2R, 3S, 4R, 5R) – 2,3,4,5,6-Pentahydroxyhexanal.

Problem 3-19

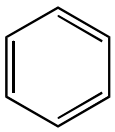
a) A: $H_2C{=}CH_2$ B: Br_2 C:



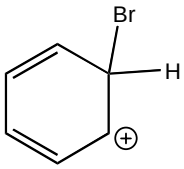
D:



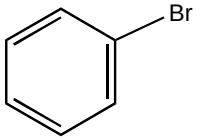
X:



Y:



Z:



U: HBr

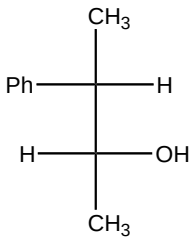
b) The reaction of bromine with an alkene is an electrophilic addition. A cyclic bromonium ion intermeditate is attacked by a Br^- ion and then a dibromoalkane (D) is formed.
For the bromation of benzene a catalyst such as $FeBr_3$ is needed. The catalyst makes the Br_2 molecule more electrophilic by forming a complex to give a $FeBr_4^-Br^+$ species that reacts as if it were Br^+. The intermediate is a non-cyclic carbocation. The net effect of the reaction of Br_2 with benzene is a substitution of H^+ by Br^+.

Problem 3-20

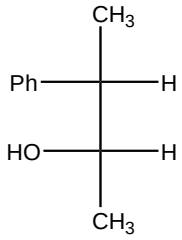
CH_3—C*H(Ph)—CO—CH_3 + $LiAlH_4$ ⟶ CH_3C*H(Ph)—C*H(OH)—CH_3

(* = stereogenic center)

Another stereogenic center is formed. Thus two diastereomeric products exist:



and



(2R,3S)-3-Phenyl-2-butanol (2S,3S)-3-Phenyl-2-butanol

Answers round 4

Problem 4-1

a) ^{1}H, ^{2}H = D, ^{12}C, ^{13}C, ^{35}Cl und ^{37}Cl.

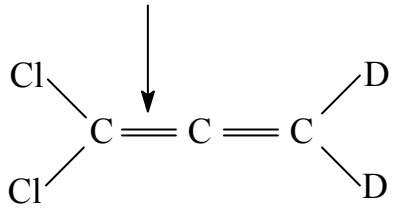
b) m/z 82 refers to $^{12}C^{35}Cl^{35}Cl$ m/z 28 refers to $^{12}C^{12}C^{2}H^{2}H$
m/z 75 refers to $^{35}Cl^{12}C_3{}^{2}H_2$ bei m/z 77 refers to $^{37}Cl^{12}C_3{}^{2}H_2$.

c) Feedstock for hydrogen: only ^{2}H = D ,
feedstock for carbon: only ^{12}C,
feedstock for chlorine: ^{35}Cl and ^{37}Cl .
Intensity (m/z 77) = 0,6 · intensity(m/z 75), $\Rightarrow$ n(m/z 77) = 0,6 · n(m/z 75)
$\Rightarrow$ **ratio (^{37}Cl)** = [0.6/(1 + 0.6)] · 100% **= 37.5%**.
ratio (^{35}Cl) = **62.5%**.

There are three isotopomers:

1. $\mathbf{C_3D_2{}^{35}Cl_2}$ p(1.) = 0.625^2 **39.06 %**
2. $\mathbf{C_3D_2{}^{35}Cl{}^{37}Cl}$ p(2.) = 2 · 0.625 · 0.375 = 0.4688 **46.88%**
3. $\mathbf{C_3D_2{}^{37}Cl_2}$ p(3.) = 0.375^2 = 0.1406 **14.06%**

d)



Problem 4-2

a) Unit cell: see textbooks

b) 71,07 pm = 2 · d_{200} · sin 9.56° $\Leftarrow$ d_{200} = 214 pm $\Leftarrow$ a = 428 pm

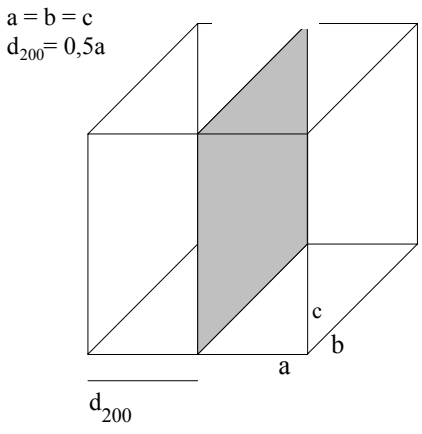
c)

$$\rho = \frac{4 \cdot (M(Fe) \cdot x + M(O))}{N_A \cdot a^3}$$

$$5{,}71 = \frac{4 \cdot (55.85 \cdot x + 16.00)}{6.022 \cdot 10^{23} \cdot (4.28 \cdot 10^{-8}\,cm)^3}$$

$\Leftarrow$ **x = 0.92** **$Fe_{0.92}O$**

200 - [illegible] face:



d) $n(Fe^{2+})$ = y $\Leftarrow$ $n(Fe^{3+})$ = 0.92 - y
2·y + 3·(0.92 - y) = 2 $\Leftarrow$ y = 0.76

Fe^{2+}: $\frac{0,76}{0,92} \cdot 100\% =$ **82.6%** **Fe^{3+}:** (100 - 82.6)% = **17.4%**

e) **$Fe^{II}_{0.76}Fe^{III}_{0.16}O$**

f) The easier the metal is to oxidize the smaller is x.
Ni^{3+} is very unstable (there are only a few compounds of trivalent nickel known) thus in Ni_xO x has the highest value;
Mn^{2+} is easy to oxidize to Mn^{3+} thus in Mn_xO x has the smallest value.

Problem 4-3

a) $K_a = \frac{c(H^+) \cdot c(Ac^-)}{c(HAc)}$; $c(H^+) = c(Ac^-)$; $1.74 \cdot 10^{-5}$ mol/L $= \frac{(10^{-4.5}\,mol/L)^2}{c_0 - 10^{-4.5}\,mol/L}$

$c_0 = 8.91 \cdot 10^{-5}$ mol/L

$\alpha = c(Ac^-)/c_0$ $\alpha = 10^{-4.5}/8.91 \cdot 10^{-5}$ **$\alpha = 0.35$**

b) $4.5 = 4.76 + \lg\frac{x \cdot 0.15}{0.14 - x \cdot 0.15}$ x = 0.331 $\Leftarrow$ **$V_{NaOH\ solution}$ = 331 mL**

c) $c(OH^-) = 8.754 \cdot 10^{-4}$ mol/1.5 L = $5.84 \cdot 10^{-4}$ mol/L $\Leftarrow$ **pOH = 3.23** **pH = 10.77**

d) $n_0(Ac^-) = 0.331 \cdot 0.15 \cdot 1.4/1.731$ mol = 0.040 mol Ac^-

$n_0(HAc) = [(0.14 - 0.331 \cdot 0.15] \cdot 1.4/1.731]$ mol = 0.073 mol HAc

$n(Ac^-) = (0.040 + 0.001)$ mol Ac^- = 0.041 mol Ac^-

n(HAc) = (0.073 – 0.001) mol HAc = 0.072 mol HAc

pH = 4.76 + log (41/72) **pH = 4.52**

e) $pH_{buffer} = pK_a$ **pH = 4.76**

f) $4.96 = 4.76 + \lg\frac{0.1mol + x}{0.1mol - x}$ (x = amount of OH^-)

$\frac{0.1mol + x}{0.1mol - x} = 1.585$ $\Leftarrow$ x = 0.0226 (not 0.023!)

The same result for the amount of acid **$n(OH^-) = n(H^+) = 0.022$ mol**

g) $n(H^+) = 0.5 \cdot 0.35$ mol = 0.175 mol

$4.56 = 4.76 + \lg\frac{x - 0,175mol}{x + 0,175mol}$ (x = amount of CH_3COOH)

$\Leftarrow$ x = 0.7734 (rounded to 0.774 or 0.78 !)

c_0 (acetic acid) = 0.78 mol/L

h) Before reaching the first equivalence point the formation of B^{2-} is not to take into consideration.

$V_{NaOH\ solution} = 0$ L $\quad 6.6\cdot10^{-5} = \dfrac{c(H^+)^2}{0.1\text{mol/L} - c(H^+)} \quad c(H^+) = 2.536\cdot10^{-3}$. pH = 2.6

$V_{NaOH\ solution} < 0.010$ L : $\quad pH = 6.6\cdot10^{-5} + \lg \dfrac{0.1\text{mol/L}\cdot V_{NaOH\ solution}}{0.001\text{mol} - 0.1\text{mol/L}\cdot V_{NaOH\ solution}}$

$V_{NaOH\ solution} = 0.010$ L (1. equi. point) : $\quad pH = ½ \cdot (pK_{a\,1} + pk_{a\,2})$

After the first equivalence point the concentration of H_2B is not to take into consideration

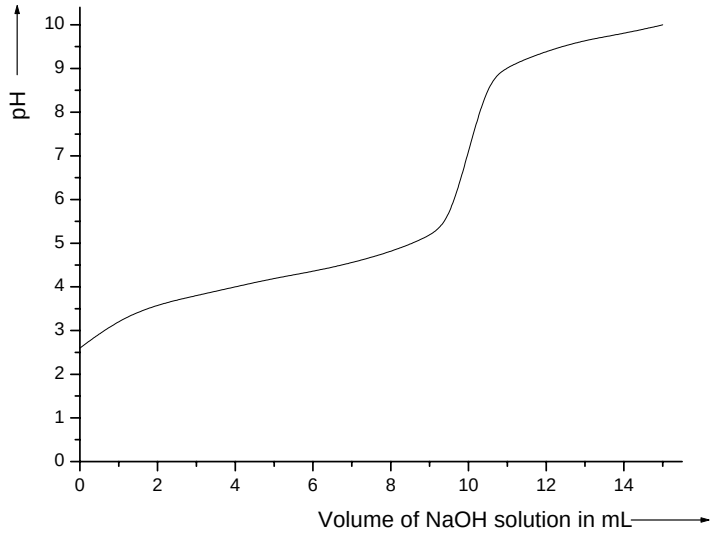
$n_0(HB^-) = 0.001$ mol. $\quad n(B^{2-}) = 0.1\text{mol/L}\cdot(V_{NaOH\ solution} - 0.010\ \text{L})$

$V_{NaOH\ solution} > 0.010$ L: $\quad pH = pK_{a\,2} + \lg[n(B^{2-})/n(HB^-)]$

$$pH = 10 + \lg \frac{0.1\text{mol/L}\cdot(V_{NaOH\ solution} - 0.010\text{L})}{0.001\text{mol/L} - 0.1\text{mol/L}\cdot(V_{NaOH\ solution} - 0.010\text{L})}$$

(pH rounded to 0.05)

V in mL	pH
0	2.60
1	3.25
2	3.60
3	3.80
4	4.00
5	4.20
6	4.35
7	4.55
8	4.80
9	5.15
9.5	5.50
10	7.10
10.5	8.70
11	9.05
12	9.40
13	9.65
14	9.80
15	10.0



i) If you multiply

$K_{a\,1} = \dfrac{c(H^+)\cdot c(HB^-)}{c(H_2B)}$ and $K_{a\,2} = \dfrac{c(H^+)\cdot c(B^{2-})}{c(HB^-)}$ and use the approximation

$c(H_2B) = c(B^{2-})$ you get $\quad K_{a\,1}\cdot K_{a\,2} = c(H^+)^2, \quad pH = ½ \cdot (pK_{a\,1} + pk_{a\,2})$.

To do a more exact calculation, you need two more equations:

$c(H_2B) + c(HB^-) + c(B^{2-}) = 0.05$ mol/L $\quad$ and $\quad c(Na^+) + c(H^+) = c(HB^-) + 2\cdot c(B^{2-}) + c(OH^-)$

0.05 mol/L $+ c(H^+) = c(HB^-) + 2\cdot c(B^{2-}) + 10^{-14}(\text{mol/L})^2 / c(H^+)$.

(Using these four equations you get pH = 7.2 at the equivalence point)

Problem 4-4

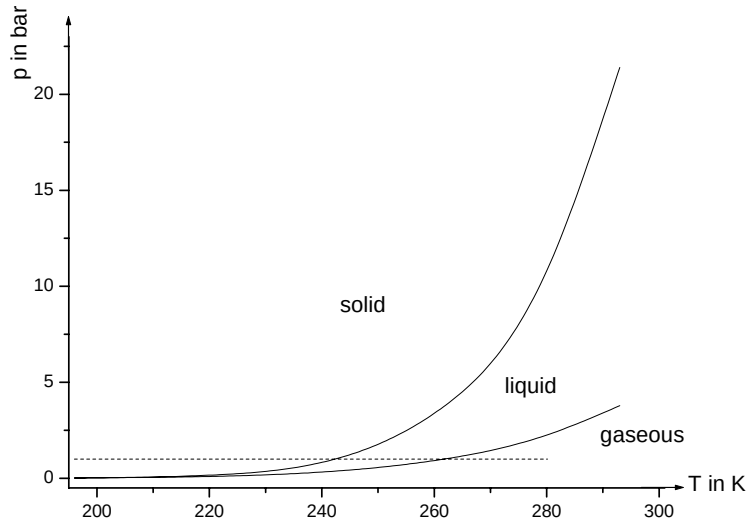
a) At the triple point $p_\ell = p_s$. $\quad -\frac{1425.7\text{K}}{T} + 10.4435 = -\frac{1871.2\text{K}}{T} + 12.7165$.

$\Leftarrow$ **T = 196 K** **p = 1477 Pa**

b) $p_\ell = 1.013\cdot10^5$ Pa, $\quad \lg 1.013\cdot10^5 = -\frac{1425.7\text{K}}{T} + 10.4435$ **T = 262 K**

c) (i) $p(SO_2(s)) = 21.4\cdot10^5$ Pa (ii) $p(SO_2(\ell)) = 3.78\cdot10^5$ Pa

d)



e) gaseous (293K/$1.000\cdot10^5$Pa)

f) no

Problem 4-5

a) $c^2(Ca^{2+}) = K_L$, as $c(Ca^{2+}) = c(C_2O_4^{2-})$ **$c(Ca^{2+}) = 1.10\cdot10^{-4}$ mol/L**

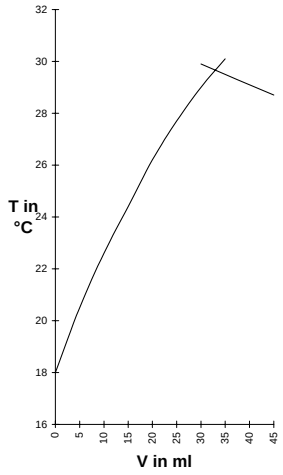
b) $c(Ca^{2+})\cdot c(CO_3^{2-}) = 1.2\cdot10^{-8}$ (mol/L)^2 $\Leftarrow$ $c(CO_3^{2-}) = \frac{1.2\cdot10^{-8}(\text{mol/L})^2}{c(Ca^{2+})}$ (1)

$c(Ca^{2+})\cdot c(C_2O_4^{2-}) = 2.0\cdot10^{-9}$ mol/L)^2 $\Leftarrow$ $c(C_2O_4^{2-}) = \frac{2.0\cdot10^{-9}(\text{mol/L})^2}{c(Ca^{2+})}$ (2)

$c(CO_3^{2-}) + c(C_2O_4^{2-}) = c(Ca^{2+})$ (3)

(1), (2), (3) $\Leftarrow$ **$c(Ca^{2+}) = 1.18\cdot10^{-4}$ mol/L**

c) From the diagram you read 32.5 mL to neutralize HNO_3.
$n(HNO_3) = 2\ mol/L \cdot 0.0325\ L = 0.065\ mol$
$\Leftarrow n(KOH) = 0.065\ mol$
$m(KOH) = 0.065\ mol \cdot 56.11\ g/mol$
$\Leftarrow$ **m(KOH) = 3.65 g**



d) The increase in temperature is not linear as the neutralisation takes place in a steadily increasing volume.

Problem 4-6

a) (i) Initial concentration of the acid in water: c_o.

$\frac{c(HA)_e}{c(HA)_w} = 5.4$ (1) constant amount of acid

$V_e \cdot c(HA)_e + V_w \cdot c(HA)_w = V_w \cdot c_0$, where $0.5\ L \cdot c(HA)_e + 1\ L \cdot c(HA)_w = 1\ L \cdot c_0$,

$\Leftarrow c(HA)_e = 2 \cdot c_0 - 2 \cdot c(HA)_w$ (2)

$\Leftarrow c(HA)_w = \frac{2 \cdot c_0}{5.4 + 2} = 0.27 \cdot c_0$,

27% of the acid remain in water, **73% are extracted.**

(ii) $c(HA)_{e1} = 10 \cdot c_0 - 10 \cdot c(HA)_{w1}$ (3)

$c(HA)_{w1} = \frac{10 \cdot c_0}{5.4 + 10}$

for the second extraction $c(HA)_{w1}$ means c_0 and so on.

$\Leftarrow c(HA)_{w5} = \frac{10^5 \cdot c_0}{15.4^5} = 0.115 \cdot c_0$,

11.5% of the acid remain in water, **88.5% are extracted.**

b) The acid exists only in the form of the HA molecule. This can be guarenteed by lowering the pH by hydrochloric acid.

c) $c(HA)_e = 0.864\ mol/L \quad \Leftarrow \quad c(HA)_w = (0.864\ mol/L)/5.4 = 0.16\ mol/L$

$10^{-4.25}\ mol/L = \frac{10^{-3.5}\ mol/L \cdot c(A^-)}{0.16 mol/L}$

$c(A^-) = 2.85 \cdot 10^{-2}\ mol/L$

$c_0(HA) = c(HA)_e + c(HA)_w + c(A^-)$

$c_0(HA) = (0.864 + 0.16 + 2.85 \cdot 10^{-2})\ mol/L$ **$c_0(HA) = 1.05\ mol/L$**

d) i) $D = \dfrac{0{,}864}{0{,}16 + 2{,}85 \cdot 10^{-2}}$ **D = 4,58**

ii) $D = \dfrac{c(HA)_e}{c(HA)_w + c(A^-)}$ where $c(HA)_e = K_D \cdot c(HA)_w$

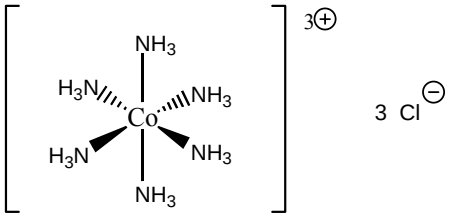
$K_a = \dfrac{c(H^+) \cdot c(A^-)}{c(HA)_w}$ $\Leftarrow$ $c(A^-) = \dfrac{c(HA)_w \cdot K_a}{c(H^+)}$

$\Leftarrow D = \dfrac{c(HA)_w \cdot K_D}{c(HA)_w \cdot [1 + K_a / c(H^+)]}$ $\Leftarrow$ $\mathbf{D} = K_D \cdot \dfrac{c(H^+)}{K_a + c(H^+)}$

Problem 4-7

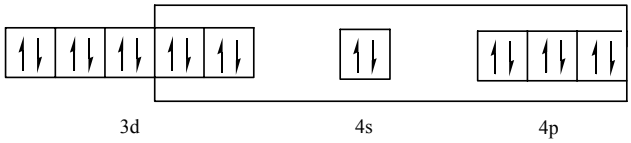
a) empirical formula of A: $Cl_3CoN_6H_{18}$

b) constitutional formula of A



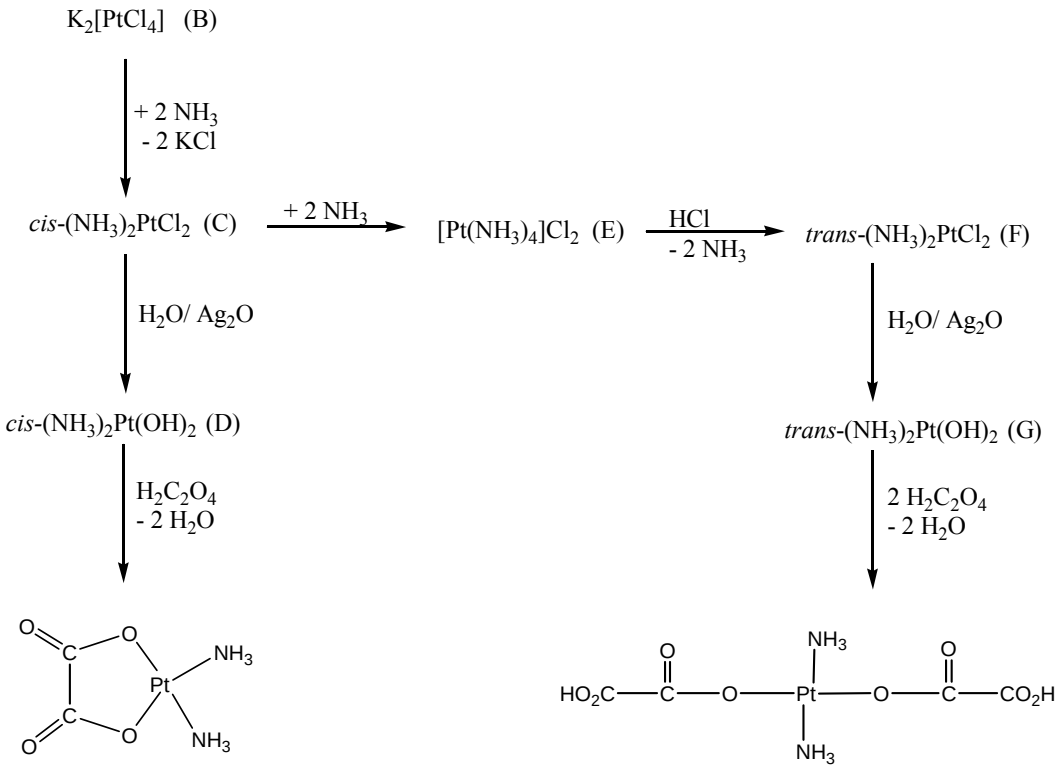
octahedron

c) electron configuration



six NH_3-ligands: d^2sp^3-hybrid.

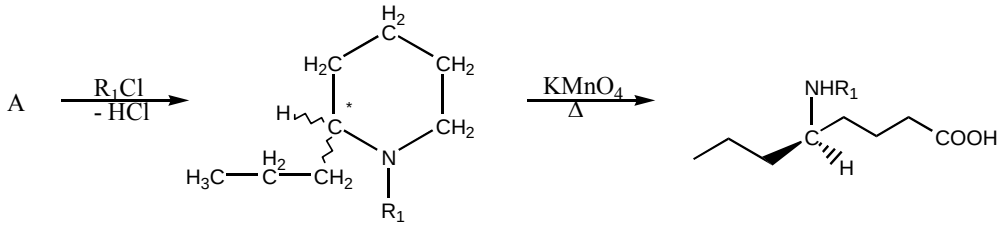
d)



Compound C is used as a drug against cancer (Cisplatin).

Problem 4-8

a)

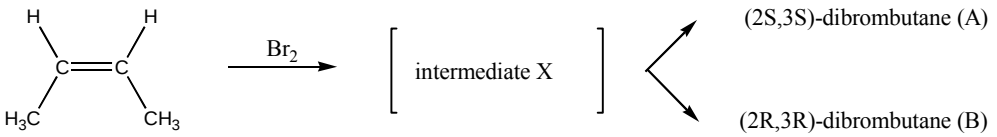


b) (5R)-5-Aminooctanoic acid

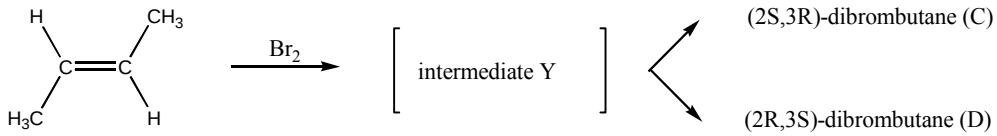
c) R

Problem 4-9

a)



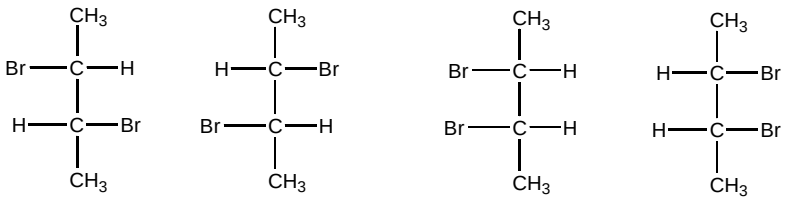
cis-2-butene



trans-2-butene

A: B: C: D:

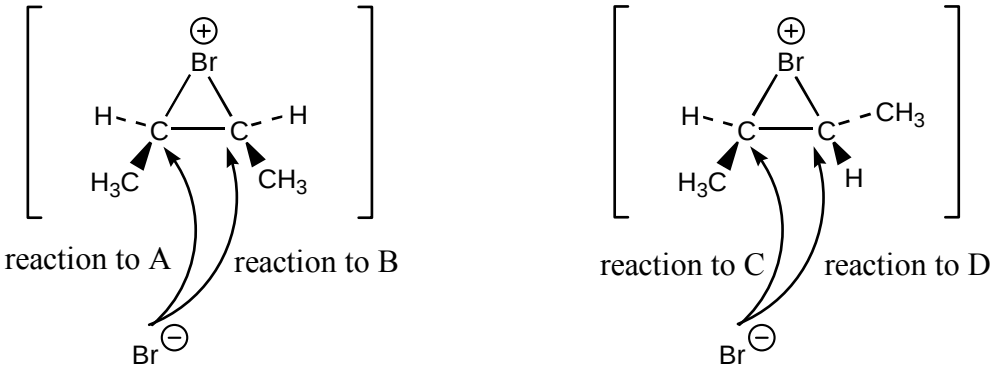
b)



S,S R,R R,S S,R

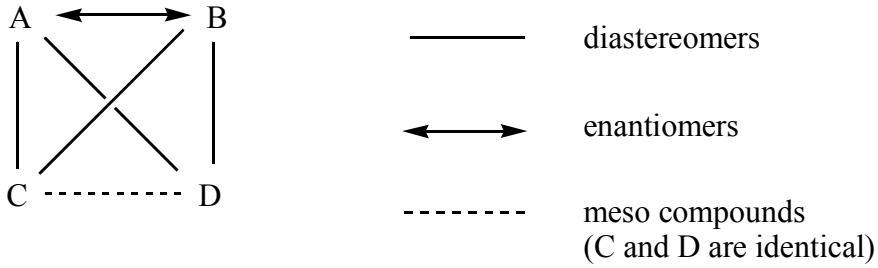
c) Intermediates

X: Y:



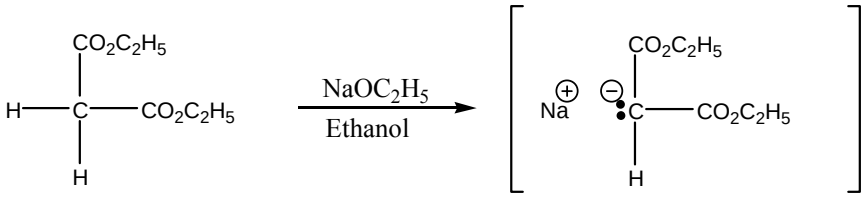
bromonium ions

Stereoisomers



Problem 4-10

a)

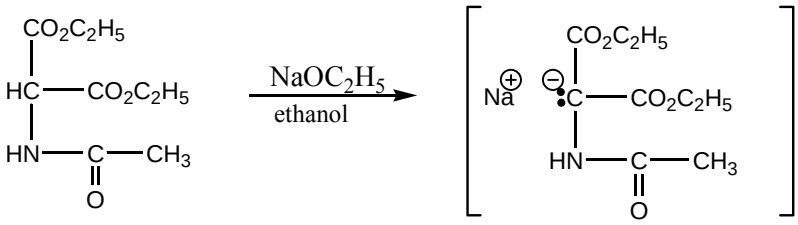


A

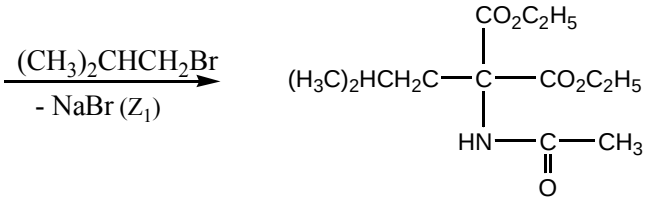
Course of the reaction:

Malonic ester is more acidic than many other carbonyl compounds (pK_a = 13) because its α-hydrogen atoms are flanked by two carbonyl groups. Thus malonic ester is easily converted into its enolate anion by reaction with sodium ethoxide in ethanol. The enolate ion, in turn, is a good nuclephile that reacts rapidly with alkyl halides.

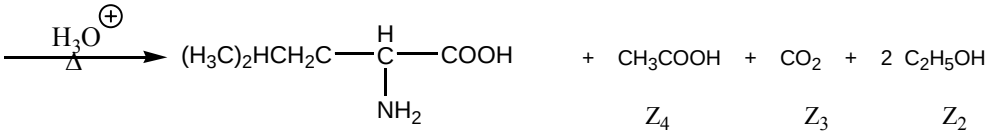
b)



X



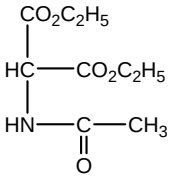
Y



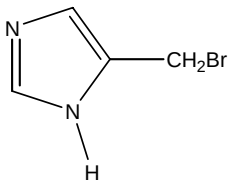
leucine

c) no, because a racemic mixture is formed

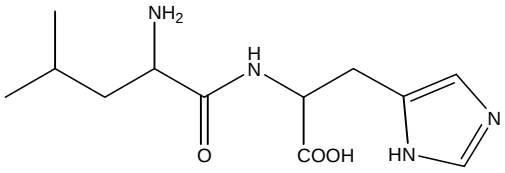
d)



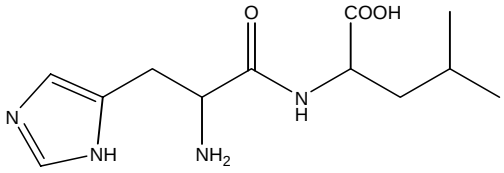
and



e)



H-Leu-His-OH



H-His-Leu-

35th International Chemistry Olympiad

Athens, Greece

Theoretical Examination

Thursday, 10 July 2003

SECTION A: General

QUESTION 1

The molar solubility s (mol/L) of $Th(IO_3)_4$ as a function of the solubility product K_{sp} of this sparingly soluble thorium salt is given by the equation:

(a) $s = (K_{sp}/ 128)^{1/4}$ ( ) (b) $s = (K_{sp}/ 256)^{1/5}$ ( ) (c) $s = 256\ K_{sp}^{1/4}$ ( )

(d) $s = (128\ K_{sp})^{1/4}$ ( ) (e) $s = (256\ K_{sp})^{1/5}$ ( ) (f) $s = (K_{sp}/128)^{1/5} / 2$ ( )

QUESTION 2

Which one of the following equations must be used for the exact calculation of $[H^+]$ of an aqueous HCl solution at any concentration c_{HCl}? ($K_w = 1\times10^{-14}\ M^2$).

(a) $[H^+] = c_{HCl}$ ( ) (b) $[H^+] = c_{HCl} + K_w/[H^+]$ ( )

(c) $[H^+] = c_{HCl} + K_w$ ( ) (d) $[H^+] = c_{HCl} - K_w/[H^+]$ ( )

QUESTION 3

The molar mass of glucose ($C_6H_{12}O_6$) is 180 g/mol and N_A is the Avogadro constant. Which <u>one</u> of the following statements <u>is not correct</u>?

(a) An aqueous 0.5 M solution of glucose is prepared by dissolving 90 g of glucose to give 1000 mL of solution. ( )

(b) 1.00 mmol amount of glucose has a mass of 180 mg. ( )

(c) A 0.0100 mole amount of glucose comprises of $0.0100\times24\times N_A$ atoms . ( )

(d) 90.0 g glucose contain $3\times N_A$ atoms of carbon. ( )

(e) 100 mL of a 0.10 M solution contain 18 g of glucose. ( )

QUESTION 4

If the density of a liquid compound B is ρ (in g/cm^3), M is the molar mass of B and N_A is the Avogadro constant, then the number of molecules of B in 1 litre of this compound is:

(a) $(1000 \times \rho) / (M \times N_A)$ ( )

(b) $(1000 \times \rho \times N_A) / M$ ( )

(c) $(N_A \times \rho) / (M \times 1000)$ ( )

(d) $(N_A \times \rho \times M) / 1000$ ( )

QUESTION 5

The equilibrium constant of the reaction:

$$Ag_2CrO_4(s) + 2Cl(aq)^- \rightleftharpoons 2AgCl(s) + CrO_4^{2-}(aq)$$

is given by the equation:

(a) $K = K_{sp(Ag2CrO4)} / K_{sp(AgCl)}^2$ ( )

(b) $K = K_{sp(Ag2CrO4)}\ K_{sp(AgCl)}^2$ ( )

(c) $K = K_{sp(AgCl)} / K_{sp(Ag2CrO4)}$ ( )

(d) $K = K_{sp(AgCl)}^2 / K_{sp(Ag2CrO4)}$ ( )

(e) $K = K_{sp(Ag2CrO4)} / K_{sp(AgCl)}$ ( )

QUESTION 6

How many mL of 1.00 M NaOH must be added to 100.0 mL of 0.100 M H_3PO_4 solution to obtain a phosphate buffer solution with pH of about 7.2? (The pK values for H_3PO_4 are $pK_1 = 2.1$, $pK_2 = 7.2$, $pK_3 = 12.0$)

(a) 5.0 mL ( )

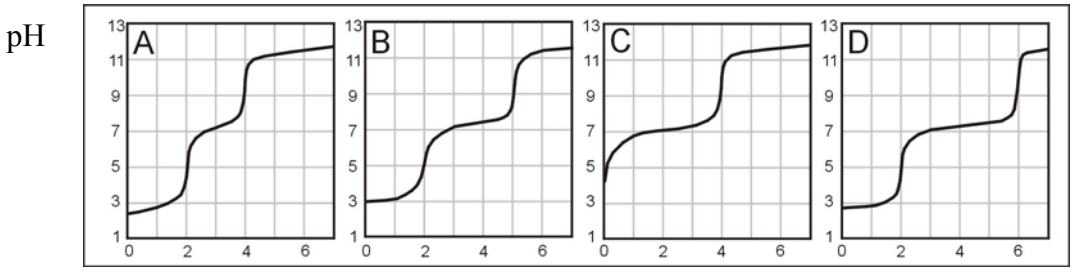
(b) 10.0 mL ( )

(c) 15.0 mL ( )

(d) 20.0 mL ( )

QUESTION 7

Solutions containing H_3PO_4 and/or NaH_2PO_4 are titrated with a strong base standard solution. Associate the contents of these solutions with the titration curves (pH vs. volume of titrant) shown in the figure. (for H_3PO_4: $pK_1 = 2.1$, $pK_2 = 7.2$, $pK_3 = 12.0$)



(case a) The sample contains H_3PO_4 only.

Curve A ( ), Curve B ( ), Curve C ( ), Curve D ( )

(case b) The sample contains both in a mole ratio H_3PO_4 : NaH_2PO_4 2:1.

Curve A ( ), Curve B ( ), Curve C ( ), Curve D ( )

(case c) The sample contains both in a mole ratio H_3PO_4 : NaH_2PO_4 1:1.

Curve A ( ), Curve B ( ), Curve C ( ), Curve D ( )

QUESTION 8

A fuel/oxidant system consisting of N,N-dimethylhydrazine $(CH_3)_2NNH_2$ and N_2O_4 (both liquids) is commonly used in space vehicle propulsion. Components are mixed stoichiometrically so that N_2, CO_2 and H_2O are the only products (all gases under the reaction conditions). How many moles of gases are produced from 1 mol of $(CH_3)_2NNH_2$?

(a) 8 ( )

(b) 9 ( )

(c) 10 ( )

(d) 11 ( )

(e) 12 ( )

QUESTION 9

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

(a) F ( )

(b) (4/3) F ( )

(c) (3/2) F ( )

(d) 2 F ( )

(e) 3 F ( )

QUESTION 10

Identify particle X in each of the following nuclear reactions:

(case a) $^{68}_{30}Zn + {}^{1}_{0}n \rightarrow {}^{65}_{28}Ni + X$ alpha ( ), beta ( ), gamma ( ), neutron ( )

(case b) $^{130}_{52}Te + {}^{2}_{1}H \rightarrow {}^{131}_{53}I + X$ alpha ( ), beta ( ), gamma ( ), neutron ( )

(case c) $^{214}_{82}Pb \rightarrow {}^{214}_{83}Bi + X$ alpha ( ), beta ( ), gamma ( ), neutron ( )

(case d) $^{23}_{11}Na + {}^{1}_{0}n \rightarrow {}^{24}_{11}Na + X$ alpha ( ), beta ( ), gamma ( ), neutron ( )

(case e) $^{19}_{9}F + {}^{1}_{0}n \rightarrow {}^{20}_{9}F + X$ alpha ( ), beta ( ), gamma ( ), neutron ( )

QUESTION 11

10.0 mL of 0.50 M HCl and 10.0 mL of 0.50 M NaOH solutions, both at the same temperature, are mixed in a calorimeter. A temperature increase of ΔT is recorded. Estimate the temperature increase if 5.0 mL of 0.50 M NaOH were used instead of 10.0 mL. Thermal losses are negligible and the specific heats of both solutions are taken as equal.

(a) $(1/2) \times \Delta T$ ( )

(b) $(2/3) \times \Delta T$ ( )

(c) $(3/4) \times \Delta T$ ( )

(d) ΔT ( )

QUESTION 12

Natural antimony consists of the following 2 stable isotopes: ^{121}Sb, ^{123}Sb. Natural chlorine consists of the following 2 stable isotopes: ^{35}Cl, ^{37}Cl. Natural hydrogen consists of the following 2 stable isotopes: ^{1}H, ^{2}H. How many peaks are expected in a low resolution mass spectrum for the ionic fragment $SbHCl^{+}$?

(a) 4 ( )

(b) 5 ( )

(c) 6 ( )

(d) 7 ( )

(e) 8 ( )

(f) 9 ( )

QUESTION 13

The smallest diffraction angle of a monochromatic beam of X-rays in a certain experiment is 11.5°. Based on this we must expect a beam of X-rays diffracted at:

(a) 22.0 degrees ( )

(b) 22.5 degrees ( )

(c) 23.0 degrees ( )

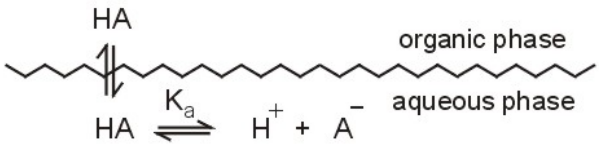
(d) 23.5 degrees ( )

(e) 24.0 degrees ( )

(f) 24.5 degrees ( )

QUESTION 14

The undissociated form of a weak organic acid HA can be extracted from the aqueous phase by a water-immiscible organic solvent according to the scheme:



Regarding this extraction, are the following statements correct (Y) or not (N)?

(a) The distribution constant (K_D) of the acid HA depends on the pH of the aqueous phase. Y N

(b) HA can be efficiently extracted only from acidic aqueous solutions. Y N

(c) The distribution ratio (D) of the acid HA depends on the pH of the aqueous phase. Y N

(d) The distribution ratio (D) of the acid HA depends mainly on its concentration. Y N

QUESTION 15

Regarding Beer's law, are the following statements correct (Y) or not (N)?

(a) The absorbance is proportional to the concentration of the absorbing compound. Y N

(b) The absorbance is linearly related to the wavelength of the incident light. Y N

(c) The logarithm of transmittance is proportional to the concentration of the absorbing compound. Y N

(d) The transmittance is inversely proportional to the logarithm of absorbance. Y N

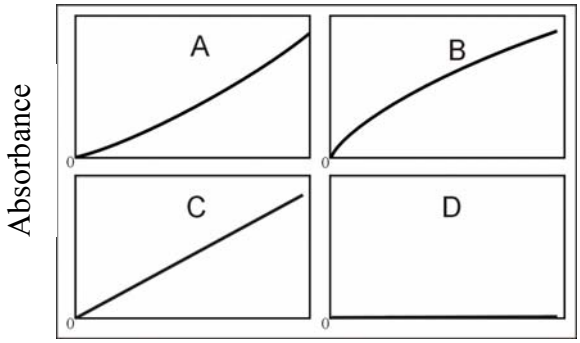
(e) The transmittance is inversely proportional to the concentration of the absorbing compound. Y N

QUESTION 16

Calculate the corresponding wavelength in nanometers (nm) for monochromatic radiation with the following numerical characteristics

(case a) 3000 Å	150 nm ( ), 300 nm ( ), 600 nm ( ), 5000 nm ( )
(case b) 5×10^{14} Hz	150 nm ( ), 300 nm ( ), 600 nm ( ), 5000 nm ( )
(case c) 2000 cm^{-1}	150 nm ( ), 300 nm ( ), 600 nm ( ), 5000 nm ( )
(case d) 2×10^{6} GHz	150 nm ( ), 300 nm ( ), 600 nm ( ), 5000 nm ( )

QUESTION 17



The absorbance of solutions of the weak acid HX were obtained. Associate the expected form of the resulting working curve with those shown in figure, under the following conditions:

(case a) Pure aqueous solutions of HX were used. Only the undissociated species HX absorb.
Curve A ( ), Curve B ( ), Curve C ( ), Curve D ( )

(case b) Pure aqueous solutions of HX were used. Only the anionic species X^- absorb.
Curve A ( ), Curve B ( ), Curve C ( ), Curve D ( )

(case c) All solutions of HX contain an excess of a strong base. Only the undissociated HX species absorb.
Curve A ( ), Curve B ( ), Curve C ( ), Curve D ( )

(case d) All solutions of HX contain an excess of a strong acid. Only the undissociated HX species absorb.
Curve A ( ), Curve B ( ), Curve C ( ), Curve D ( )

(case e) Pure aqueous solutions of HX were used. Both HX and X^- absorb. Measurements were obtained at a wavelength where the molar absorptivities of X^- and HX are equal and different than zero.
Curve A ( ), Curve B ( ), Curve C ( ), Curve D ( )

QUESTION 18

Which of the following acids is the strongest?

(a) perchloric acid, $HClO_4$ ( )

(b) chloric acid, $HClO_3$ ( )

(c) chlorous acid, $HClO_2$ ( )

(d) hypochlorous, HClO ( )

(e) All of them are equally strong because they all contain chlorine ( )

QUESTION 19

Which structure describes best the crystal system of iron in which the coordination number is 8?

(a) simple cubic ( )

(b) body-centered cubic ( )

(c) cubic closest packed ( )

(d) hexagonal closest packed ( )

(e) none of the above ( )

QUESTION 20

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

(a) B ( )

(b) C ( )

(c) N ( )

(d) Mg ( )

(e) Al ( )

QUESTION 21

Which second period (row) element has the first six ionization energies (IE in electron volts, eV) listed below?

IE_1	IE_2	IE_3	IE_4	IE_5	IE_6
11	24	48	64	392	490

(a) B ( )

(b) C ( )

(c) N ( )

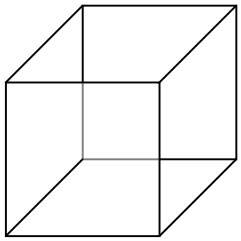
(d) O ( )

(e) F ( )

QUESTION 22

Silver metal exists as a face-centered cubic (fcc) packed solid.

(a) Draw an fcc unit cell.



(b) How many atoms are present in the fcc unit cell?

(c) The density of silver has been determined to be 10.5 g/cm^3 . What is the length of each edge of the unit cell?

(d) What is the atomic radius of the silver atoms in the crystal?

QUESTION 23

Are the following statements correct	(Y) or not (N)?	
(a) HF boils at a higher temperature than HCl.	Y	N
(b) HBr boils at a lower temperature than HI	Y	N
(c) Pure HI can be produced by reacting concentrated sulfuric acid with KI.	Y	N
(d) Ammonia solutions are buffer solutions because they contain the conjugate pair $NH_3 - NH_4^+$.	Y	N
(e) Pure water at 80°C is acidic.	Y	N
(f) During electrolysis of an aqueous KI solution with graphite electrodes, the pH near the cathode is below 7.	Y	N

QUESTION 24

Under certain conditions of concentration and temperature HNO_3 reacts with Zn and its reduction products are NO_2 and NO in a molar ratio 1:3. How many moles of HNO_3 are consumed by 1 mol of Zn?

(a) 2.2 ( )
(b) 2.4 ( )
(c) 2.6 ( )
(d) 2.8 ( )
(e) 3.0 ( )
(f) 3.2 ( )

SECTION B: PHYSICAL

QUESTION 25: Muon

The muon (μ) is a subatomic particle of the lepton family which has same charge and magnetic behavior as the electron, but has a different mass and is unstable, i.e., it disintegrates into other particles within microseconds after its creation. Here you will attempt to determine the mass of the muon using two rather different approaches.

a) The most common spontaneous disintegration reaction for the muon is :

$$\mu \rightarrow e + \bar{\nu}_e + \nu_\mu,$$

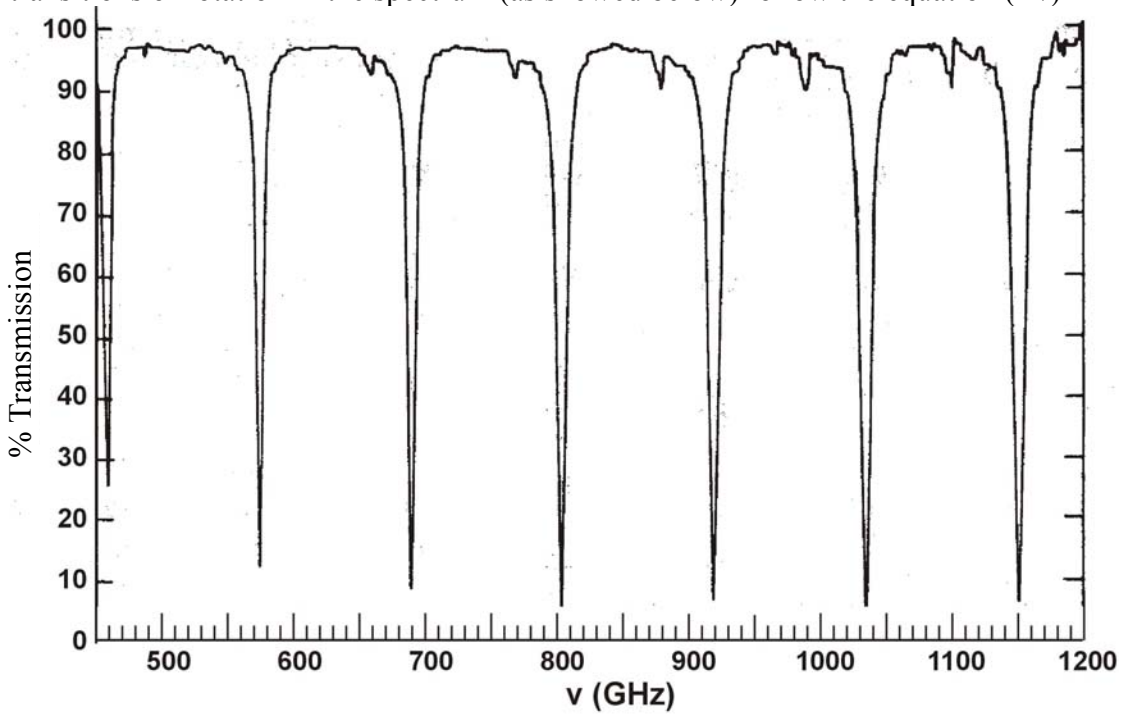
where $\bar{\nu}_e$ is the electron antineutrino, and ν_μ the muon neutrino. In a given experiment using a stationary muon, $\bar{\nu}_e + \nu_\mu$, carried away a total energy of 2.000×10^{-12} J, while the electron was moving with a kinetic energy of $1.4846\text{x}10^{-11}$ J. Determine the mass of the muon.

b) Many experiments have studied the spectroscopy of atoms that have captured a muon in place of an electron. These exotic atoms are formed in a variety of excited states. The transition from the third excited state to the first excited state of an atom consisting of a ^{1}H nucleus and a muon attached to it was observed at a wavelength of 2.615 nm. Determine the mass of the muon.

AUFGABE 26: CO-Spektrum

In diatomic molecules the energy of the states of rotation is given $E_J = B\cdot J\cdot (J+1)$. J is the quantum önumber of the molecule and B is the constant of rotation. B, the reduced mass μ and the bond length R follow the equation: $B = \frac{h^2}{8\pi^2\mu R^2}$.

Usually you observe spectroscopic transitions with photon energies, which are equal to the energy difference between according states of the molecule ($h\cdot\nu = \Delta E$). The observed transitions of rotation occur between adjacent levels of rotation, $\Delta E = E_{J+1} - E_J = 2\cdot B\cdot(J+1)$. Thus consecutive transitions of rotation in the spectrum (as showed below) follow the equation $(\Delta\nu) = 2$ B.



Using the diagram calculate the following values of $^{12}C^{16}O$ in appropiate units:

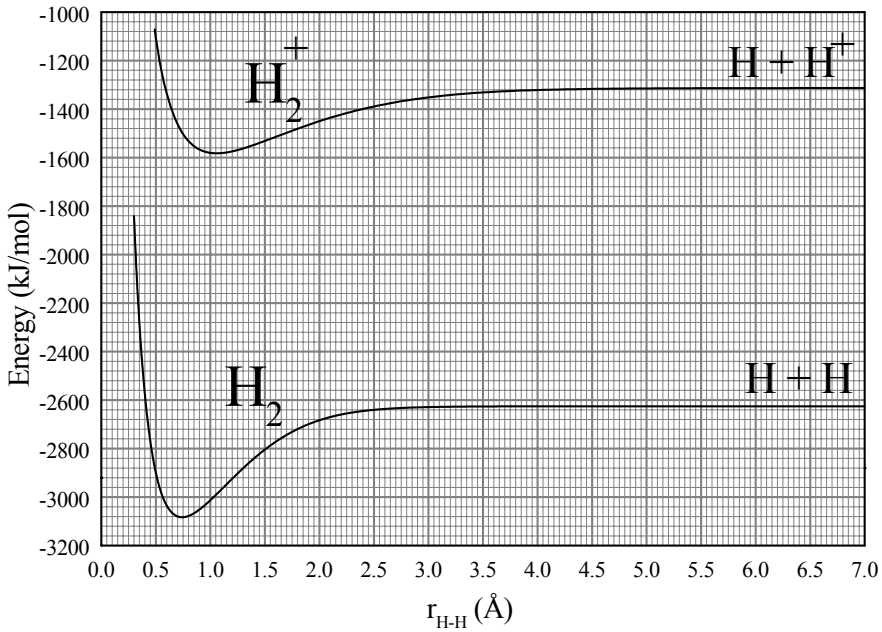
Δν

a) B

b) R

QUESTION 27: Hydrogen molecule

In the following graph are presented potential energy curves of the H_2 molecule and its cation H_2^+.
Using the information provided on this graph, give numerical answers with appropriate units to the following



questions:

1. What are the equilibrium bond lengths of H_2 and H_2^+?

2. What are the binding energies of H_2 and H_2^+?

3. What is the ionisation energy of the H_2 molecule?

4. What is the ionisation energy of the H atom?

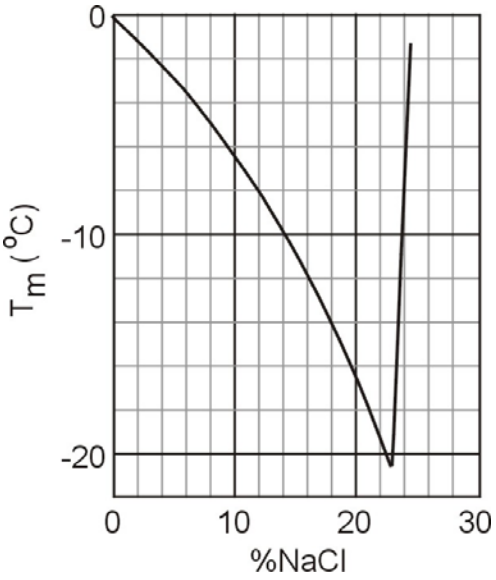
5. If we use electromagnetic radiation of frequency $3.9 \cdot 10^{15}$ Hz in order to ionise H_2, what will be the velocity of the extracted electrons? (ignore molecular vibrational energy)

QUESTION 28: Cryoscopy

Chemists often need a bath in which to carry out a process that has a temperature below the water freezing point (0 °C) and well above the CO_2 sublimation point (–78 °C). In this case they mix water ice prepared at its melting point and NaCl. Depending on the quantities used temperatures as low as –20 °C can be reached.

We prepare a cold bath mixing 1 kg of ice at 0 °C with 150 g of NaCl in a thermally insulated container. Circle the letters Y or N to indicate if the following statements are correct (Y) or not (N).

1. The mixing process is spontaneous Y N
2. The change of entropy during the mixing process is negative Y N
3. This diagram depicts the freezing point of aqueous solutions of NaCl as a function of the composition of the solution (per cent by weight). What is is the freezing point of the bath based on the diagram?



4. If an equal mass of $MgCl_2$ were used instead of NaCl, would the freezing point be higher? Y N

QUESTION 29: Pool **(5 points)**

A very large swimming pool filled with water of temperature equal to 20°C is heated by a resistor with a heating power of 500 W for 20 minutes. Assuming the water in the pool is not in any contact with anything besides the resistor, determine the following quantities:

a) The heat delivered to the water

b) Is the change of entropy of the resistor positive, negative, or zero?
   (i) $\Delta S_{res} > 0$ ( )
   (ii) $\Delta S_{res} = 0$ ( )
   (iii) $\Delta S_{res} < 0$ ( )

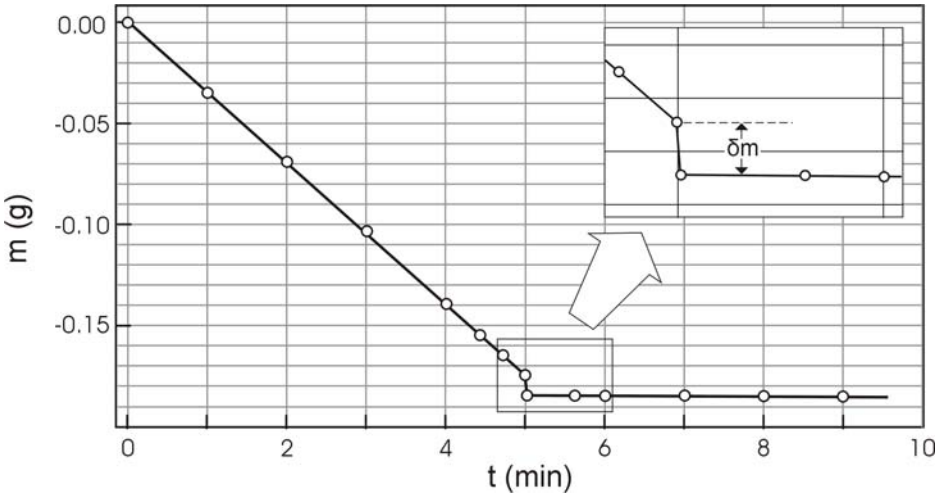
c) Is the change of entropy of the water positive, negative, or zero?
   (i) $\Delta S_{pool} > 0$ ( )
   (ii) $\Delta S_{pool} = 0$ ( )
   (iii) $\Delta S_{pool} < 0$ ( )

d) Is the change of entropy of the system positive, negative, or zero?
   (i) $\Delta S_{total} > 0$ ( )
   (ii) $\Delta S_{total} = 0$ ( )
   (iii) $\Delta S_{total} < 0$ ( )

e) Is the process reversible? Y N

QUESTION 30: Gas velocity

The experiment described here gives a simple way to determine the mean velocity u of the molecules in the gas phase of a volatile liquid. A wide shallow container (a Petri dish) half filled with ethanol is placed on an electronic balance with its lid next to it and the balance is zeroed at time t=0. Balance readings are recorded as shown on the diagram. At t = 5 min the lid is placed



over the dish. The liquid no longer evaporates, but the trapped molecules push against the lid, hence lowering the measurement of the balance by δm. Therefore, the force exerted on the lid is f = δm g. The force is also equal to the rate of change of the momentum of the evaporating molecules, i.e., f = ½ u dm/dt. Using the data provided determine the mean velocity of ethanol molecules at 290 K. Assume g = 9.8 m s^{-2}.

SECTION C: Organic

PROBLEM 31: Ester identification

2.81 g of an optically active diester **A**, containing only C, H and O were saponified with 30.00 mL of a 1.00 M NaOH solution. Following the saponification, the solution required 6.00 mL of a 1.00 M HCl solution to titrate the unused NaOH, only. The saponification products were an optically inactive dicarboxylic acid **B**, MeOH and an optically active alcohol **C**. Alcohol **C** reacted with I_2/NaOH to give a yellow precipitate and C_6H_5COONa.
The diacid **B** reacted with Br_2 in CCl_4 to give a single, optically inactive product (compound **D**).
Ozonolysis of **B** gave only one product.

1. Determine the molecular mass of compound **A**.

$M_{\mathbf{A}}$ =

2. Give the structural formulas of **A**, **B**, and **C** without stereochemical information.

A	B	**C**

3. Give the possible stereochemical formulas (with bold and dashed bonds) for **C**.

Possible Stereochemical Formulas for C

4. Give the stereochemical formula for **D**, using a Fischer projection.

Stereochemical Formula for D

5. Give the stereochemical formula for **B**.

Stereochemical Formula for B

The diester **A** also reacted with Br_2 in CCl_4 and was converted to a mixture of two compounds (**E**, **F**) both optically active.

6. Give all the possible stereochemical formulas for **E** and **F**, using Fischer projections. Name all the stereogenic centers as either *R* or *S* on all the formulas.

Possible Stereochemical Formula(s) for E	**Possible Stereochemical Formula(s) for F**

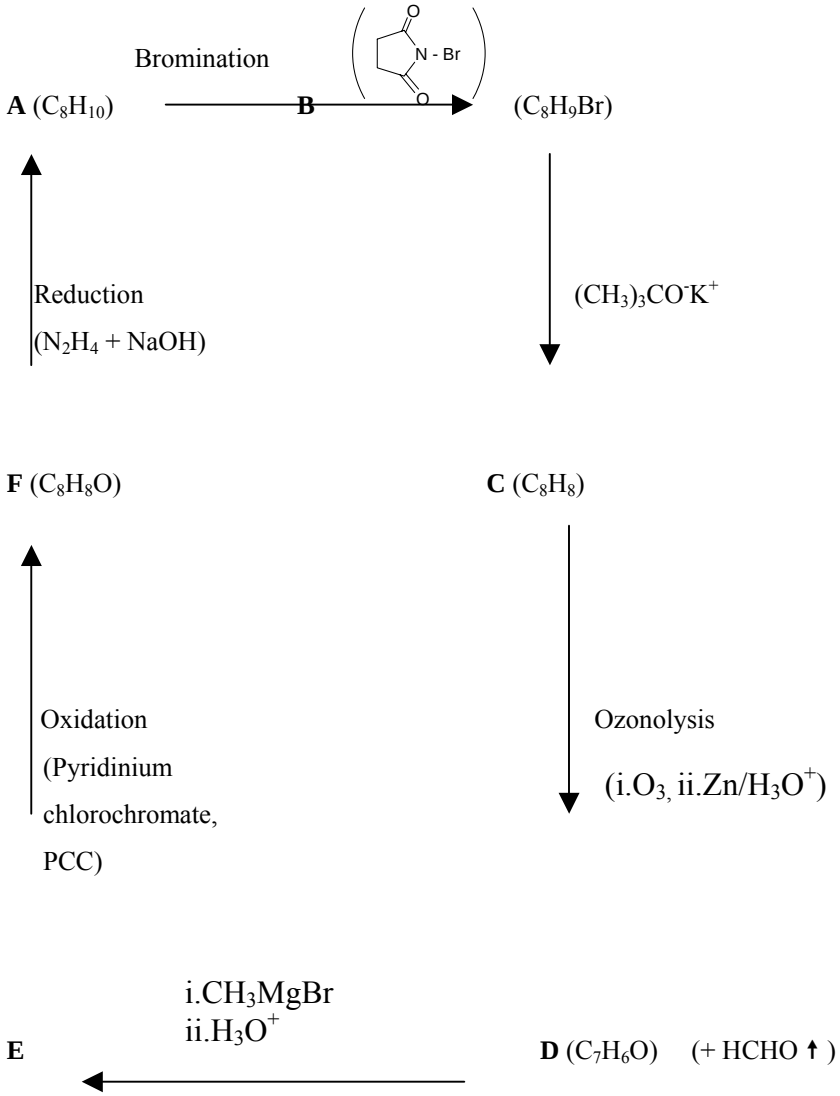
If we use $Na^{18}OH$ for the saponification of compound **A**, would the oxygen isotope be incorporated in (either or both of) the products **B** and **C**?

7. Mark the correct answer:

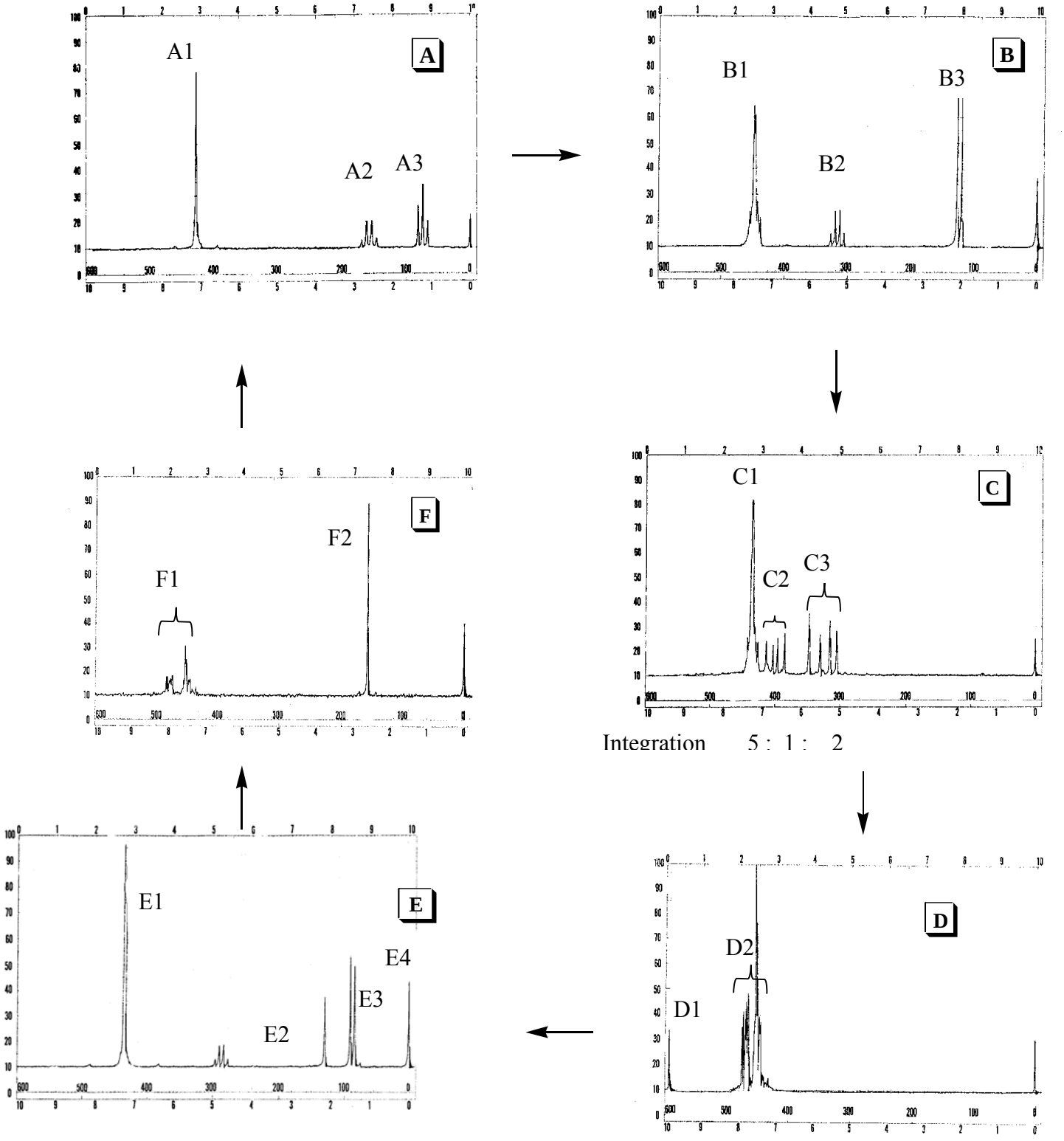
a. Only **B** ( ) b) Only **C** ( ) c) Both **B** and **C** ( )

PROBLEM 32: NMR puzzle

An organic compound **A** (C_8H_{10}) gives the following chain of reactions:



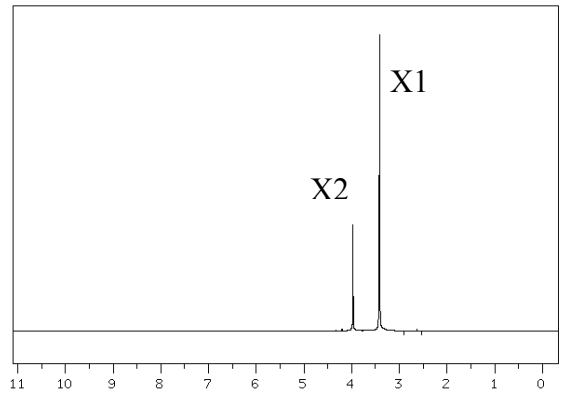
Based on the ^{1}H-NMR spectra given, draw the structures of compounds **A**, **B**, **C**, **D**, **E** and **F**, and match the groups of the hydrogen atoms of each compound to the corresponding ^{1}H-NMR peaks, as shown in the example.



General remarks: NMR spectra were recorded in $CDCl_3$ on a 60 MHz Perkin Elmer Spectrometer. Under ordinary conditions (exposure to air, light and water vapour) acidic impurities may develop in $CDCl_3$ solutions and catalyse rapid exchange of some particular protons.

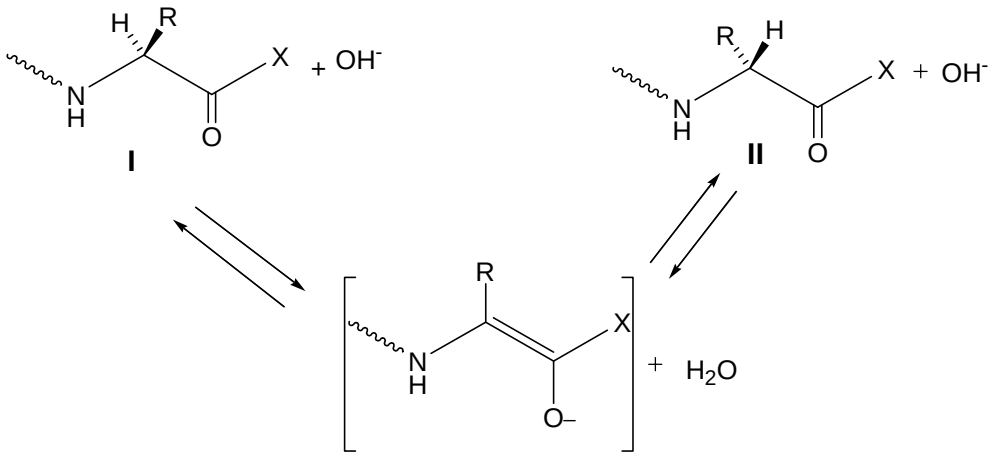
EXAMPLE

X1 X2
CH_3OH



PROBLEM 33: Peptides

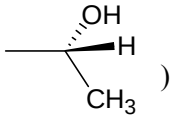
Racemization of α-aminoacids and peptides can occur by an α-enolization mechanism and both heat and the presence of strong bases greatly accelerate the process:



intermediate

1. Draw stereochemical formulas I and II (with bold and dashed bonds) for the aminoacid components of the mixture that has reached equilibrium through the α-enolization mechanism described above operating on each of the following hydroxyaminoacids A and B:

A: serine (R = $–CH_2OH$)

B: (2*S*,3*R*)-threonine (R = 

)

A

I

II

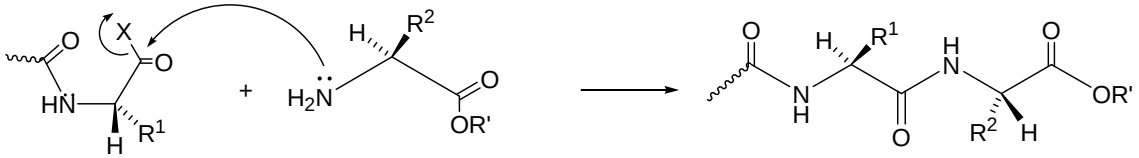
B

I	**II**

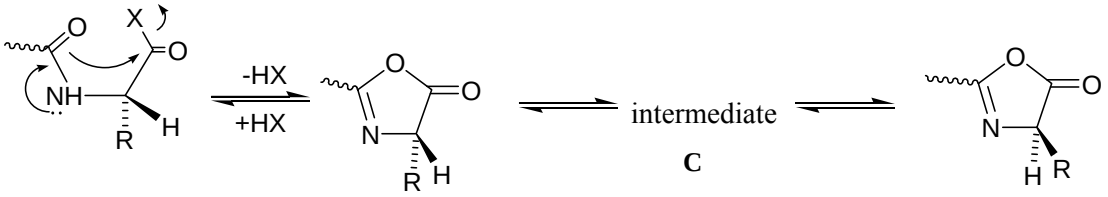
2. Mark the box that corresponds to the correct definition of the relationship between the structures you have drawn in each of the above cases A and B.

	enantiomeric	diastereomeric
A $_{I, II}$	☐	☐
B $_{I, II}$	☐	☐

During peptide synthesis, in order to form a new peptide bond the carboxyl group has to be activated, that is, it must bear a good leaving group, represented in a simplified scheme below:



It is at this stage of the synthesis that a second racemization mechanism may occur; the amidic carbonyl oxygen is five atoms away from the activated carboxyl group and can intramolecularly attack the activated carboxyl forming a five membered cyclic intermediate (an azalactone) which quickly equilibrates its hydrogen at the stereogenic center, represented in a simplified scheme below:



azalactone azalactone

3. Write a structure for the intermediate **C** that interconverts the two azalactones and thus explains the scrambling of the stereochemistry at the stereogenic center:

Intermediate **C**

Azalactones are very reactive substances that can still react with the amino group of an aminoacid. Therefore, the coupling reaction can proceed to completion albeit affording racemized or epimerized products.

4. If *N*-benzoyl glycine, $C_9H_9NO_3$, is warmed to 40˚C with acetic anhydride it is converted into a highly reactive substance, $C_9H_7NO_2$. (P_1)

A: Propose a structure for this substance.

P_1

B: Write the reaction product (s) of the substance you proposed above with *S*-alanine ethyl ester (P_2) (the side chain R of the aminoacid alanine is a methyl group) using stereochemical formulas (with bold and dashed bonds) for both reactants and product.

P_1 + **P_2** → Product

SECTION D: Inorganic

QUESTION 34: Aluminium

One of the largest factories in Greece, located near the ancient city of Delphi, produces alumina (Al_2O_3) and aluminium metal using the mineral bauxite mined from the Parnassus mountain. Bauxite is a mixed aluminium oxide hydroxide – $AlO_x(OH)_{3-2x}$ where $0<x<1$.

Production of Al metal follows a two-stage process:

(i) Bayer process: Extraction, purification and dehydration of bauxite (typical compositions for industrially used bauxites are Al_2O_3 40-60%, H_2O 12-30%, SiO_2 free and combined 1-15%, Fe_2O_3 7-30%, TiO_2 3-4%, F, P_2O_5, V_2O_5, etc., 0.05-0.2%). This involves dissolution in aqueous NaOH, separation from insoluble impurities, partial precipitation of the aluminium hydroxide and heating at 1200°C. Complete and balance the following chemical reactions of stage (i)

$$Al_2O_3 + OH^- + \rightarrow [Al(OH)_4(H_2O)_2]^-$$

$$SiO_2 + OH^- \rightarrow SiO_2(OH)_2^{2-}$$

$$SiO_2(OH)_2^{2-} + \rightarrow CaSiO_3\downarrow +$$

$$[Al(OH)_4(H_2O)_2]^- \rightarrow \downarrow + OH^- + H_2O$$

$$Al(OH)_3 \rightarrow Al_2O_3 +$$

ii) Héroult-Hall process: Electrolysis of pure alumina dissolved in molten cryolite, Na_3AlF_6. Typical electrolyte composition ranges are Na_3AlF_6 (80-85%), CaF_2 (5-7%), AlF_3 (5-7%), Al_2O_3 (2-8% intermittently recharged). Electrolysis is carried out at 940°C, under constant pressure of 1 atm, in a carbon-lined steel cell (cathode) with carbon anodes. Balance the main reaction of the electrolysis:

$$Al_2O_3(l) + C(anode) \rightarrow Al(l) + CO_2(g)$$

Since cryolite is a rather rare mineral, it is prepared according to the following reaction. Complete and balance this reaction:

$$HF + Al(OH)_3 + NaOH \rightarrow Na_3AlF_6 +$$

During the electrolysis process several parallel reactions take place that degrade the graphite (C) anodes or reduce the yield.

iii) By using the thermodynamic data given below, which are taken to be independent of temperature, determine the thermodynamic quantities ΔH, ΔS and ΔG at 940°C for the reaction:

$C(graphite) + CO_2(g) \rightarrow 2CO(g)$.

	Al(s)	Al_2O_3(s)	C (graphite)	CO(g)	CO_2(g)	O_2(g)
Δ_fH^o (kJ.mol^{-1})	0	−1676	0	−111	−394	
S^o (J.K^{-1}.mol^{-1})	28	51	6	198	214	205
$\Delta_{fus}H$ (kJ.mol^{-1})	11	109				

iv) At the same temperature and using the data from the table in part (iii) determine the quantities ΔH and ΔG for the reaction

$2Al(l) + 3CO_2(g) \rightarrow Al_2O_3(l) + 3CO(g)$

given that $\Delta S = -126$ J K^{-1} mol^{-1}. (Show your calculations)

v) Pure aluminium is a silvery-white metal with a face-centered cubic (fcc) crystal structure. Aluminium is readily soluble in hot concentrated hydrochloric acid producing the cation $[Al(H_2O)_6]^{3+}$, as well as in strong bases at room temperature producing hydrated tetrahydroxyaluminate anion, $[Al(OH)_4]^-$(aq). In both cases liberation of H_2 occurs. AlF_3 is made by treating Al_2O_3 with HF gas at 700°C, while the other trihalides, AlX_3, are made by the direct exothermic reaction of Al with the corresponding dihalogen. Write all 4 chemical reactions described above.

vi) The $AlCl_3$ is a crystalline solid having a layer lattice with 6-coordinate Al(III), but at the melting point (192.4°C) the structure changes to a 4-coordinate molecular dimer, Al_2Cl_6. The covalently bonded molecular dimer, in the gas phase and at high temperature, dissociates into trigonal planar $AlCl_3$ molecules.
For the molecular dimer Al_2Cl_6, in the gas phase, two different Al — Cl distances (206 and 221 pm) were measured. Draw the stereostructure of the dimer, and write down the corresponding Al — Cl distances.

vii) What is the hybridization of the Al atom(s) in Al_2Cl_6 and $AlCl_3$?

QUESTION 35: Kinetics **(10 points)**

The acid-catalyzed reaction $CH_3COCH_3 + I_2 \rightarrow CH_3COCH_2I + HI$ was found to be first order with respect to hydrogen ions. At constant hydrogen ion concentration the time needed for the concentration of iodine to be reduced by 0.010 mol L^{-1} was measured under various concentrations of the reactants.

i) Based on the information provided in the table, fill in the blanks.

$[CH_3COCH_3]$ (mol L^{-1})	$[I_2]$ (mol L^{-1})	Time (min)
0.25	0.050	7.2
0.50	0.050	3.6
1.00	0.050	1.8
0.50	0.100	3.6
0.25	0.100	…
1.50	…	…
…	…	0.36

ii) Derive the rate law for the reaction and calculate the rate constant.

iii) Calculate the time needed for 75% of CH_3COCH_3 to react in excess I_2.

iv) Show graphically the dependence of the rate on $[CH_3COCH_3]$ and on $[I_2]$, for fixed initial concentration of the other reagents.

v) If the rate is doubled by raising the temperature by 10°C from 298 K, calculate the activation energy for this reaction.

Fundamental constants

Quantity	Symbol	Value	Unit
Speed of light	c	299 792 458	$m\ s^{-1}$
Permeability of vacuum	μ_0	$4\pi \times 10^{-7}$ = 12.566 370 614…x 10^{-7}	$N\ A^{-2}$
Permittivity of vacuum	ε_0	$1/\mu_0 c^2$ = 8.854 187 817 x 10^{-12}	$C^2\ m^{-2}\ N^{-1}$ or $F\ m^{-1}$
Planck constant	h	6.626 068 76 x 10^{-34}	J s
Electron charge	e	1.602 176 462 x 10^{-19}	C
Electron mass	m_e	9.109 381 88 x 10^{-31}	kg
Proton mass	m_p	1.672 621 58 x 10^{-27}	kg
Avogadro constant	N_A	6.022 141 99 x 10^{23}	mol^{-1}
Faraday constant	F	96 485.3415	$C\ mol^{-1}$
Boltzmann constant	k	1.380 650 3 x 10^{-23}	$J\ K^{-1}$
Molar gas constant	R	8.314 472	$J\ K^{-1}\ mol^{-1}$
Atomic mass unit	u	1.660 538 73 x 10^{-27}	kg

Source: *Physics Today* **55** BG6 (2002)

Common unit conversions

The unit 1 M is commonly used as an abbreviation for 1 mol dm^{-3}.

1 L = 1 dm^3 = 1000 cm^3

1 Å = 10^{-10} m

1 cal = 4.184 J

Useful formulas

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

$$E_n = \frac{-Z^2 e^2}{(4\pi\varepsilon_0) 2n^2 \alpha},\ \alpha = \frac{\left(\frac{h}{2\pi}\right)^2 (4\pi\varepsilon_0)}{\mu e^2}$$

$2\ d\ \sin\theta = n\ \lambda$ $\qquad$ $\text{Kinetic Energy} = \frac{1}{2}mv^2$ $\qquad$ $k = Ae^{-\frac{E_a}{RT}}$

35th International Chemistry Olympiad

Athens, Greece

Practical Examination

Tuesday, 8 July 2003

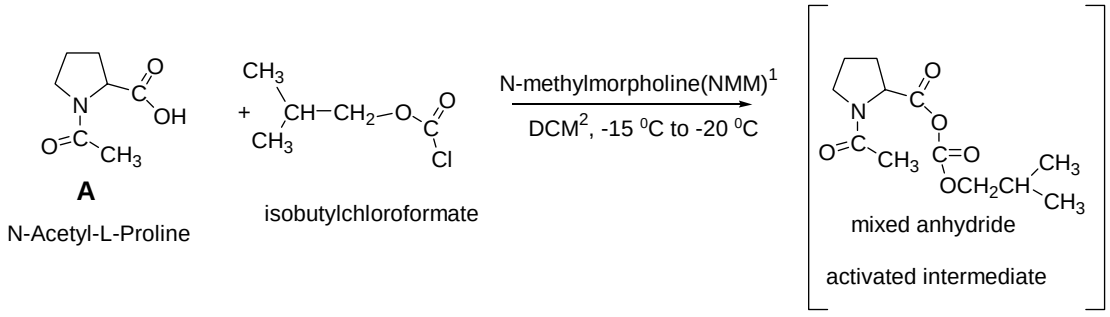
Synthesis of the dipeptide *N*-acetyl-*L*-prolinyl-*L*-phenylalanine methyl ester (Ac-*L*-Pro-*L*-Phe-OCH_3)

Introduction

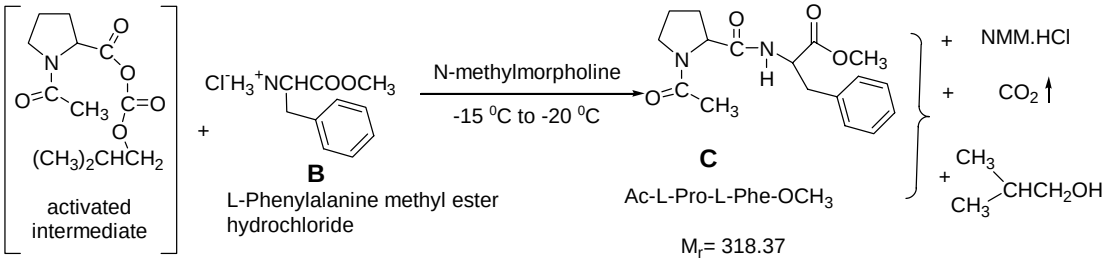
Peptide synthesis is now a well-refined art and many of their synthetic procedures can be readily adapted to the elementary laboratory. Interest in peptides, always high, has heightened even more with the recent discovery of the importance of the so-called "opiate" peptides as well as of other biological active peptides.

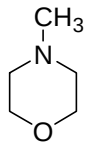
In this experiment the one-pot procedure for synthesizing the title dipeptide from its components, suitably protected amino acids, is described.

STEP 1



STEP 2



[1] *N*-methylmorpholine (NMM) = 

[2] DCM = Dichloromethane

Procedure

STEP 1

Place the 1.50 g (0.0095 mol) sample of *N*-acetyl-*L*-proline (labelled **AcPro**), which you have been given, into a 50-cm^3 round-bottomed flask. Add 20 cm^3 dichloromethane (labelled **DCM**) in the graduated cylinder. Use some of the 20 cm^3 DCM to wash out the AcPro vial and add the remaining DCM also into the round-bottomed flask. Plug the flask with a septum, clamp it loosely to a support stand and cool it to –15 °C to –20 °C in the ice/sodium chloride cold bath provided by the supervisor. Allow approximately 5 minutes for cooling. Add 1.2 cm^3 (0.0109 mol) of *N*-methylmorpholine (labelled **NMM**) to the flask, by means of a syringe. Then, slowly add 1.5 cm^3 (0.0116 mol) isobutylchloroformate (labelled **IBCF**) to the flask by means of a second syringe. During the addition, swirl the reaction mixture gently by hand, and continue swirling for another 10 min. The temperature should remain in the range $–20^o$ to $–15^oC$.

STEP 2

Remove the septum and quickly add all the *L*-phenylalanine methyl ester hydrochloride (2.15 g, 0.0100 mol), (labelled **$HCl{\cdot}H_2NPheOCH_3$**) using the polypropylene powder funnel. Plug the flask again with the septum. Immediately add 1.2 cm^3 (0.0109 mol) of *N*-methylmorpholine (labelled **NMM**) using a third syringe, while the reaction mixture is swirled by hand. *ATTENTION: Leave the needle part of the syringe in the septum for the remainder of the reaction*. Allow the reaction to proceed for 60 min at –15 °C to –20 °C, swirling periodically by hand.

During this waiting period you are highly advised to start working on the Analytical Chemistry experiment.

After 60 min at $–20^oC$ to $–15^oC$, remove the 50 cm^3 round-bottomed flask from the ice/sodium chloride bath and place the flask in the 250 cm^3 beaker and let it warm up to room temperature. Transfer the contents of the flask into the 50 cm^3 separating funnel by means of the glass funnel. Rinse the flask with a small amount of dichloromethane (3-5 cm^3), which is in a vial (labelled **DCM**). Wash the organic layer successively with two 20 cm^3 portions of 0.2 M aqueous HCl solution, two 20 cm^3 portions of 1% aqueous $NaHCO_3$ solution (read caution comment in next paragraph) and finally one 10 cm^3 portion of saturated solution of sodium chloride (labelled **brine**).

Important
After each washing allow the separating funnel to stand for enough time, so that the two phases separate completely. Also, take into consideration that the organic phase (DCM) is always the lower layer and contains the product. All the aqueous washings are collected in the same Erlenmeyer flask (empty if necessary). ***CAUTION: Keep in mind, also, that during washing with 1% $NaHCO_3$, the CO_2 liberated is exerting pressure on the separating funnel stopper, so be sure to let the gas out through the stopcock before and after each shaking, while holding the funnel upside down.***

Before continuing, wash the glass funnel, the 50 cm^3 cylinder and the 50 cm^3 round-bottomed flask with water and then dry them with acetone. Your supervisor will show you where to dispose of the water and the acetone.

Pour the organic layer into a clean 50 cm^3 Erlenmeyer flask. Add the anhydrous sodium sulfate, which is in a vial labelled **Na_2SO_4**, to the Erlenmeyer flask containing the organic layer. The organic phase should become clear. Filter it through the cleaned and dried funnel, whose stem you have previously stuffed with a small piece of cotton to trap any solids, into the cleaned and dried 50 cm^3 round-bottomed flask. Rinse the Erlenmeyer flask with a small amount of dichloromethane (3-5 cm^3). Removal of the organic solvent is done under reduced pressure, using a rotary evaporator apparatus. This will be done for you by a laboratory supervisor, who will add 20 cm^3 of diethylether to the residue in your flask, which will cause precipitation of your product. After cooling for 5 minutes in the ice bath, scrape the walls of the flask with a spatula, filter by suction the crystallized dipeptide through a fritted glass funnel. Wash twice with diethylether (5 cm^3 each time).

Leave the product on the filter under suction for at least 3 minutes. Then collect it on weighing paper, weigh it in the presence of a supervisor and then transfer it into a sample vial and label it with your student code. Write the mass of your product (**C**) on the label and on your answer sheet (on the next page).

TLC- Analysis

You have two Eppendorfs, one empty and one with a tiny amount of substance **B**. Put a small amount of **C** into the empty Eppendorf, and dissolve both **B** and **C** in a few drops of methanol. Use the supplied capillary tubes to apply small samples of these solutions to the TLC plate. Develop the TLC plate with a solution of chloroform-methanol-acetic acid (7:0.2:0.2) as eluant. The appropriate amount of eluant has been placed in the proper vial by the supervisor.

After the elution, analyze the TLC-plate using a UV-lamp. Clearly mark the starting line, solvent front and the UV-active spots.

Draw the diagram in the box on the answer sheet. Determine the R_f values.

Finally place the TLC-plate in a small plastic bag with a sealing strip and put it in an envelope provided by the supervisor. Write your student code on the envelope.

The examination committee will check the quality of the *N*-acetyl-*L*-prolinyl-*L*-phenylalanine methyl ester that you have prepared by determining its angle of optical rotation and consequently its specific rotation, $[a]^t_{D,}$ using an accurate polarimeter apparatus.

TITRATION OF ASCORBIC ACID WITH POTASSIUM IODATE

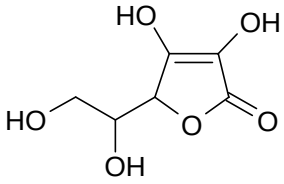
Introduction

Ascorbic acid (vitamin C, $C_6H_8O_6$, symbolized below as $AscH_2$) is a weak acid and undergoes the following dissociation steps:

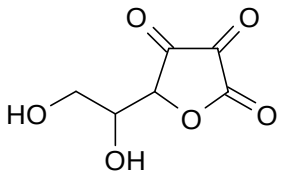
$$AscH_2 \rightleftharpoons AscH^- + H^+ \qquad K_{a1} = 6.8\times10^{-5}$$
$$AscH^- \rightleftharpoons Asc^{2-} + H^+ \qquad K_{a2} = 2.7\times10^{-12}$$

Ascorbic acid is readily oxidized to **dehydroascorbic acid** according to the half reaction:

$$C_6H_8O_6 \rightleftharpoons C_6H_6O_6 + 2H^+ + 2e^-$$



Ascorbic acid ($C_6H_8O_6$)



Dehydroascorbic acid ($C_6H_6O_6$)

A typical titrant used for the redox titration of ascorbic acid is potassium iodate, KIO_3. If the titration is carried out in 1 M HCl medium, then the reaction proceeds as follows:

$$3C_6H_8O_6 + IO_3^- \rightleftharpoons 3C_6H_6O_6 + I^- + 3H_2O$$

The end point is detected by the reaction of the first excess of iodate with iodide ions already present in the solution, producing I_2 which colours starch indicator blue:

$$IO_3^- + 5I^- + 6H^+ \rightleftharpoons 3I_2 + 3H_2O$$

Principle of the method
Ascorbic acid will be titrated by using a solution of potassium iodate of known concentration. The titration will be carried out in 1 M HCl, while starch solution will be used as indicator to detect the end point.

Procedure

Preparation of burette
Rinse the burette with deionized water at least three times. Rinse twice with solution of potassium iodate and fill. Record the initial volume of titrant ($V_{initial}$).

Titration of unknown sample
Obtain the unknown solution in a clean 250-mL volumetric flask. Record batch number of solution given. Dilute to the mark with deionized water and shake well. Use a pipette to transfer 25.00 mL of this solution into a 250-mL conical flask. Use a graduated cylinder to transfer 25 mL of 2 M HCl into the same flask and shake well. Add 40 drops of starch solution and titrate the solution with potassium iodate up to a permanent blue colour. Record final volume of titrant (V_{final}) (titration 1). Repeat the procedure as many times as necessary. Calculate the concentration of ascorbic acid (mg $C_6H_8O_6$/mL of solution). Each time refill the burette with solution of potassium iodate.

Questions

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

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

Balance the above reaction.

2. If V_1 and V_2 are the volumes of KIO_3 solution (titrant) required for the titration of 25.00 mL of the ascorbic acid solution given to you, in 1 and 5 M HCl, respectively, then the two volumes are related by the following relationship: (Circle the correct answer)

a. $V_2 = (3/2)\ V_1$
b. $V_2 = (2/3)\ V_1$
c. $V_2 = V_1$
d. none of the above

About the history of the International Chemistry-Olympiads (IChO)

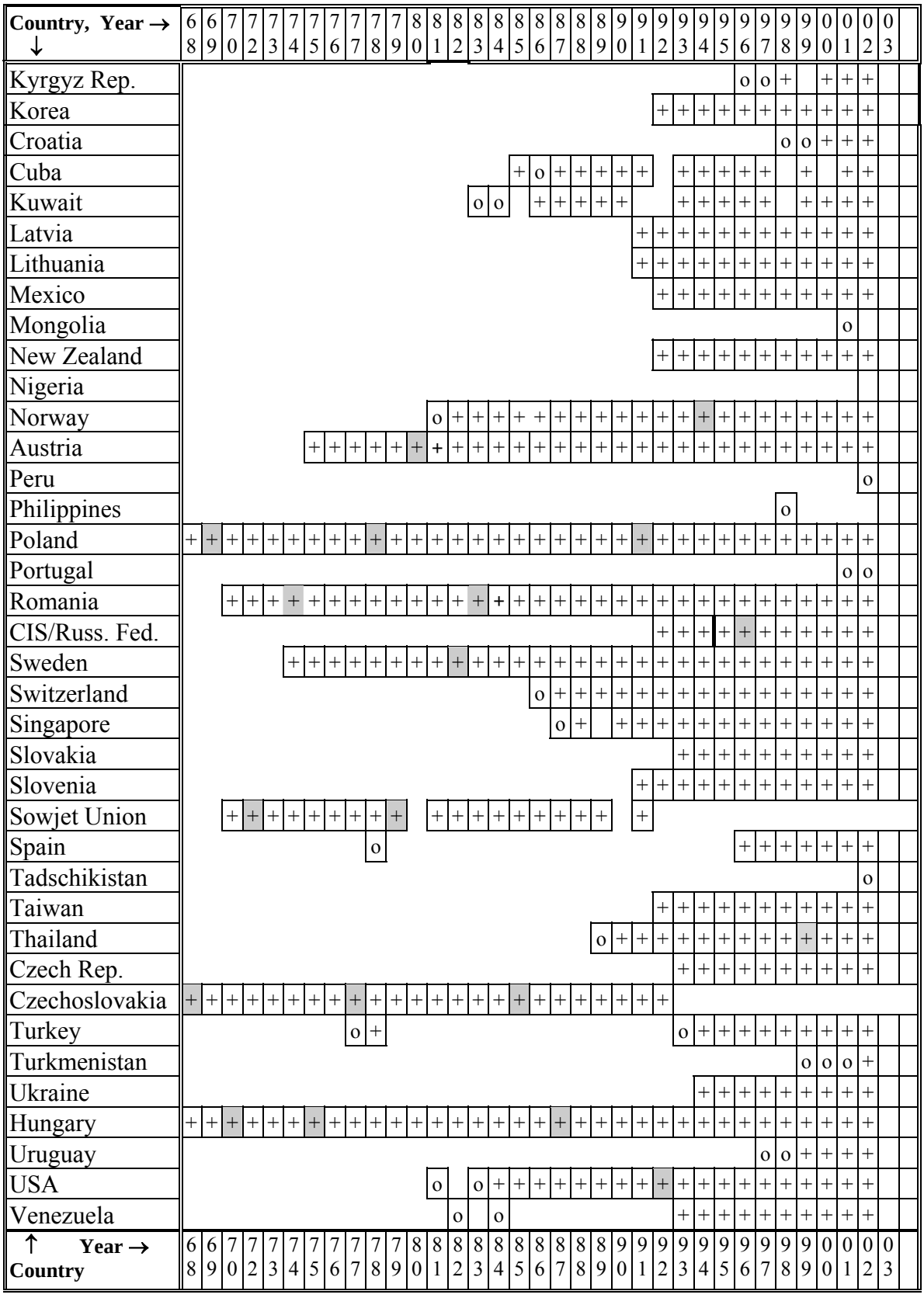
The idea of chemistry olympiads was born 1968 during an Czechoslovakian national olympiad that was attended by observers from Poland and Hungary. These three countries participated in the first IChO 1968 in Prague. The participating countries of the following years are shown in the table.

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
Egypt																																o	o	+	
Argentina																											+	+	+	+	+	+	+	+	
Azerbaijan																													o	o		+	+	+	
Australia																			o	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	
Belgium							+	+	+			+				+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	
Brazil																													o	o	+	+	+	+	
Bulgaria	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	
P. R. China																			+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	
Denmark														+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	
DDR	o	+	+	+	+	+	+	+	+	+	+	+	+	+		+	+	+	+	+	+	+													
Germany					o	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+		
Ivory Coast																																			
Estonia																										+	+	+	+	+	+	+	+		
Finland								o	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+		
France												o	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+		
Greece																+	+	+	+		+	+	+	+	+	+	+	+	+	+	+	+	+		
United Kingdom												o		o	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+		
The Netherlands												+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+		
India																													o	o	+	+	+	+	
Indonesia																												o	+	+	+	+	+	+	
Iran																									+	+	+	+	+	+	+	+	+	+	
Ireland																												o	o	+	+	+	+	+	
Iceland																																o	o	+	
Italy												+	+	+	+	+	o	o	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+		
Japan																																		o	
Yugoslavia							+	+	+	+				+	+	+	+	+	+															o	
Canada																o	o	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	
Kazakhstan																												o	o	+	+	+	+	+	
Kenya																													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


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
Kyrgyz Rep.
Korea
Croatia
Cuba
Kuwait
Latvia
Lithuania
Mexico
Mongolia
New Zealand
Nigeria
Norway
Austria
Peru
Philippines
Poland
Portugal
Romania
CIS/Russ. Fed.
Sweden
Switzerland
Singapore
Slovakia
Slovenia
Sowjet Union
Spain
Tadschikistan
Taiwan
Thailand
Czech Rep.
Czechoslovakia
Turkey
Turkmenistan
Ukraine
Hungary
Uruguay
USA
Venezuela
↑ 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		
Vietnam																												+	+	+	+	+	+	+			
Belarus																												+	+	+	+	+	+	+			
Cyprus Rep.																					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		
Number of delegations	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				

Number of delegations 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	KWT	C	DK
.													YU	B	C
.														YU	S
.														CDN	B
25														CH	CH
.														KWT	KWT

(List of abbreviations see page 99)

	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	TW	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	TW	RC	IR	H
5	SU	CS	NL	A	GUS	SGP	**D**	**D**	IR	H	RO	TW
.	H	RO	USA	GUS	H	ROK	GB	USA	RUS	RA	H	A
.	PL	F	I	**D**	**D**	TW	SK	UA	ROK	RUS	TW	SK
.	RO	A	**D**	RO	CDN	CZ	TW	CZ	RC	AUS	UA	BLR
.	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	TW	UA	A	**D**	**D**
.	A	AUS	A	AUS	P	RO	AUS	BLR	AUS	RO	RA	ROK
.	USA	SGP	AUS	NL	NZ	DK	SGP	SGP	CDN	TW	BLR	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	BLR	MEX	CDN
.	C	S	LV	LT	F	SK	LT	T	BLR	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	TW	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
.					YVA	CY	CY	BG	MEX	CY	FIN	SLO
.					CY	GR	B	S	CH	LV	B	EST
.					KWT	TR	GR	LT	CY	DK	S	S
.						YVA	FIN	E	E	NZ	CY	YVA
40						C	YVA	B	FIN	GR	EST	CY
.						KWT	KWT	GR	BG	KZ	LV	HR
.							C	FIN	YVA	E	SLO	I
.								YVA	GR	IRL	YVA	RI
.								C	B	B	BR	N
45								KWT	RI	KS	E	AZ
.									KWT	YVA	N	IRL
.									C	RI	RI	E
.											GR	LV
.											ROU	GR
50											C	BR

(List of abbreviations see page 99)

	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012
IChO held in	IND	NL	GR	D	TW	ROK						
1	RC	RC										
.	ROK	T										
.	USA	TW										
.	RUS	ROK										
5	IR	A										
.	TR	UA										
.	IND	USA										
.	AUS	PL										
.	TW	IND										
10	T	**D**										
.	SGP	IR										
.	PL	H										
.	RO	RUS										
.	F	CDN										
15	SK	TR										
.	H	AUS										
.	VN	GB										
.	CZ	SGP										
.	RA	E										
20	BLR	SK										
.	C	BLR										
.	**D**	VN										
.	GB	FIN										
.	UA	F										
25	A	LT										
.	MEX	CZ										
.	DK	KZ										
.	CDN	LV										
.	EST	NL										
30	RI	RO										
.	HR	RA										
.	I	EST										
.	N	HR										
.	BG	BG										
35	CY	NZ										
.	KZ	I										
.	B	DK										
.	LT	SLO										
.	NZ	N										
40	CH	YVA										
.	E	MEX										
.	FIN	BR										
.	SLO	S										
.	NL	RI										
45	LV	TM										
.	BR	B										
.	S	IRL										
.	YVA	CH										
.	IRL	C										
50	GR	CY										

(List of abbreviations see page 99)

List of abbreviations

A	Austria
AUS	Australia
AZ	Azerbaijan
B	Belgium
BG	Bulgaria
BLR	Belarus
BR	Brazil
C	Cuba
CDN	Canada
CH	Switzerland
CI	Iceland
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
J	Japan
KS	Kyrgyz Republic
KWT	Kuwait
KZ	Kasakhstan
LV	Latvia
LT	Lithuania
MEX	Mexico
MGL	Mongolei
KZ	Kasakhstan
LV	Latvia
LT	Lithuania
P	Portugal
PE	Peru
PL	Polen
RA	Argentina
RI	Indonesia
RC	People’s Republic of 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
TR	Turkey
TW	Taiwan (Chinese Taipeh)
UA	Ukraine
USA	United States of America
VN	Vietnam
WAN	Nigeria
YU	Yugoslavia
YVA	Venezuela