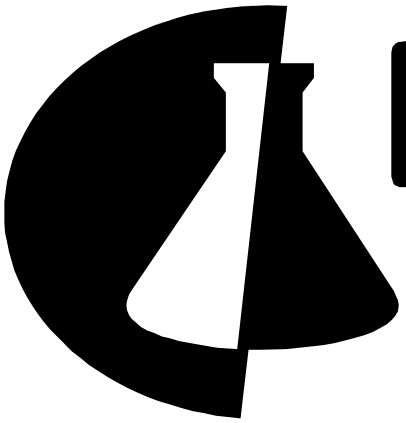

IChO

45. International Chemistry Olympiad Russia 2013

National German Competition

Volume 19

Preface

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

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

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

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

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

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

In the appendix you find tables of historical interest.

Wolfgang Hampe

This booklet including the problems of the 45th IchO and the latest statistics is available as of September 2013 from
http://www.icho.de (button:"Aufgaben")

Contents

Part 1: The problems of the four rounds

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

Part 3: The problems of the IChO

Part 4: Appendix

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Part 1

The problem set of the four rounds

First Round

Problem 1-1 Acids and Bases

Robert Boyle describes acids as pure substances which dye solutions of indicators characteristically.

a) Are the following substances pure substances, homogeneous or heterogeneous mixtures? Fill in the following table.

Expanded polystyrene	*α-tin*	*brass*
ammonium chloride fumes	*armored concrete*	*air+*
aqueous solution of sodium chloride	*β-sulfur*	*bath foam*
ice/water mixture	*sodium chloride*	

Pure substance	Homogeneous mixture	Heterogeneous mixture
...	...	...
...	...	...

Arrhenius stated that acids dissociate in hydronium cations and acid residue anions when dissolved in water and bases dissociate in metal cations and hydroxyl anions.
Subsequently the acidic or basic reaction of aqueous solutions is based on a surplus of hydronium cations and hydroxyl anions, respectively.

b) The basic reaction in water of some compounds cannot be explained by the theory of Arrhenius. Give three examples of such compounds.

Nowadays the Brønsted definition is widely used.

c) Describe how acids and bases are defined by the Brønsted theory.

Brønsted says that there are so called conjugate acids and bases.

d) Explain what a conjugate acid base pair is.

Given the species: NH_3, H_2O, HS^-, $H_2PO_4^-$, HCN, HCl, SO_4^{2-}, H_3CCOO^-

e) Fill in the table and complete the free fields.

Conjugate acid	Conjugate base
...	....
...	...

Na_2CO_3, $Al_2(SO_4)_3$, Na_2S, KCl, Cl_2 are dissolved in water.

f) Write the equations for the reactions with water. State whether the solutions react acidic, basic or neutral.

The pH value of an aqueous solution shows whether it is neutral, acidic or basic. The range of the pH values reaches normally from 0 to 14.

g) How is the pH value defined? Explain the origin of the range of values from 0 to 14. Derive why a neutral solution at room temperature has a pH of 7.

At 60 °C water has a H_3O^+ concentration of $10^{-6.51}$ mol/L.

h) Is it possible to form an acid by heating water? Explain the higher H_3O^+ concentration compared with water at 25 °C.

If a sufficient amount of acid is dissolved in water the degree of dissociation or protolysis shows whether the solution reacts strongly or weakly acidic.
An aqueous solution of an acid with c(HA) = 0.04 mol/L has a pH value of 3.

i) Calculate the degree of dissociation (in %) and state whether it is a weak or a strong acid.

j) Calculate the pH of aqueous solutions of nitric acid, acetic acid and sulfuric acid each with concentrations of c = 0.2 mol/L. Write the results with two decimals.
pK_a (HNO_3) = -132 pK_a (H_3CCOOH) = 4.75
pK_{a1} (H_2SO_4) = -3.00 pK_{a2} (H_2SO_4) =1.92

Problem 1-2 Preparations

Gerda is desperate: After the 4th round of the German IChO selection process she checks the lab cupboards. Besides a container with 5 L of NaOH standard solution she finds some other aqueous solutions which cannot be used in their given concentrations.
"What a waste" she thinks when she recognizes that the 1 L bottles are more than half-full.

Bottle 1	Bottle 2	Bottle 3
123 g NaOH dissolved in 700 g of H_2O d = 1.15 g/ml	H_2SO_4 (72 %) d = 1.65 g/ml	120.4 g $MgCl_2$ (free from water) + 600 g H_2O d = 1.14 g/ml

She wants to dilute these solutions in order to use them in the chemical lab.

a) Calculate the volume of each solution (in mL) which has to be filled up to 1 L to get a solution of c = 2 mol/L.

After the end of the 4th round some saturated solutions are empty and have to be freshly prepared.

b) Calculate the mass of sodium chloride to prepare a saturated aqueous solution of 2 L. Such a solution contains 26.5 % of mass of NaCl (ϑ = 20 °C, d = 1188.7 kg/m^3).

c) *Determine a general equation for the concentrations of Ca^{2+} and OH^- in a saturated solution of calcium hydroxide as a function of the solubility product.*

d) *Calculate the mass of calcium hydroxide ($Ca(OH)_2$) and barium hydroxide ($Ba(OH)_2 \cdot 8\ H_2O$) to prepare 1 L of saturated solutions. Give the mass with two decimals.*
$K_{sp}(Ca(OH)_2) = 3.89 \cdot 10^{-6}$, $K_{sp}(Ba(OH)_2) = 4.27 \cdot 10^{-3}$,
$\vartheta = 20$ °C, $d = 1000\ kg/m^3$ for both solutions.

e) *How can you prepare a saturated solution of a salt without any weighing? Make a proposal!*

Problem 1-3 Organic Acid?

The aqueous solution of a substance **A** shows an acidic reaction. When 766 g of **A** are burned in oxygen 1.837 g of carbon dioxide and 0.376 g of water are generated.

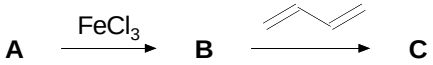
a) *Determine the empirical formula of **A**.*

The ^{1}H-NMR spectrum (in DMSO) shows two signals with the relation 1:2. The shifts of the peaks are 8.59 ppm (s) and 6.58 ppm (s). In the ^{13}C-NMR spectrum two signals at 149.79 ppm (s) and 115.67 ppm (s) are observed.

b) *Deduce the molecular formula of **A**. Account for your decision using the NMR signals. Sketch the structural formula and write down the name of the substance!*

c) *Explain by using resonance structures why **A** shows an acidic reaction.*

The reaction of **A** with an aqueous solution of iron(III) chloride gives compound **B**.
The reaction of **B** with an excess of buta-1,3-diene at 100 °C leads to compound **C**:



d) *Complete the reaction scheme!*

e) *Sketch all isomers of **C** formed in this reaction. Determine the kind isomerism of these isomers.*

The combination of **A** and **B** served in former times as a pH electrode. The standard potential of the half-cell is $E^0 = + 0.70$ V.

f) *Write down the equation for the redox reaction.*

g) *Calculate the potential of this half-cell for pH = 5.5*
(25 °C, c(Ox) = c(Red) = 1 mol/L)

Second Round (homework)

Problem2-1 Nothing but Unknown Substances

There is no carbon in the unknown substance A. If 19.5 g of A is annealed in the absence of air a ternary, white, crystalline compound B and a gas C form. In the presence of air gas C burns with a light blue flame. The elementary analysis of B shows 24.5 % (w/w) of carbon and 28.6 % (w/w) of nitrogen.

When annealed with carbon another ionic compound D also results in compound B, too, but without the gas. D reacts with acids to form urea among other substances. The elementary analysis of D shows 14.0 % (w/w) of carbon und 32.6 % (w/w) of nitrogen.

An aqueous solution of B reacts with an aqueous solution of iron(III) chloride to form a red solution of compound E. Compound F forms if B reacts with elementary sulfur. F reacts with an aqueous solution of iron(III) chloride, too, to form a red solution of compound G.

The reaction of an aqueous solution of E with an aqueous solution of Mohr's salt [$(NH_4)_2Fe(SO_4)_2 \cdot 6\ H_2O$] in a molar ratio of 1 : 1 leads to the complex compound H. In H the iron cations of both oxidation states are octahedral coordinated.

a) Write down the names and the empirical formulae of the unknown substances A - H.

b) Give the equation of the reaction of D to B. Assign the oxidation states to all atoms. What is the name of this reaction?

c) Draw the Lewis structure of the anion of D.

d) Give 5 examples of existent isoelectronic compounds which have the same number of atoms as D.

e) Calculate the volume (25 °C, 1013 hPa) of the gas C which is formed in the reaction of A.

f) Which colour of compound H do you expect? Which magnetic property should H show in an inhomogeneous magnetic field? Account for your decision by using an MO scheme and its occupation with electrons.

In a reaction of an aqueous solution of B with chlorine a ring-shaped compound I occurs. Compound J forms when I reacts with ammonia at 150 °C. J may react with formaldehyde to give a thermosetting plastic.

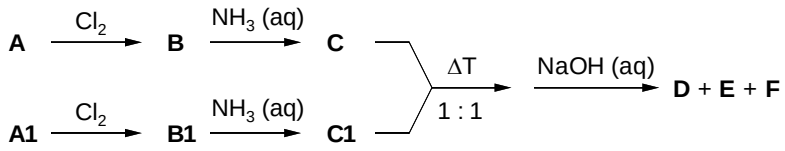
g) Write down the names and the empirical formulae of I and J. Draw the Lewis structure of I (only one resonance form is necessary).

The reaction of an aqueous solution of F with an aqueous solution of silver nitrate gives a white solid K which dissolves readily in a solution of ammonia but is insoluble in nitric acid. You get a colorless solid L if K reacts with a solution of bromine in diethyl ether at low temperatures. L reacts to a red compound M when melted.

h) Write down the names and the empirical formulae of K, L and M. Compound L may be formally assigned to the compounds of a group of elements of the periodical system. Which group is it? Give a short explanation.

Problem 2-2 An "Organic" Riddle

The unsaturated hydrocarbons A and A1 react according to the following not balanced equations to form the compounds D, E and F.



Consider the following information:

- C and C1 are heated in the molar ratio of 1 : 1.
- The elementary analysis of D, E and F provides the following data:
  D: 55.82 % C, 11.71 % H, 32.47 % N
  E: 59.88 % C, 12.01 % H, 28.11 % N
  F: 62.98 % C, 12.30 % H, 24.72 % N
- D, E and F are heterocyclic compounds.
- D, E and F are bases.
- D, E and F can be catalytically dehydrated to form aromatic heterocyclic compounds.
- The ^{1}H-NMR spectrum ($CDCl_3$) of compound D shows to singlets in the ratio 1 : 4 (chem. shift: 1.66 ppm, 2.84 ppm).
- If D, E and F react with an N-alkylation agent the compounds D*, E* and F* form. During this reaction D, E and F add 4 methyl groups each.

a) Complete the reaction scheme above with the compounds A to C and A1 to C1. (Stereochemical aspects have to be considered!)
Write down the names and the empirical formulae of the unknown substances D, E and F. Draw line-bond structures of all possible stereoisomers of D, E and F which indicate the overall shape of the molecules.
(Instructions: Bond receding into page 
Bond coming out of the paper plane 

Mark the stereogenic centers with an asterisk, determine the absolute configuration using the CIP convention. Write down the kind of stereoisomerism which the possible stereoisomers show.
Calculate the percentage of the yield of the isomers of D, E and F relating to the total yield. Assume that the reactivity of C and C1 is approximately the same.

The hydroxide salts of D*, E* and F* are heated. Each of the salts of E* and F* give a mixture of products, the salt of D* provides either the formation of only one product X (reaction way 1) or a mixture of a liquid compound Y and a gaseous compound Z (d = 1.064 kg/m^3, 1013 hPa, ϑ = 25 °C, reaction way 2).

b) Show the scheme of both ways of reaction with the structural formulae of X, Y and Z.

c) What is the name of the described reaction sequence (N-methylation, hydroxide formation and heating)? Draw a general reaction scheme and state whether the formation of a certain product is favoured. Account for your decision.

d) Which ways of reaction and which products do you predict if you start with compound E? Specify the reaction schemes with structural formulae. Mark the preferentially formed products in reaction ways with more than one product. (Stereochemical aspects do not need to be considered!)

Problem 2-3 Technical Chemistry

Consider generally and especially in this problem:
The reaction constants K_p, K_c, K_a, K_b and K_{sp} are non-dimensional. Whether a constant is K_p or K_c depends on whether the reacting agents are gaseous or dissolved.
If you use the equations for these equilibrium constants you have to fill in the numbers representing the pressures/concentrations dimensionless i.e. you have to divide the given pressures/concentrations by the standard pressure (p° = 1,000 bar)/standard concentration (c° = 1 mol/L).

The double contact process is an important method to produce sulfuric acid. During this synthesis sulfur dioxide is oxidized to sulfur trioxide:

$$2\ SO_2 + O_2 \rightleftharpoons 2\ SO_3 \quad (1)$$

A unit produces 500 t of sulfur trioxide per day. In this unit 99.8 % of the inserted sulfur dioxide react to sulfur trioxide.

a) Which mass of sulfur reacts per day to produce 500 t of sulfur trioxide? Which quantity of heat is released in the reaction to form 500 t of sulfur trioxide per day from

sulfur dioxide (referred to standard conditions)? Calculate the mass of sulfur dioxide which would be released into the environment if there is no waste gas cleaning.

b) *Calculate K_p and ΔG for the formation equation (1) of sulfur trioxide at 600 °C and at 700 °C using the thermodynamic data given below.*

c) *Calculate K_p at 700 °C using the van't Hoff isobar based on the values at 600 °C. Compare $K_{p,\ 700\ °C}$ with the value from b) and give reasons why there could be differences.*

In the production process of SO_2 sulfur is burned at first at a temperature in the range of 1400 to 1600 °C with less than the necessary amount of air followed by a second step of total oxidation of SO_2 with an excess of air at a temperature below 700 °C.

d) *Give the reasons why SO2 is oxidized at 1500 °C with a lack of air first and why the total oxidation is carried out at 700 °C.*

With this process you get a mixture (practically free of SO_3) in which SO_2 has a volume percentage of 10 %, oxygen of 11 % and nitrogen 0f 79 %. This mixture is passed into a contact oven. There the equilibrium establishes at 600 °C and the actual pressure of p_{act} = 1.02 bar.

e) *Calculate the volume percentage of the components of the gas mixture in equilibrium. What is the value of the relative conversion (in %) of sulfur dioxide? Use in this calculation K_p = 65.1.*
(Hint: In the calculation there will occur a cubic equation which has to be solved up to two decimals.)

In an experiment to study the equilibrium of the reaction (1) the following mole fractions at 1000 K and $1.013 \cdot 10^5$ Pa are found in equilibrium:

x_{SO_2} = 0,309, x_{SO_3} = 0,338, x_{O_2} = 0,353

f) *Calculate K_p and ΔG at 1000 K with these data!*

Data: R = 8.314 J · mol^{-1} · K^{-1}, Standard pressure p° = 1.000 bar
Air: 21 % (of vol.) O_2, 79 % (of vol.) N_2
M(O) = 16.0 g · mol^{-1}, M(S) = 32.1 g · mol^{-1}.

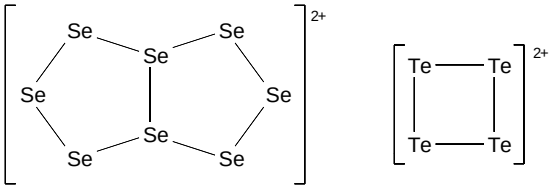
Thermodynamic Data (25 °C):

	$H°_f$/kJ · mol^{-1}	S^0 /J · mol^{-1} · K^{-1}	c_p / J · mol^{-1} · K^{-1}
SO_2	-297	249	46,5
O_2	0	205	31,9
SO_3	-396	257	59,0

Problem 2-4 Extraordinary Ions

Dissolving selenium and tellurium in hot concentrated sulfuric acid leads to intensively colored solutions of polychalkogen cations.

In the case of selenium green Se_8^{2+} forms, in the case of tellurium pink Te_4^{2+}:

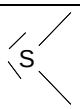
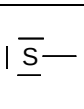
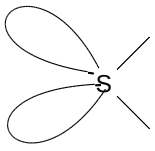
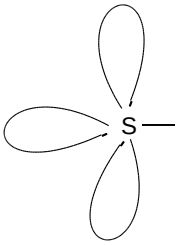
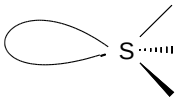


a) Write down the equations for both dissolving processes. Assigns oxidation states!

Oxidation of the lighter homologue sulfur with antimony pentafluoride leads to salt ionic compounds which possess S_4^{2+}-four-membered rings analogous to Te_4^{2+}.

b) Explain why the S_4^{2+} cation is often termed in literature as pseudoaromatic compound. Use the number of valence electrons and the resulting Lewis structure and electron distribution.

Different to oxygen, the lightest element of the chalcogen group, which often forms double bonds, the element sulfur mostly generates covalent single bonds. Similar to the molecular structures of Se_8^{2+} and Te_4^{2+} shown above and following the octet rule you may assign the following modes of bonding and formal charges to sulfur atoms:

Bond			
Bond with orbitals			
Formal charge	±0	−1	+1

c) Draw based on the three given modes of bonding three spatial molecular structures of S_4^{2+} cations which are different to the four membered ring structure and assign formal charges. Use  to indicate nonbonding electron pairs.

Three spatulas full of potassium chloride, three spatulas of lithium chloride, ¼ spatula of calcium sulfide and one spatula of sulfur are thoroughly mixed and heated in a porcelain crucible in a hood.

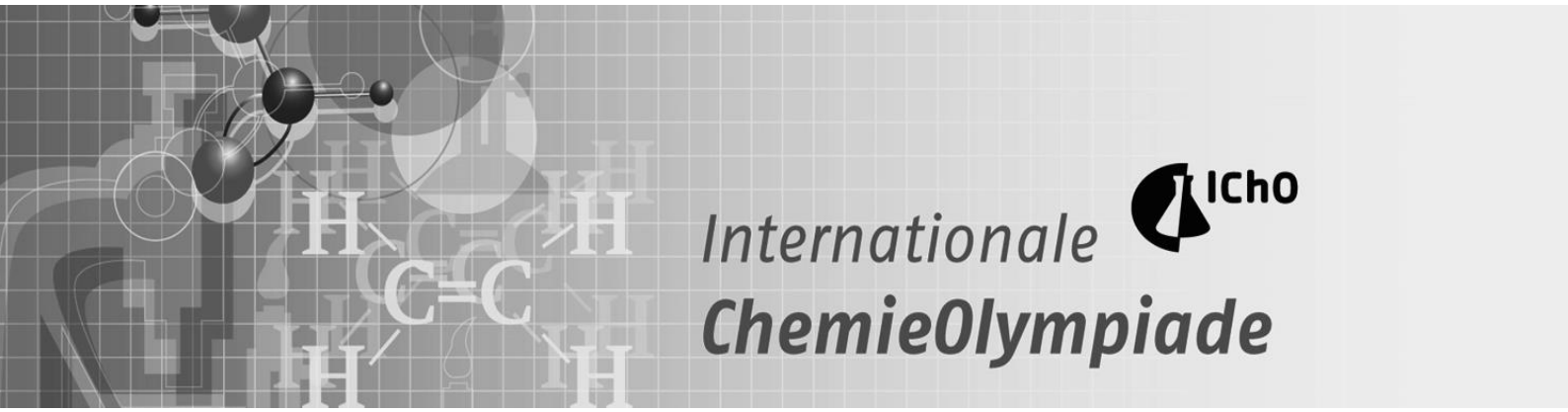
In the molten mass an intense colour is observed, the absorption maximum of which lies at approximately 17000 cm^{-1}.
After cooling down this colour vanishes and a white solid comes to existence.

d) Which colour does the molten mass show? Which sulfur containing particle X is responsible for the colour? Draw the Lewis structure of X!

e) Give a reason why the colour vanishes when the molten mass is cooled down!

Elementary sulfur is insoluble in water but dissolves well in an aqueous solution of (poly)sulfide.

f) Explain why sulfur dissolves in an aqueous solution of (poly)sulfide.



Problems Round 3

Test 1 Göttingen 2013: Problems 3-01 to 3-10

Test 2 Göttingen 2013: Problems 3-11 to 3-20

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

Good Luck

Useful formulas and data

$\Delta G^0 = \Delta H^0 - T \cdot \Delta S^0$ $\Delta G^0 = - \Delta E \cdot z \cdot F$ $\Delta G^0 = - R \cdot T \cdot \ln K$

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

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

Nernst equation : $E = E^0 + \frac{R \cdot T}{z \cdot F} \cdot \ln (c_{Ox}/c_{Red})$

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

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

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

with $c^0 = 1$ mol/L, $p^0 = 1.000 \cdot 10^5$ Pa

Rate laws

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

Arrhenius equation: $k = A \cdot e^{-Ea/(R \cdot T)}$ A pre-exponential factor; E_a activation energy

Law of Lambert and Beer: $A = \varepsilon \cdot c \cdot d$ A absorbance; ε molar absorption coefficient; d length of the cuvette; c concentration

Transmission $T = \frac{I}{I_0}$ Absorbance $A = \lg \frac{I_0}{I}$ with I Intensity

Speed of light $c = 3.000 \cdot 10^8$ ms^{-1}

Gas constant $R = 8.314$ JK^{-1}mol^{-1}

Faraday constant $F = 96485$ Cmol^{-1}

Avogadro constant $N_A = 6.022 \cdot 10^{23}$ mol^{-1}

Planck constant $h = 6.6261 \cdot 10^{-34}$ Js

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

1 Å $= 10^{-10}$ m

A periodic table was provided

Third Round Test 1

Problem 3-01 Multiple Choice

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

a) Mark a typical frequently used reducing agent.

A	F_2	**B**	H_2	**C**	I_2	**D**	N_2	**E**	O_2

b) Assign one of the following statements to each of the elements Li, Na, Be, Mg, B, Al, C, Si, N, P, Cu, Ag and Au.

01 … it forms hydrogen compounds with the formula E_nH_{2n+2} which explode in contact with oxygen and which are liquid at room temperature if $n \geq 3$.

02 … it forms three-center two-electron bonds to stabilize its electron deficit. The oxo acid of this element is not a Brønsted-acid,

03 … its phosphate (but not its sulfate) is hardly soluble. It forms organometallic Grignard reagents.

04 … its phosphate (but not its sulfate) is hardly soluble. It shows red flame coloration.

05 … it's a noble metal which dissolves in hot concentrated sulfuric acid.

06 … it's a highly non-noble metal which forms a passivating oxide coating. It forms dimer covalent hydrides and chlorides.

07 … it's a very rare element which forms covalent hydrides and chlorides.

08 … it's very reactive and forms salts which are very soluble in water.

09 … may form double bonds and exists in modifications of different colour.

10 … it may form branched frameworks with multiple bonds.

11 … it exists as diatomic molecule.

12 … it does not react with a solution of silver nitrate but is soluble in aqua regia forming complexes with quadratic-planar coordination.

13 … its ions show a green flame colouring and are used to identify halides in plastic.

c) Which of the following unusually written formulae represents more than one compound?

A	CAgNO	**B**	CH_4O	**C**	CK_2O_3	**D**	C_2H_3Cl	**E**	C_2H_6O

d) Which of the following reactions is a redox reaction?

A	$2\ CrO_4^{2-} + 2\ H_3O^+ \rightleftharpoons Cr_2O_7^{2-} + 3\ H_2O$	**B**	$Zn + H_2O \rightleftharpoons ZnO + H_2$
C	$SO_2 + 2\ H_2S \rightleftharpoons 3\ S + 2\ H_2O$	**D**	$2\ H_2 + O_2 \rightleftharpoons 2\ H_2O$
E	$(CH_3CO)_2O + H_2O \rightleftharpoons 2\ CH_3COOH$		

e) Which is a carcinogen degradation product of methanol?

A	CH_4	**B**	CO_2	**C**	CH_3CH_2OH	**D**	HCOOH	**E**	CH_2O

Problem 3-02 Free of Limescale

Devices for heating water are susceptible to limescale. Tap water contains Ca^{2+}, CO_3^{2-} and HCO_3^- ions amongst others. By heating this water precipitation of solid calcium carbonate is favored.

a) Give two reasons for this precipitation.

A scaled electric kettle had to be cleaned with an acid.
In a normal household usually vinegar essence which is a 25% aqueous solution of acetic acid is available. This corresponds to a concentration of 4.30 mol/L.

b) Calculate the pH of vinegar essence and the concentration of the acetic anions. (Assume for simplification that activities are equal to concentrations.)

Vinegar essence was diluted until pH = 2.3 was reached.
200 mL of this diluted *vinegar essence was given into a water boiler. After all limescales vanished the solution had a pH of 5.00.*

c) Calculate the mass of calcium carbonate which was dissolved by the essence. (Mention simplifications used in your calculation.)

pK_a(Acetic acid) = 4.76

Problem 3-03 Bromine Oxides

A yellow-orange product was prepared by means of ozonization of a bromine solution in trichlorofluoromethan at -78 °C. The product turned out to be a bromine oxide **A**.
Heating oxide A from -78 °C to -5°C gave rise to the formation of two other products, a golden-yellow bromine oxide **B** and a deep brown bromine oxide **C.**
Let the general formula of a bromine oxide be Br_xO_y.

a) Write down the oxidation state of bromine in Br_xO_y as a function of x and y.

The reaction of these oxides with iodide ions in acidic solution has been used for the analysis of these oxides: $a\ Br_xO_y + b\ I^- + c\ H^+ \longrightarrow d\ Br^- + e\ I_2 + f\ H_2O$

b) Determine the stoichiometric factors a to f depending on x and y.

Iodine formed in this reaction was determined by titration with a solution of thiosulfate (c = 0.065 mol/L). The bromide from the same sample was determined by potentiometric titration with silver nitrate solution (c = 0.020 mol/L)). Results:

	V($Na_2S_2O_3$ sol.), c = 0.065 mol/L in mL	V($AgNO_3$ sol.), c = 0.020 mol/L in mL
Oxide **A**	10.3	6.7
Oxide **B**	17.7	14.4
Oxide **C**	8.74	14.2

c) Give the equations of the reactions of the titrations.

*d) Determine the empirical formulae of the **A**, **B** and **C**.*
*Write down the equations for the reactions of **A**, **B** and **C** with iodide ions.*

e) Calculate the mass of the samples used for the analysis.

f) Draw the Lewis structures of the bromine A, B and C. If there is mesomerism it is sufficient to draw one resonance structure. Tip: Substitute hydrogen in the corresponding oxo acids.

Problem 3-04 Gluconic acid

Gluconic acid (HA) and its salts are use as acid regulators for food.
A platinum electrode with hydrogen (p = 1 bar, T = 298 K) bubbling over its surface dips into a solution of gluconic acid (c = $1.00 \cdot 10^{-3}$ mol·L^{-1}) which contains sodium gluconate (c = $3.00 \cdot 10^{-2}$ mol·L^{-1}). The potential of this electrode is -0.315 V towards the standard hydrogen electrode.

a) Determine the acid constant of gluconic acid.

To titrate 50 mL of an aqueous solution which contains 1.36 g of gluconic acid 34.7 mL of a sodium hydroxide solution (c = 0.200 mol·L^{-1}) were consumed.

b) Determine the molar mass of gluconic acid from these data.

c) Calculate the pH value at the equivalence point of this titration precisely. Propose an appropriate indicator.

(If you could not solve a) use $K_a = 1.50 \cdot 10^{-4}$ an.)

Problem 3-05 Halogens

Halogens are very reactive and show a high electron affinity. Though chlorine has the highest electron affinity fluorine is a stronger oxidation agent. Table 3-05.1 provides different data of halogens.

Tab. 3-05.1. Selected data of halogens (X = hal)

	Bond length d(X-X) / pm	Hydration enthalpy X^- (g) → X^- (aq) / kJ · mol^{-1}	Electron affinity X (g) + e– → X^- (g) /kJ · mol^{-1}	Bond energy X-X (25 °C) /kJ · mol^{-1}
Fluorine	144	-458	-328	159
Chlorine	198	-384	-349	243
Bromine	228	-351	-325	193
Iodine	266	-307	-295	151

a) Reflect using the data above which factors determine the oxidation power of halogens.

Write down all steps which finally lead to the formation of halides ($(X_2 \longrightarrow ... \longrightarrow X^-$ (aq)) starting from elementary halogens.

Justify the fact that fluorine has a higher oxidation power by using the data of the table.

b) Account for the course of the bond energies X-X.

Halogens react mostly as oxidation agents. However, some halogen species can be reduction agents. Furthermore halogens may react with themselves in a redox reaction.

c) Give one equation each of a reaction of chlorine or another chlorine species

i) which reacts as oxidation agent,

ii) which reacts as reduction agent,

iii) which reacts as oxidation and reduction agent.

Avoid identical reactions and reaction partners in i) to iii), respectively.

All halogens form hydrogen compounds HX (X = F, Cl, Br, I), which dissolve in water very well. However, the acidity of these solutions is very different.

d) Arrange the hydrohalic acids in the direction of rising acidity.
Account for your decision!

e) Calculate the degree of protolysis (in %) of hydrofluoric acid with the concentration c = 0.1 mol/L. (pK_a(HF) = 3.19)

The only known oxo acid of fluorine is HOF.

f) Draw the Lewis structure of HOF and apply oxidation numbers.
Witch shape of the molecule would you expect according to the VSEPR model?

At 25 ° C HOF is an unstable gas which decays to form hydrogen fluoride and oxygen with a half-life of 30 minutes. HOF decays in water, too.

g) Write down the equation for the reaction of HOF with water.

Problem 3-06 Properties of State, Equilibria

The table below shows the atomization heat ($\Delta_{at}H°$) and the heat of formation ($\Delta_f H°$) for different allotropes of carbon. The atomization heat is needed to form free gaseous atoms of the given compound. (Graphite is the most stable modification of carbon under standard conditions.)

	$\Delta H_{at}°/(kJmol^{-1})$	$\Delta H_f°/(kJmol^{-1})$
$C_{graphite}$	718.9	u
$C_{diamond}$	717.0	v
C(g)	0	w
$C_2(g)$	x	831.9

a) Determine u, v, w and x.

b) Calculate the carbon-carbon bond energy in diamond (y) and in gaseous C_2 (z).

The carbon-carbon bond energy in graphite is 473.3 kJ mol^{-1}.

c) Compare this value to the atomization heat of graphite. What is the quantity you can deduct from the comparison?

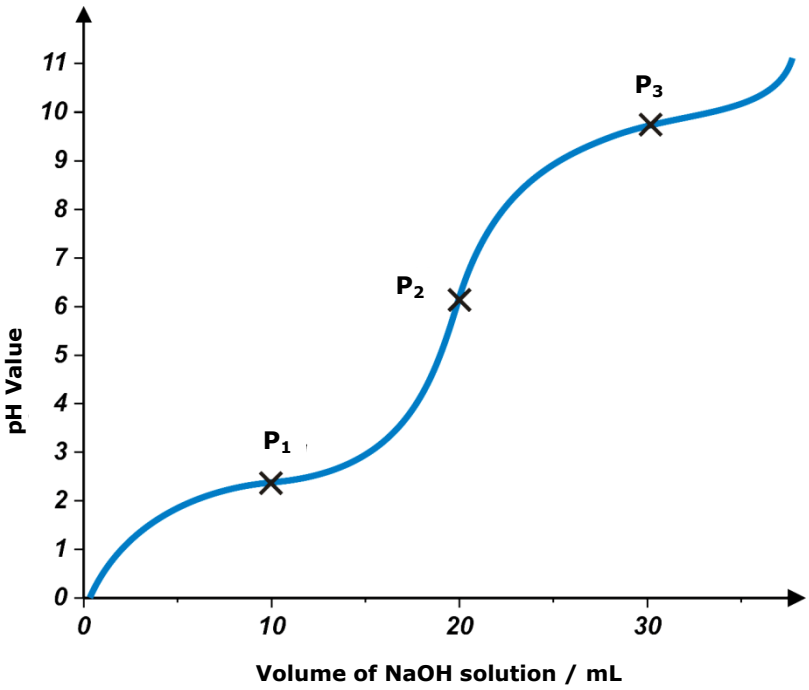
Iodine is an essential trace element for life. At high temperatures an equilibrium between $I_2(g)$ and I(g) establishes.
The following table summarizes the initial pressure of $I_2(g)$ and the total pressure when the equilibrium is reached at the given temperatures:

T in K	1073	1173
$p(I_2)_0$ in bar	0.0639	0.0693
p_{total} in bar	0.0760	0.0930

d) Calculate $\Delta H°$, $\Delta G°$ and $\Delta S°$ at 1100 K. Assume that $\Delta H°$ and $\Delta S°$ are independent of temperature with in the temperature range given in the table.

Problem 3-07 Properties of Aminoacetic Acid

Aminoacetic acid in an acidic solution is titrated with a solution of sodium hydroxide to give the following titration curve:



There are three inflection points: P_1 (pH = 2.35), P_2 (pH = 6.07) and P_3 (pH = 9.78).

a) *Which compound(s) is (are) existent at these inflection points? What is the ratio of the amount of the respective compounds if there is more than one?*

Acetic acid is a liquid while aminoacetic acid is a solid.

b) *Account for this difference.*

An aqueous solution of $NH_2CH_2CONHCH(CH_3)COOH$ is heated.

c) *Which compound(s) is (are) formed?*

d) *Show how you could prepare phenylalanine starting from 3-phenylpropanoic acid, ammonia and bromine (reaction equation).*

e) *Visualize the stereochemical situation of S-phenylalanine.*

Problem 3-08 Reaction Quiz

Complete the reaction equations below.

1. $HCHO + CH_3CHO \longrightarrow$

2. $(CH_3)_2C{=}CH_2 + Br_2 \longrightarrow$

3. $(CH_3)_2C{=}CH_2 + HBr \longrightarrow$

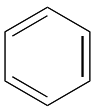
4. $(CH_3)_2C{=}CH_2 + KMnO_4 \xrightarrow{H_2O}$

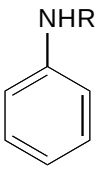
5. $(CH_3)_2C{=}CH_2 + O_3 \longrightarrow$

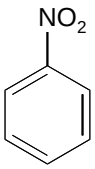
6. $CH_3CH_2C{\equiv}CH + H_2O \longrightarrow$

7. $CH_3CH_2CHO + LiH \longrightarrow$

8. $CH_3MgBr + C_2H_5COCH_3 \longrightarrow$

9.  $+ C_2H_5COCl \xrightarrow{Kat.}$

10.  $+ HNO_3 \xrightarrow{H_2SO_4}$

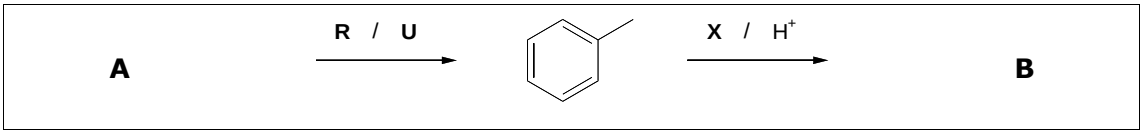
11.  $+ ClNHR \longrightarrow$

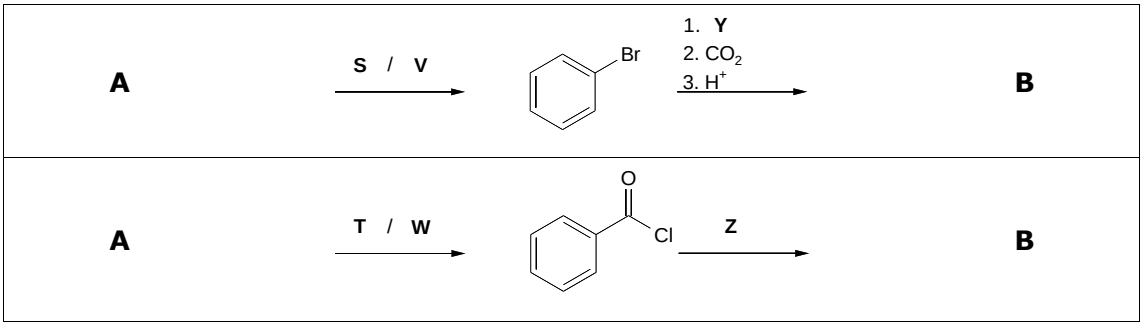
12. $H_2NCH(CH_3)COOH + H_2NCH_2COOH \longrightarrow$

Problem 3-09 A Versatile Organic Compound

Compound **A** is the prime example for an aromatic compound. While **A** is strongly carcinogen and thus should not be used in labs, some of the derivatives of this compound are less poisonous and often used. This problem deals with an acid **B** which is a derivative of **A**.

There are different ways to synthesize **B**:





*a) Draw the structural formulae of **A** and **B**. Propose suitable reagents **R**, **S**, **T**, **U**, **V**, **W**, **X**, **Y** and **Z** which could be used in the reactions above. Some compounds may appear repeatedly.*

b) Which of the three aromatic intermediates would you use taking into account ecological and economic reasons? Account for you decision considering dangerousness and availability of the intermediate and of the chemicals needed for the reaction.

Because of its many derivatives B has a large-scale importance. Some examples are given in the table below (M = Na or K, BnOH = Phenylmethanol)**:**

B		$MHCO_3$		**C**
B	$SOCl_2$	**I**	EtOH	**D**
			BnOH	**E**
			½ Na_2O_2	½ **F**

*c) Draw the structural formulae of the compounds **C**, **D**, **E*** and **F** and give their names. *Give an application for at least two of these compounds. Which compound represents **I**?*

Concern came up recently that **B** elicits hypersensitivity and that it is poisonous for cats and dogs even in small amounts. It is discussed whether the carcinogen **A** may form from **B** before **B** is catabolized by amino acetic acid to form hippuric acid, a peptide.

d) Draw the structural formula of hippuric acid. Mark the most acidic proton.

It is taken for granted that by using the radical initior **F** compound **A** and a derivative of **A** ($C_{12}H_{10}$) are found in plastic materials.

*e) Propose a mechanism for the decay of F to A. Which compound $C_{12}H_{10}$ can also form during the reaction of **F** to **A** (structural formula)?*

Third Round Test 2

Problem 3-11 Multiple Choice

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

a) Which of the following elements exists at 25 °C and 1 bar in several modifications?

A Bromine	**B** Argon	**C** Phosphor	**D** Nitrogen	**E** Sodium

b) Which pure substance is solid under standard conditions?

A Benzoic acid	**B** Bromine	**C** Acetic anhydride	**D** Gallium	**E** Palmitic acid

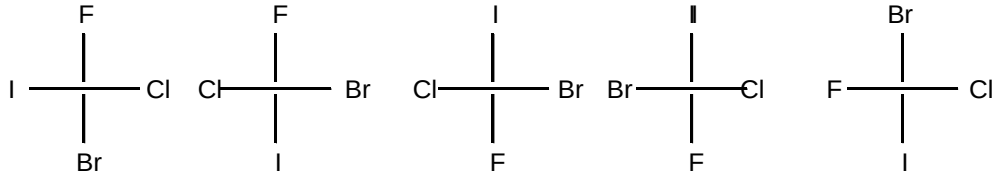
c) Which substances comproportionate in an acidified aqueous solution under standard conditions?

A Cr^{3+} and CrO_4^{2-}	**B** H_2S and H_2SO_4	**C** Ag and Ag^{2+}	**D** I^- and IO_3^-	**E** NO^{2-} and NO^{3-}

d) Which is the correct order for the standard potentials of Cu^{2+}/Cu, Fe^{3+}/Fe^{2+}, Zn^{2+}/Zn in acidic solution?

A $E(Cu^{2+}/Cu) > E(Fe^{3+}/Fe^{2+}) > E(Zn^{2+}/Zn)$	**B** $E(Cu^{2+}/Cu) > E(Zn^{2+}/Zn) > E(Fe^{3+}/Fe^{2+})$
C $E(Fe^{3+}/Fe^{2+}) > E(Zn^{2+}/Zn) > E(Cu^{2+}/Cu)$	**D** $E(Zn^{2+}/Zn) > E(Fe^{3+}/Fe^{2+}) > E(Cu^{2+}/Cu$
E $E(Fe^{3+}/Fe^{2+}) > E(Cu^{2+}/Cu) > E(Zn^{2+}/Zn))$	**F** $E(Zn^{2+}/Zn) > E(Cu^{2+}/Cu) > E(Fe^{3+}/Fe^{2+})$

e) Four of the following Fischer projections represent the same compound, one represents the enantiomer. Which one is it?



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

f) The basis of which of the following titration methods is not a redox reaction?

A Argento-metry	**B** Ceriometry	**C** Complexo-metry	**D** Iodometry	**E** Permangano-metry

g) Which of the following species has an unpaired electron?

A K_2MnO_4	**B** $[Ti(H_2O)_6]^{4+}$	**C** NO_2	**D** $[PdCl_4]^{2-}$	**E** BH_3

h) Which group contains no double bond?

A Acetyl group	**B** Alkyl group	**C** Allyl group	**D** Cyclohexyl group	**E** Vinyl group

Problem 3-12 Quantitative Analysis

A mixture of salts contained sodium carbonate, sodium oxalate and sodium chloride. A sample of 0.7371 g was dissolved in water. 20.0 mL of diluted hydrochloric acid (c = 0.2000 mol/L) were added, the obtained solution was boiled and after cooling down titrated with a solution of sodium hydroxide (c = 0.1016 mol/L). Consumption: 8.25 mL with phenolphthalein as indicator.

At 800 °C a second sample of 0.6481 g was annealed to constant weight. In doing so a poisonous gas evolved. The residue was dissolved in water, 50.0 mL of diluted hydrochloric acid (c = 0.2000 mol/L) were added. This solution, too, was annealed to constant weight and in the same way as above titrated with the solution of sodium hydroxide. Consumption: 14.70 mL.

Hint: Sodium carbonate free of water melts at 854 °C.

a) Write down the equations of the reactions of this analysis.

b) Calculate the percentage of the composition of the mixture.

Problem 3-13 Applications of the Nernst Equation

In one half cell of an electrochemical cell a silver electrode dips into a solution of silver nitrate with c($AgNO_3$) = 0.010 mol/L. In the second half cell a silver electrode dips into a silver nitrate solution, too, yet its concentration is unknown. The difference in potentials is 0.024 V at 298 K.
It is not said which electrode is the anode, which is the cathode.

a) Calculate the concentration of the silver nitrate solution in the second half cell.

Given are the standard potentials of the following half reactions:

$Sn^{2+} + 2\ e^- \longrightarrow Sn$ $\quad E°_1 = -0.14$ V

$Sn^{4+} + 2\ e^- \longrightarrow Sn^{2+}$ $\quad E°_2 = +0.15$ V

b) Determine the equilibrium constant for the reaction
$Sn(s) + Sn^{4+}(aq) \rightleftharpoons 2\ Sn^{2+}(aq)$.

Given are the standard potentials of the following half reactions:

$Hg_2^{2+} + 2\ e^- \longrightarrow 2\ Hg$ $\quad E°_3 = +0.79$ V

$Hg_2Cl_2 + 2\ e^- \longrightarrow 2\ Hg + 2\ Cl^-$ $\quad E°_4 = +0.27$ V

c) Calculate the solubility S (in mg/L) of Hg_2Cl_2 in water at 298 K. The mercury cation in the aqueous phase is Hg_2^{2+}.

You are given the following set of standard electrode potentials and half cell reactions of chlorine:

$E°(ClO_4^- + 8\ H^+ / Cl^- + 4\ H_2O) = 1.38$ V

$E°(ClO_3^- + 3\ H^+ / HClO_2 + H_2O) = 1.21$ V

$E°(HClO_2 + 2\ H^+ / HClO + H_2O) = 1.64$ V

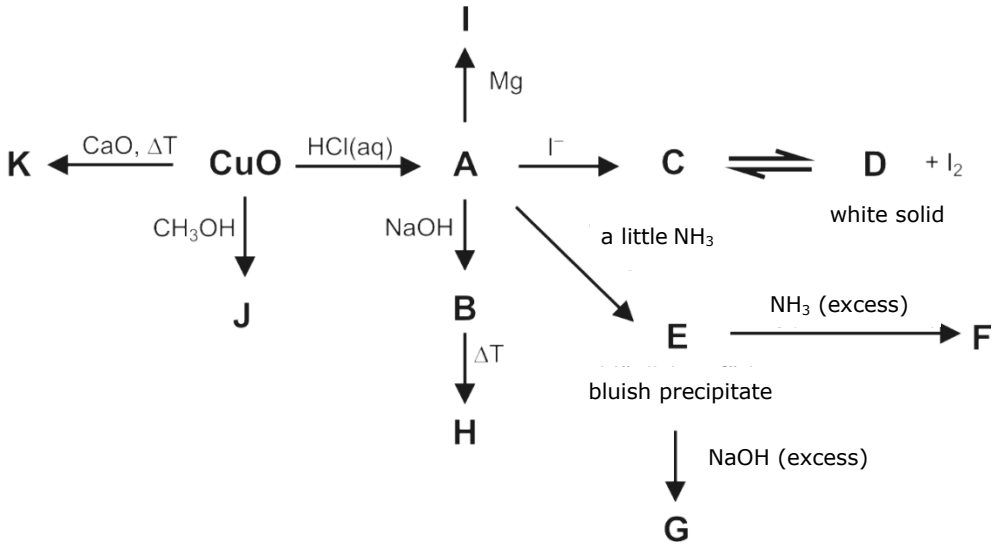
$E°(HClO + 1\ H^+ / ½\ Cl_2 + H_2O) = 1.63$ V

$E°(½\ Cl_2 / Cl^-) = 1{,}36$ V

d) Calculate the following potentials
$E°(ClO_4^- + 2\ H^+ / ClO_3^- + H_2O)$ and $E°(HClO_2 + 3\ H^+ / ½\ Cl_2 + 2\ H_2O)$.

Problem 3-14 Copper and Copper Compounds

Given the following scheme:



*a) Determine the copper containing species **A** to **K**! Write down all reaction equations.*

Copper(II) oxide can be used for the C,H,O-elementary analysis of organic compounds. Thereby a precisely weighed sample of the organic compound reacts with copper(II) oxide at high temperatures in a combustion train. In a school lab the gaseous products are channeled through two small tubes, one filled with calcium chloride, the other with sodium hydroxide. The change of mass of the two tubes is determined. Oxygen may be used as carrier gas.

b) Explain shortly how the C,H,O-elementary analysis works and what the function of the two tubes is. How are the amounts of carbon, hydrogen and oxygen found? Write down relevant reaction equations.

The copper containing compound X crystallizes with water of hydration. The elementary analysis gives 24.09 % mass of carbon and 4.04 % mass of hydrogen. The electrolysis of an aqueous solution of 1.256 g of X leads to an increase of 399.7 g of copper at a platinum electrode.

c) Determine the empirical formula of X.

Figure 1 shows the result of a thermogravimetric examination. The loss of mass of 9.1 % is due to the total loss of hydration water. X contains 1 mol of water per 1 mol of X.

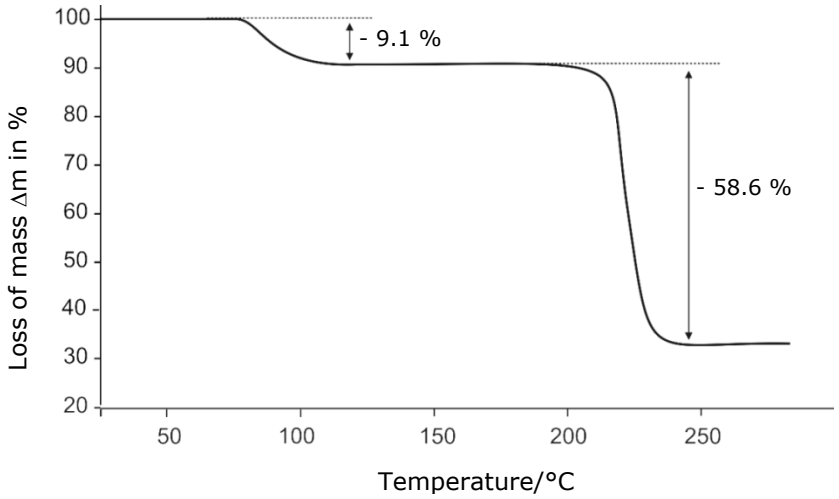


Fig. 1 Thermogravimetric Analysis of compound X.

(R., Musumeci, A., Spectrochimica Acta A: Molecular and Biomolecular Spectroscopy 67(1) (2007), 48-57)

d) Determine the molar mass and the molecular formula of X.

An IR spectrum (fig.2) is consulted to determine the compound X more precisely.

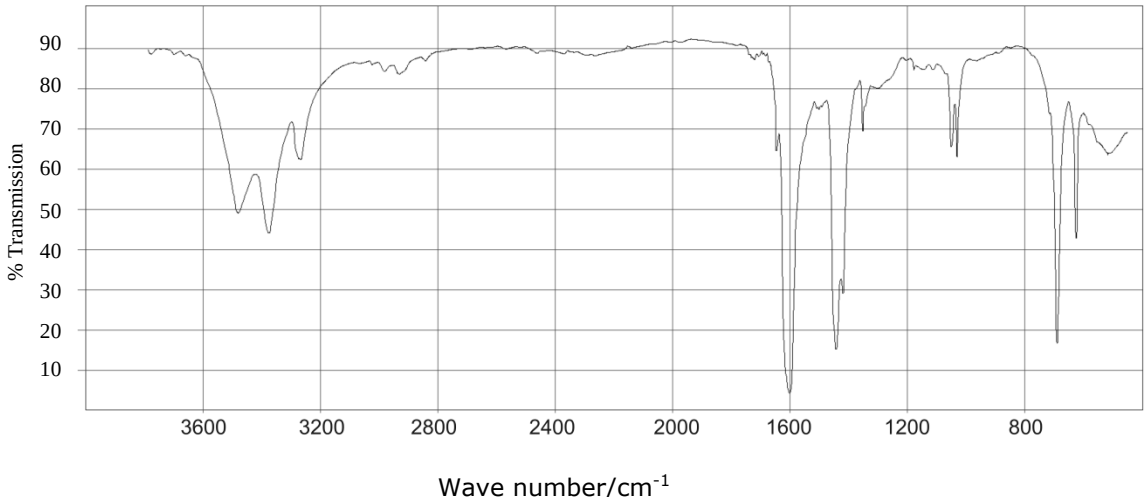


Fig. 2. IR spectrum of X (NIST Chemistry WebBook, http://webbook.nist.gov/chemistry)

(A table of vibrational frequencies of some functional groups is provided.)

e) Determine compound X and account for your decision.

There is a solid copper compound and you do not know the oxidation state.

f) Name a property (or properties) to be analyzed in order to find out the oxidation state of copper definitely. Account for your answer.

Problem 3-15 Oxides and Peroxides

When Carl Scheele in 1774 added sulfuric acid to pyrolusite, a modification of manganese dioxide, he obtained a gas A which turned out to be an element.

Fig 1[1] Pyrolusite

a) Give the name of A. Write the reaction equation for Scheele's experiment.

b) Why couldn't Scheele use hydrochloric acid to obtain A? Write a reaction equation.

Pyrolusite has a tetragonal structure (Fig.2) with a = b = 4.4 Å, c = 2.9 Å in its unit cell.

c) Calculate the density of pyrolusite.

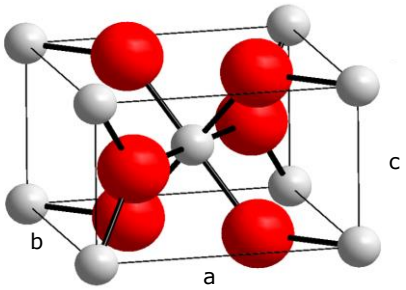


Fig. 2[2]

When element A appears in compound with cesium mass fraction is 19.39 %, in a compound with hydrogen 94.12 %.

d) Determine the empirical formulae of these compounds.

e) Write the equation for the reaction of the compounds described in d).

[1] From Wikipedia

[2] From Wikipedia

Sometimes you find the inscription "manganese peroxide" on containers with pyrolusite.

f) Is this a correct name?
Give exactly two other examples each of oxides and peroxides with the formula MO_2 (M = metal).

Problem 3-16 Kinetics, Historical and in General

Potassium permanganate is very popular as standard solution for redox titrations because of its oxidation power and of its low toxicity. In the quantitative analysis the complete reaction is crucial. The kinetic of the permanganate reaction was often investigated.
In 1904 Anton Skrabal published the article „Zur Kinetik der Reaktion von Kaliumpermanganat und Oxalsäure" in the „Zeitschrift für Anorganische Chemie" (About the kinetic of the reaction of potassium permanganate in the Journal for Inorganic Chemistry).
He writes in the introduction:
„The reaction of permanganate with oxalic acid proceeds in the following way: The first drops of the permanganate solution are very slowly consumed; then there is a period with a nearly immediate reaction and near to the end the process of decolourization is slowing down.
The retardation observed in the beginning cannot be found if some of the reaction product of manganous sulfate is added from the outset. [...] Because of the acceleration of the reaction by addition of manganous salt we can assume that there is an oxidation state between $Mn(OH)_2$ and $Mn(OH)_7$ which oxidizes the oxalic acid better than the highest one. [...] At first the manganate reacts with the manganous salt to form a manganic ion."
(Hint: The appendixes "*ous*" and "*ic*" indicate different oxidation states, "*ous*" stands for the lower, "*ic*" for the higher oxidation state. Scrabal assumed that the *ous*- and the *ic*-state differ only by exactly one oxidation number.)

a) Give the formula for manganous sulfate.

b) Write down the equation for the reaction of permanganate with oxalic acid in an acidic solution.

c) Write down the equation for the reaction of permanganate ions with manganous ions to form manganic ions. What is the name of this type of reaction?

The free manganic ion is not stable in water. It exists as a trioxalato complex in a great excess of oxalic-acid ions.

When the complex decomposes oxalate is oxidized to carbon dioxide and the manganic ions are reduced. For this decomposition Skrabal measured the following data amongst others:

t in min	0	9.0	18.0	25.0	32.0	44.0	50.0	56.0
c(complex) in mmol/L	20.07	15.30	11.70	9.51	7.74	5.34	4.47	3.74

d) This reaction cannot be of 0. order? Explain why.
Show that in the total interval of measuring the reaction is of 1. order and determine the rate constant k.

Skrabal made his experiments in the winter of 1903/1904. The data above were detected at 14 °C. At 30 °C the rate constant of the reaction is $k_{30°C} = 3.80 \cdot 10^{-3}\ s^{-1}$.

e) Calculate the activation energy of the decomposition reaction assuming that the activation energy and the pre-exponential factor A are independent of temperature.
(If you could not solve d) assume $k = 3.6 \cdot 10^{-2}$ min.)

f) Determine the half-life of the complex at 80 °C.
(If you could not solve e) assume $E_a = 92.0\ kJ \cdot mol^{-1}$.)

g) Give the reaction orders and the units of the rate constant of the reactions (i) to (iii) by using the units of concentration as „conc" and the units of time as „time".

(i) $C_{12}H_{22}O_{11} + H_2O \xrightarrow{(H_3O^+)} 2\ C_6H_{12}O_6$

$$v = -\frac{d[C_{12}H_{22}O_{11}]}{dt} = k_i \cdot c(C_{12}H_{22}O_{11}) \cdot c(H_3O^+)$$

(ii) $2\ NH_3(g) \xrightarrow{\text{at a wolfram suface}} N_2 + 3\ H_2$ $\quad v = -\frac{d[NH_3]}{dt} = k_{ii}$

(iii) $H_2 + Br_2 \longrightarrow 2\ HBr$ in the beginning is $\quad v = \frac{d[HBr]}{dt} = k_{iii} \cdot c(H_2) \cdot c(Br_2)^{1/2}$

h) Give equations for a uni- and a bimolecular reaction. Use A, B, ... for the reacting species.

For the reaction $A + B \longrightarrow X \longrightarrow C + D$ with the intermediate X, the reaction diagram at the end of problem 3-16 can be drawn.

i) What do the energetic values I to V represent in detail?

j) Given the following statements mark the correct ones:

i) The reaction order can be determined by measuring the half-life as a function of the concentrations of the reacting species.

ii) The reaction order can be determined by measuring the rate constant as a function of the concentration of the reacting species.

iii) The reaction order can be determined by measuring the rate constant as a function of temperature.

iv) In a reaction of 1. order the half-life is independent of the concentrations of the reacting species.

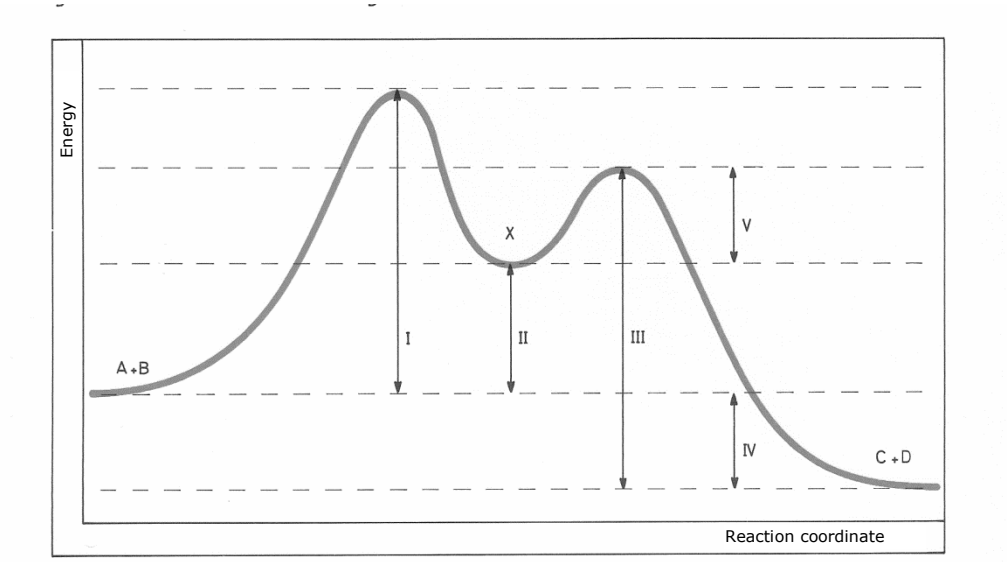
v) In a reaction of 2. order the half-life is dependent of temperature.

vi) In a reaction of 1. order the rate constant is independent of the concentrations of the reacting species.

vii) In a reaction of 1. order the rate constant is independent of temperature.

viii) In a reaction of 2. order the rate constant is dependent of temperature.

Diagram to part i) and j)

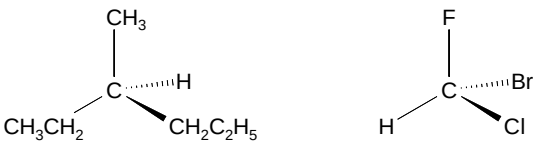


Problem 3-17 Stereoisomerism

Stereoisomeric compounds can be named unambiguously by using the R/S convention (Cahn, Ingold, Prelog 1951).

The method used employs sequence rules to the four substituents directly attached to the stereogenic center. These sequence rules are based on the atomic number of these and more outward atoms.

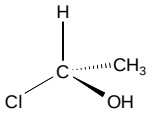
The following two compounds have the R configuration:



a) Assign priorities to the substituents. Explain how you then find the R conformation.

b) Assign R or S to the following compound:

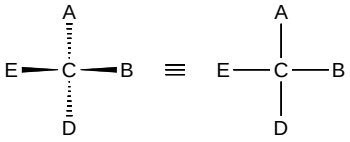
i)

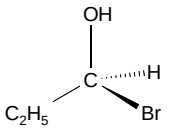
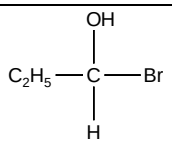
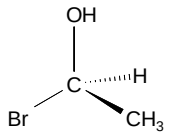
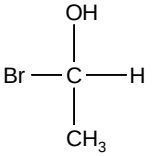
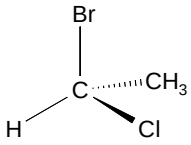
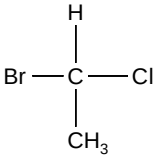


ii) Exchange in the molecule above the substituents Hydrogen and CH_3. Which confirmation do you get?

iii) Exchange in the molecule of ii) OH and CH_3. Which confirmation do you get?

Another good possibility to draw the structure of stereochemical compounds unambiguously is the "Fischer Projection". The correlation between a 3D image and a Fischer projection is shown in the image below:



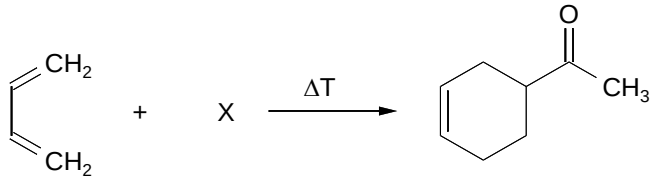
Pair 1		
Pair 2		
Pair 3		

c) Do the 3D image and the Fischer projection show identical ore different confirmations?

If they are different write down the kind of stereoisomerism.

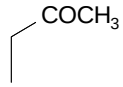
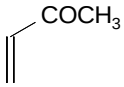
Problem 3-18 Cycloaddition Reactions

The following is typical for a cycloaddition reaction:

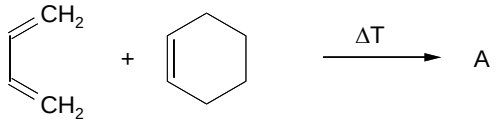


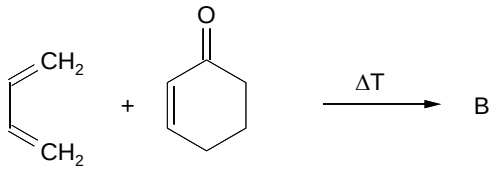
1,3-Butadiene Product

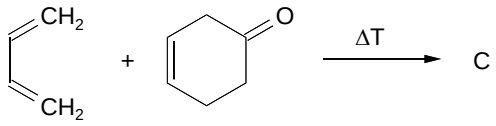
a) Chose compound X from the given compounds 1 to 3 so that it leads in the reaction above to the given product. Name the product.

Compound 1	Compound 2	Compound 3
		

b) Which products would you expect to obtain from the following reactions? Write down the structural formulae.







c) Which of the three compounds which react with 1,3-butadiene is the most reactive? Account for your decision.

d) What is the product of the addition reaction of two molecules of 1,3-cyclopentadiene (C_5H_6)?

1,3-Butadiene reacts with maleic acid diethylester as well as with fumaric acid diethyl-ester. Both, maleic acid and fumaric acid are dicarboxylic acids. They have the same empirical formulae ($C_4H_4O_4$) and differ only in their configuration.

e) Write the equations for both reactions. Draw 3-D structures of both products.

(Hint: ◀ in front of the paper plane ⁞⁞⁞ behind the paper plane)

Problem 3-19 Pyrrole: Properties and Structure

Pyrrole (C_4H_5N) is an unsaturated compound with a ring shaped structure. It is found in small amounts in coal tar and liquid at room temperature. Although pyrrole appears to be both an amine and an unsaturated carbon hydrate its chemical properties are not

consistent with either of these structural features. On the other hand pyrrole easily undergoes electrophilic substitution.

a) Draw the structural formula of pyrrole.

b) Sketch the structural formula of the pyrrole ring including the p_z orbitals. Mark the number of π electrons in each p_z orbital using dots. Explain why pyrrole does not have the properties of an amine and of an unsaturated carbon hydrate.

Pyrrole reacts with nitric acid to form 2-nitropyrrole with a yield of more than 80%.

*c) Determine, **X**, **Y** and **Z** in the following reaction scheme:*

$$HNO_3 + H_2SO_4\,(konz) \longrightarrow \mathbf{X} + H_2O + HSO_4^-$$

$$\text{Pyrrol} + \mathbf{X} \longrightarrow [\ \mathbf{Y}\ ] \xrightarrow{H_2O} \text{2-Nitropyrrol} + \mathbf{Z}$$

*d) Account for the high yield by drawing the resonance forms of the intermediate **Y**. For comparison draw possible resonance forms of the intermediate of the reaction to form 3-nitropyrrole.*

Pyrrole has a dipole moment.

e) Mark the positive and the negative side of the dipole. Account for your decision by drawing the resonance forms of pyrrole.

Fourth Round (theoretical problems)

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

Problem 4-01 Dissolving Silver and Gold

Silver can be dissolved in concentrated nitric acid forming NO.

a) Write down a balanced equation for this reaction. Use only species which are mentioned in the table below.

b) Show that this reaction under standard conditions is thermodynamically possible using the data from the table below.

c) Show that gold cannot be dissolved in this way. Use the value -45 kJ/mol as the result of b).

Standard values at 298 K

	$\Delta H°_f$ in kJ/mol	S° in $JK^{-1}mol^{-1}$	$\Delta G°_f$ in kJ/mol
Ag(s)		42.7	
$Ag^+(aq)$	105.9		77.1
N_2		191.5	
$NO_3^-(aq)$	-206.6		-110.5
NO(g)	90.3	210.6	
$H_2(g)$		130.6	
$O_2(g)$		205.0	
$H^+(aq)$	0		0
$H_2O(l)$	-285.9	69.9	

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

$E°(Au^{3+} + 3\ e^- \longrightarrow Au) = 1.42$ V

Problem 4-02 Kinetics[3]

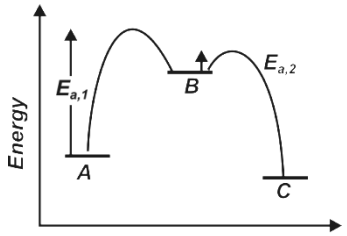
There are two consecutive reactions of first order given with their rate constants.

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C\ .$$

Under certain conditions you may use the method of the steady state approximation to work out the overall rate of the reaction $A \longrightarrow C$.

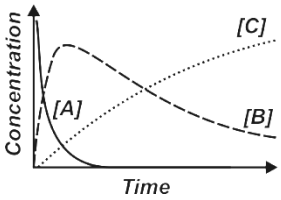
The following figure shows the typical energy profile of a reaction to which the steady state approximation will apply:

[3] All plots of the following page from Keeler, Wothers, Chemical Structure and Reactivity, Oxford 2008

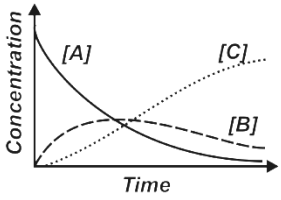


The three plots below show typical variations in the concentrations of A, B and C:

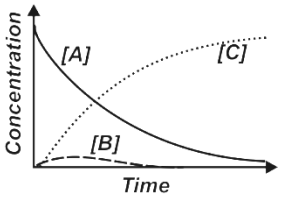
i)



ii)



iii)



a) Which of them matches the energy profile above? Give a short explanation.

A possible ion–molecule reaction mechanism for the synthesis of ammonia in interstellar gas clouds is shown below

$$N^+ + H_2 \longrightarrow NH^+ + H \qquad k_1$$
$$NH^+ + H_2 \longrightarrow NH_2^+ + H \qquad k_2$$
$$NH_2^+ + H_2 \longrightarrow NH_3^+ + H \qquad k_3$$
$$NH_3^+ + H_2 \longrightarrow NH_4^+ + H \qquad k_4$$
$$NH_4^+ + e^- \longrightarrow NH_3 + H \qquad k_5$$
$$NH_4^+ + e^- \longrightarrow NH_2 + 2H \qquad k_6$$

b) Use the steady state approximation to derive equations for the concentrations of the intermediates NH^+, NH_2^+, NH_3^+ and NH_4^+ in terms of the reactant concentrations $[N^+]$, $[H_2]$ and $[e^-]$. Treat the electrons as you would any other reactant.

c) Determine the rate law for the production of NH_3 as a function of $[N^+]$ and $[H_2]$. Give an expression for the overall rate constant k in terms of the rate constants for the elementary steps, k_1 to k_6.

Under acid conditions and in aqueous solution methanoic acid is oxidized by bromine:

$$HCOOH + Br_2 + 2\ H_2O \longrightarrow CO_2 + 2\ Br^- + 2\ H_3O^+$$

The experimental determined rate law is $v = k_{obs} \cdot \frac{[Br_2] \cdot [HCOOH]}{[H_3O^+]}$.

d) Find a simple two step mechanism for this reaction and show how this rate law comes about from this reaction mechanism.
(Hint: The first step could be a fast equilibrium; the second step is very slow.)

Problem 4-03 The Chemical Chameleon

Manganese exhibits all oxidation states from +II to +VII and shows a lot of redox reactions.

Due to their characteristic colour (Tab. 1) manganese compounds are often used in qualitative and quantitative analysis. However, the stability of the ions varies strongly.

Tab.1: Colours of manganese in different oxidation states. The colours may vary with different ligands.

Oxidation state	Mn (VII)	Mn (VI)	Mn (V)	Mn (IV)	Mn (III)	Mn (II)
Colour	purple	green	blue	brown	strong purple-red	pink

a) Write down the electron configuration of manganese in the electron ground state.

b) Which is the most stable oxidation state of manganese? Account for your answer!

Oxidation reactions with permanganate are very important in the quantitative analysis. They are based on the great oxidation power of the permanganate anion MnO_4^-, which depends strongly on the pH value.

c) Write down equations of reduction reactions of permanganate anions in
i) acidic ii) neutral iii) basic solutions.
(Include electrons in your equations e.g. $Cl_2 + 2\ e^- \rightleftharpoons 2\ Cl^-$)

Iron in acidic solution is titrated with potassium permanganate solution.

d) In which oxidation state should iron be? Which acid should be used to acidify the iron solution? Account for your decision.

e) How do you realize the endpoint of the titration?

A good preliminary test for manganese is the reaction with oxidizing agents. The sample is triturated with a 3 to 6-fold amount of a mixture of equal parts of potassium nitrate and sodium carbonate and then heated to redness in a magnesia trough. In the presence of manganese a dark green colour of the product can be observed. If it is dissolved in water and acidified the colour changes to red violet and a brown precipitate forms.

f) Write down equations of all described reactions of this preliminary test and in the solution. Start with $MnSO_4$.

In the qualitative separation scheme of cations manganese precipitates in the ammonium sulfide group as pink manganese(II) sulfide.

(Saturation concentration of H_2S in water: $c_{total}(H_2S)$ = 0.1 mol/L; residual concentration of manganese(II) after the quantitative precipitation $c_{res} = 10^{-5}$ mol/L;
($K_{a1}(H_2S) = 10^{-6.9}$, $K_{a2}(H_2S) = 10^{-12.9}$, $K_{sp}(MnS) = 10^{-13}$)

g) As of which pH manganese cations can be precipitated as manganese sulfide in a saturated hydrogen sulfide solution?

If an aqueous solution of manganese(II) cations is treated with a solution of sodium hydroxide a beige white precipitate forms which when exposed to air becomes gradually brownish. If this brownish precipitate is dissolved in conc. sulfuric acid or in conc. phosphoric acid a strong purple-red solution forms.

h) Write down an equation for the precipitation and the following reaction(s).

i) Which product(s) do you expect when an aqueous solution of manganese(II) cations is treated with a solution of ammonia?

Manganese forms four tetraoxomanganese ions MnO_4^{n-} in different oxidation states.

j) Write down the empirical formulae, apply the particular oxidation states und the names. Don't use the name "manganate" with the appropriate oxidation state but give the chemical name (as sulfite instead of sulfate(IV)).

The reaction of potassium permanganate with sodium sulfite in a strongly basic solution which is cooled with ice gives a sodium tetraoxomanganate X. After recrystallization a solid, $4X \cdot NaOH \cdot 48\ H_2O$, with a manganese content of 13.3 % of mass forms.
This solid is stable below 0 °C only if it does not come into contact with water and carbon dioxide. If a solution of the solid in a concentrated solution of potassium hydroxide is heated or if such a solution is diluted the solution turns green and a brown solid precipitates.

k) Which is the empirical formula of X? Which colour of X do you expect?

l) What happens if the solution of X in a solution of potassium hydroxide is diluted? Give the reaction equation.

Problem 4-04 Complex Compounds

Among the complex compounds aqua complexes with water as ligand form a very large group. These complexes form as soon as metal salts dissolve in water.
An aqueous solution of chrome alum ($KCr(SO_4)_2 \cdot 12\ H_2O$), a double salt, react strongly acidic (pH = 3).

a) Write a reaction equation which explains the acidic reaction of chrome alum!

b) Write equations for the following reactions:

To an aqueous solution of chrome alum *the following solutions are added*

i) barium chloride solution,

ii) sodium perchlorate solution,

iii) sodium hydroxide solution.

Chromium(III) chloride hexahydrate ($CrCl_3 \cdot 6\ H_2O$) dissolves in water to from a dark-green solution. Waiting for some time the colour becomes first of all brighter and then changes to violet. If the violet solution is heated the colour changes back to dark green. When cooled down the colour changes within some weeks to violet again. There is no redox reaction.

c) Explain this colour change by reaction equations.

You find another colour change when a solution of cobalt(II) chloride hexahydrate ($CoCl_2 \cdot 6\ H_2O$) is heated. The change goes reversibly from pink to blue.

d) Write a reaction equation which accounts for this change.

Ammonia, too, may act as complex ligand. Such compounds are called ammine complexes or ammoniates.

e) Write equations for the following reactions:
To an aqueous solution of cobalt(III) chloride hexaammoniate ($CoCl_3 \cdot 6\ NH_3$) the following solutions are added

i) silver nitrate solution,

ii) sodium hydroxide solution.

The molar electrolytic conductivity of aqueous solutions of $CoCl_3 \cdot (NH_3)_5$, $CoCl_3 \cdot (NH_3)_5 \cdot H_2O$ and $CoCl_3 \cdot (NH_3)_6$ is detected. One of them shows a conductivity of 475, the second of 357 and the third of 232 $S \cdot cm^2 \cdot mol^{-1}$.

f) Which complex should have the smallest conductivity in an aqueous solution? Account for your decision. Assume that at the time of measure no exchange of ligands has taken place.

An aqueous solution of cobalt(III) nitrite triammoniate ($Co(NO_2)_3 \cdot 3\ NH_3$) shows nearly no conductivity.

g) Why? Draw all structural isomers of this compound!

Problem 4-05 Condensation Reactions

In condensation reactions two species react to form a new one by splitting off water.

In most cases these reactions are reversible. The position of the equilibrium is influenced by all sorts of factors. For example, in the chromate-dichromate equilibrium the pH value plays a decisive role.

a) *Write down the reaction equation of the chromate/dichromate equilibrium. Which species is predominant in acidic which one in basic solution? Through which intermediate stage does the condensation proceed? Draw a reaction equation with structural formulae which visualizes the condensation.*

The production of silicones is based on condensation reactions, too. Reactants are chloromethane (CH_3Cl) and silicon, which react at high temperatures using a copper catalyzer. Besides about 3 to 4 % of $(CH_3)HSiCl_2$ three more main products A, B and C form. These can be used as reactants to form silicones.

b) *Give the name of the three main products A, B and C and write down the reaction equations of their formation.*

Methyl chlorosilanes react with water to from silanols which then may condense to polysiloxanes (silicones).

c) *Write down equations for the reactions of A, B and C with water. Why do they react almost quantitatively?*

d) *In which of these reactions should no polymer be formed? In which reaction is the highest degree of cross linking possible?*

Looking at phosphoric acids there are a lot of polyphosphoric acids (e.g. $H_{n+2}P_nO_{3n+1}$, $H_nP_nO_{3n}$) which are generated by condensation reactions of phosphoric acids.
They can be distinguished by potentiometric titration with sodium hydroxide solution using a pH electrode.

e) *Explain why such a distinction of $H_5P_3O_{10}$, $H_6P_4O_{13}$ and $H_3P_3O_9$ is possible using the structural formulae of these compounds.*

The formation of anhydrides can be considered as condensation reactions, too.
By dehydration of sulfuric acid with phosphorus pentaoxide or heating of sodium hydrogensulfate the anhydride of sulfuric acid, a white solid, forms.

f) *Write the empirical formula of the white solid. Draw one structural formula of it.*

A lot of metals form polynuclear complexes in aqueous solutions (i.e. complexes with more than one metal center) the formation of which is influenced by the pH value.
Sn(II) oxide is amphoteric and dissolves in aqueous solutions of acids and alkalis forming different complex ions. An important complex is $[Sn(OH)_3]^-$.

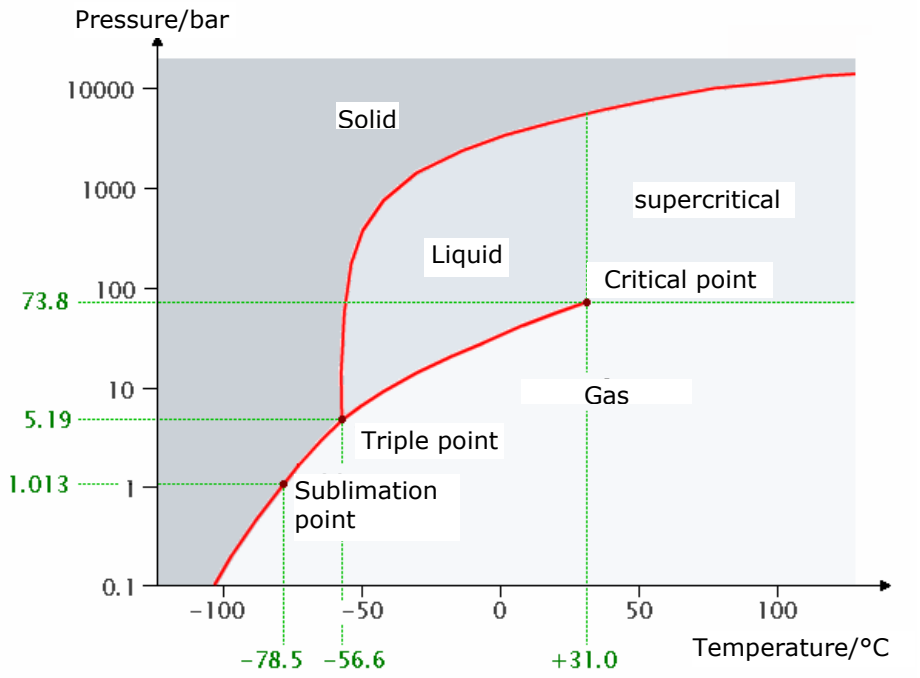
g) *Draw the Lewis structure of $[Sn(OH)_3]^-$ and determine the 3-D shape of the molecule using the VSEPR model. Write the equation of a reaction of $[Sn(OH)_3]^-$ to form a polynuclear Sn(II) complex.*

Condensation reactions are not always combined with the elimination of water, hydrogen sulfide can be eliminated, too.

h) *Which hydrogen contending arsenic sulfide compound generates arsenic(III) and arsenic(V) sulfide in a "hydrogen sulfide condensation"? Write down the reaction equations.*

Problem 4-06 Phase Diagrams

The following picture shows the phase diagram of carbon dioxide.



a) *What would happen with CO_2 gas if the pressure is gradually increased from 0.5 to 9000 bar at a temperature of -80 °C/0 °C/100 °C?*

b) *In which way is it possible to get liquid carbon dioxide under normal pressure (1,013 bar)?*

You may buy CO_2 in steel gas bottles which are able to sustain more than 100 bar. These bottles are filled with an utmost amount of carbon dioxide.

c) *In which state does CO_2 exist inside these bottles?*

Estimate the pressure inside these bottles immediately after filling using the diagram (at 25 °C). Note that the vertical axis is logarithmical.
How can you ascertain how much carbon dioxide is left in the bottle before it must be refilled?

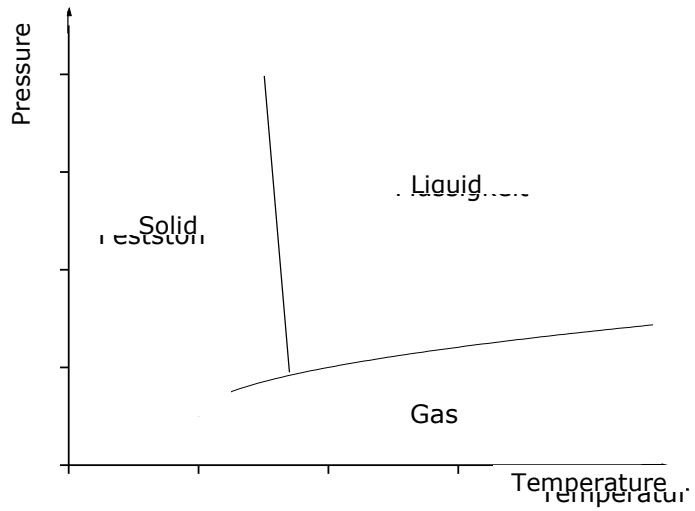
There are formulae in the collection at the beginning of the test which apply for the phase transitions of pure substances. In these equations you find expressions like $\frac{\mathrm{dp}}{\mathrm{dT}}$ and $\frac{\mathrm{d\ ln\ p}}{\mathrm{dT}}$, ΔH (molar enthalpy of the phase transition) and ΔV (difference in molar volume of the two phases).

d) Specify the relevance of the expression $\frac{dp}{dT}$ in a phase diagram.

The molar volume of a solid substance is 161.0 cm^3/mol at 1.013 bar and the melting point, 350.75 K. The molar volume of the liquid at this temperature and pressure is 163.3 cm^3/mol.
Under a pressure of 101.3 bar the freezing point changes to 351.26 K.

e) Calculate the molar enthalpy of fusion for the substance.

The following phase diagram is a little bit unusual.



f) With the help of the Clapeyron equation compare the densities of the fluid and the solid. Determine which one is smaller.

Problem 4-07 Thermodynamics in Biochemistry

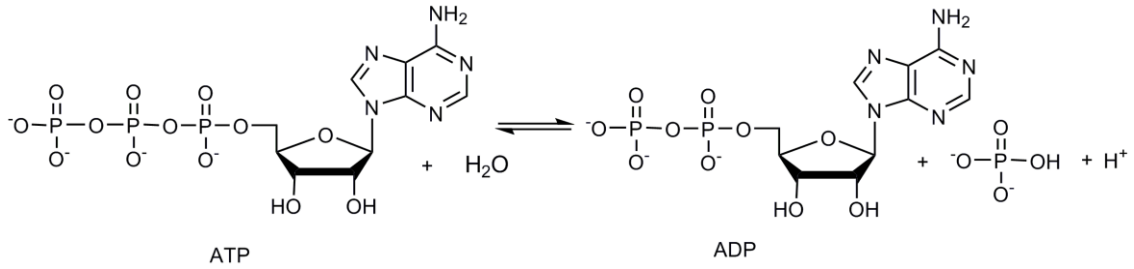
In most living cells the pH is nearly 7. In order to simplify calculations for biochemical reactions E°, K and $\Delta G°$ refer to pH = 7 and are denoted as E°', K' and $\Delta G°'$.
In equations with $\Delta G°'$ and K' for reactions at pH=7 the concentration of H^+ is therefore omitted.
The values of E° for two reactions involved in photosynthesis are

(i) $NADP^+ + H^+ + 2\ e^- \longrightarrow NADPH$ E° = -0.11 V

and (ii) $O_2 + 4\ H^+ + 4\ e^- \longrightarrow 2\ H_2O$ E° = +1.23 V.

a) Calculate the biochemical redox potential E°' for these two half-reactions.

Cells use adenosine triphosphate (ATP) as the molecular energy currency. The hydrolysis of ATP to adenosine diphosphate (ADP) is often coupled with other chemical reactions.



Biochemistry textbooks often represent this reaction as

$ATP + H_2O \rightleftharpoons ADP + P_i + H^+$ $\Delta G°' = -30.5\ kJ\ mol^{-1}$ (1)

Animals use free energy from the oxidation of their food to maintain concentrations of ATP, ADP, and phosphate far from equilibrium. In red blood cells the following concentrations have been measured:

c(ATP) = 2.25 mmol L^{-1}
c(ADP) = 0.25 mmol L^{-1}
$c(P_i)$ = 1.65 mmol L^{-1}.

b) Calculate the actual $\Delta G'$ of reaction (1) in the red blood cell at 25 °C and pH = 7.

In living cells many so-called "anabolic" reactions take place, which are at first sight thermodynamically unfavorable because of a positive ΔG. The phosphorylation of glucose is an example:

glucose + $HPO_4^{2-} \rightleftharpoons$ glucose 6-phosphate^{2-} + H_2O $\Delta G°' = +13.8$ kJ mol-1 (2)

c) Calculate first the equilibrium constant K_2' of reaction (2) and then the ratio c(glucose 6-phosphate^{2-})/c(glucose) in the red blood cell in chemical equilibrium at 25 °C and pH = 7.

To shift the equilibrium to a higher concentration of glucose 6-phosphate, reaction (2) is coupled with the hydrolysis of ATP:

$$\text{glucose} + \text{ATP}^{4-} \overset{\text{hexokinase}}{\rightleftarrows} \text{glucose 6-phosphate}^{2-} + \text{ADP}^{3-} + \text{H}^{+} \qquad (3)$$

d) Calculate $\Delta G°'$ and K_3' of reaction (3).
What is now the ratio c(glucose 6-phosphate^{2-}) / c(glucose) in the red blood cell in chemical equilibrium at 25 °C and pH = 7?

Light reactions in green plants lead to the oxidation of water and the reduction of $NADP^+$ to give NADPH as well as to the formation of ATP from ADP and P_i. Thereby the formation of 1 mol of NADPH and the oxidation of 1 mol of water is coupled with the formation of 1 mol of ATP.

e) Calculate the Gibbs energy of the overall reaction. What is the relation between $\Delta G°$ and $\Delta G°'$? Account for your statement.

The production of 1 mol of glucose in the photosynthesis apparatus requires about 8800 kJ.

f) How many photons (according to the longwave absorption peak of chlorophyll at 680 nm) are then required to form one molecule of glucose?

Problem 4-08 Reactions of Heterocycles

Pyridine (C_5H_5N) may be obtained from coal tar. It shows aromatic properties. Pyridine has a substantial dipole moment (μ = 2.26 D).

a) Draw a three-dimensional image of pyridine which shows the position of the π electrons and of the free electron pair. In which hybrid orbital is the lone electron pair located?
Account for the aromaticity of pyridine and the basic reaction using your image.
Indicate the negative end of the dipole and account for your decision.

Pyridine reacts with fuming sulfuric acid (oleum) forming a compound with low yield. Other reactions for example with bromine or nitric acid give even a lower yield.

b) Write the equation for the reaction of pyridine with sulfuric acid and name the product. Which type of reaction takes place?

c) Draw an image of the intermediate carbocation structure in 2-position as well as in 3-position. Which product (C2 or C3) provides a higher yield? Account for your decision.

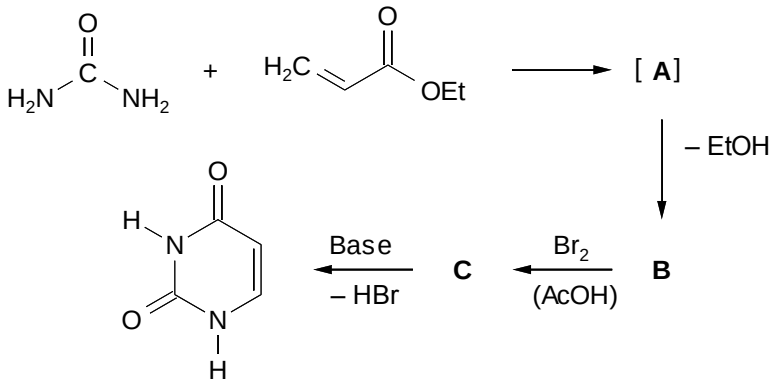
2-Chloropyridine reacts with sodium ethanolate (in anhydrous ethanol) to form 2-Ethoxypyridine in high yield.

d) Write the reaction equation. What is the name of the type of this reaction?

The two reactions in b) and d) show a great difference if they are performed with pyridine or benzene.

e) Give the difference in reactivity and yield and explain this difference by using the models of electron structure of pyridine and benzene.

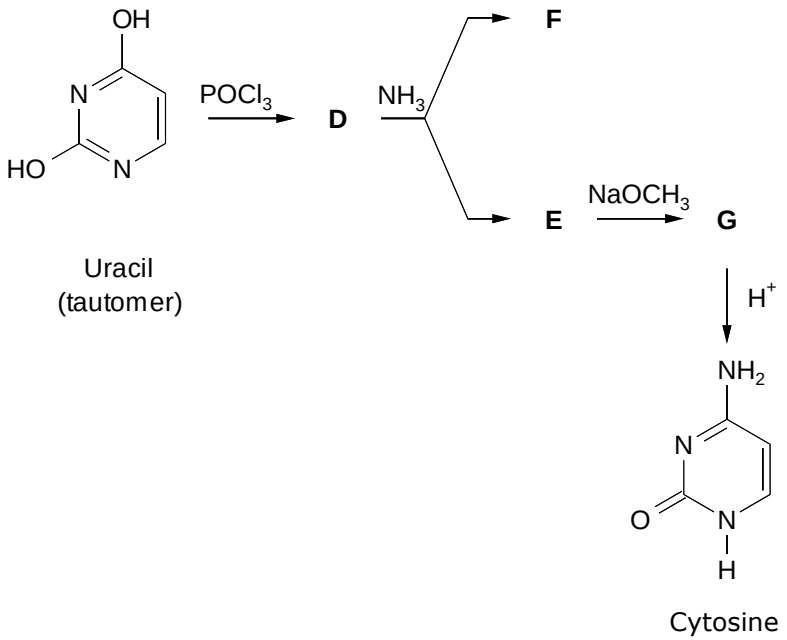
The formation of the heterocycles uracil and cytosine are illustrated by the following (unbalanced) reaction schemes.
Formation of uracil:



Uracil

*f) Draw the structural formulae of the compounds **A**, **B** and **C**.*

Formation of cytosine:



Uracil
(tautomer)

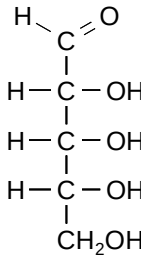
Cytosine

Remark: Reaction of uracil with $POCl_3$ in the ratio 1:2
Reaction of **D** with NH_3 in the ratio 1:1.

*g) Draw the structural formulae of the compounds of **D** to **G**.*

The smallest unit in the DNA is called nucleotide. It consists of a phophate residue, a sugar (ribose) and a heterocyclic base. In the DNA the sugar is found as 2-deoxyribose (as hemiacetal).
(See hints in problem 4-10, too.)

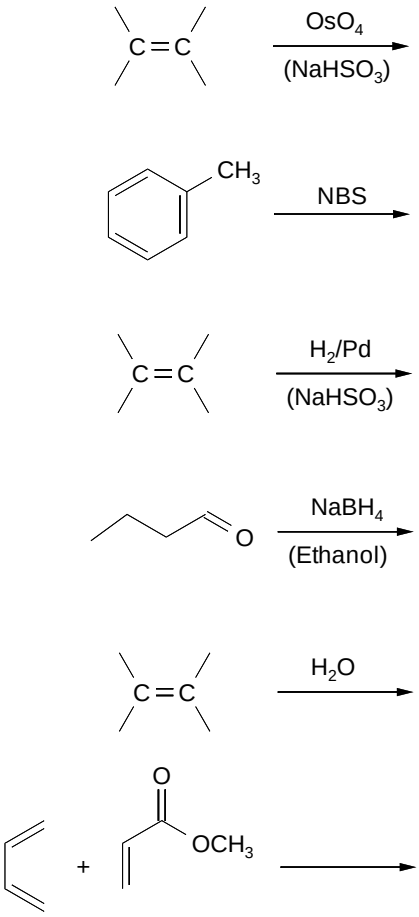
Structural formula of D-Ribose:



h) Draw the structural formula of a nucleotide consisting of a phosphate residue, a sugar (2-deoxyribose) and a heterocyclic base.

Problem 4-09 Redox Reactions

a) Complete the reaction schemes below. Determine whether each of these reactions is an oxidation, a reduction, or neither. (Don't take stereochemical aspects into account.)



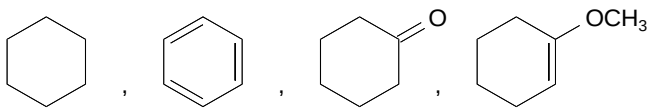
You may attach oxidation numbers to the C atoms of organic compounds, yet there are different systems.

In one of these systems, which includes the neighbor atoms and their bond orders, you get the following values.

Oxidation number of the C atoms	-IV	-II	-II	+II	+IV
Examples	CH_4	$H_2C{=}CH_2$	CH_3OH,	$HC{\equiv}N$	CO_2

b) Rank the compounds in the rows i), ii) and iii) in order of increasing oxidation level. If there are several differently substituted C atoms in a molecule take only those into account which bind to other atoms than carbon and hydrogen, too.

i) $H_2C{=}O$, CH_3OH, CO_2, HCO_2H

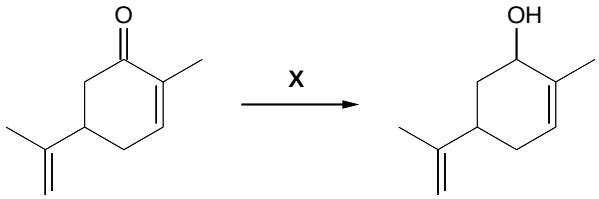
ii) 

iii) CH_3CN, $CH_3CH_2NH_2$, $NH_2CH_2CH_2NH_2$

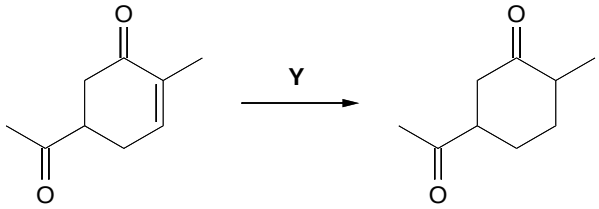
Some of the reducing agents reduce functional groups very electively.

c) Which reducing agent would you choose for the reactions i) and ii), respectively?

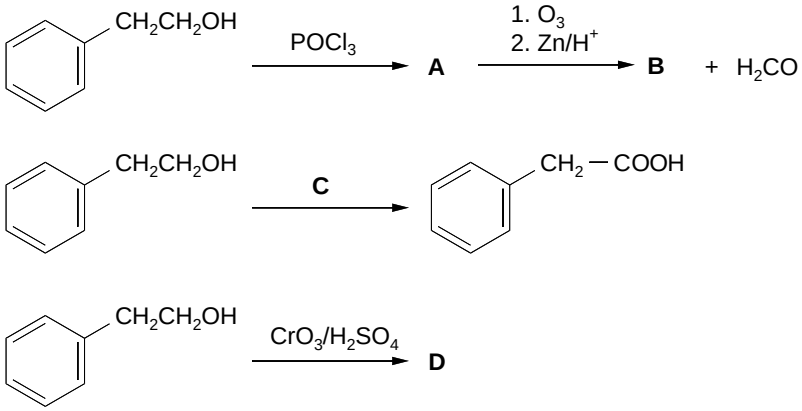
i)



ii)



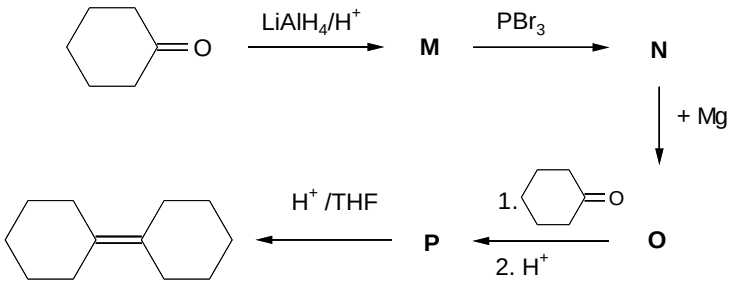
d) Complete the missing compounds A, B, C and D in the following reactions!



Trans-4-tert-butylcyclohexanol and cis-4-tert-butylcyclohexanol, respectively, are mixed with CrO_3 / H_2SO_4 ("Jones reagent").

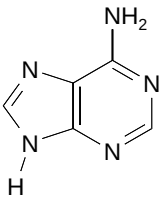
e) Which compound(s) forms (form)? Draw the most stable conformation of the reactants and of the products.

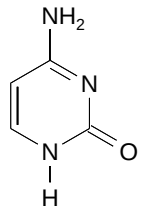
f) Complete the structural formulae of the missing compounds M, N, O and P in the following reaction scheme.

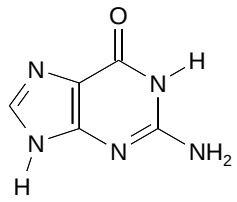


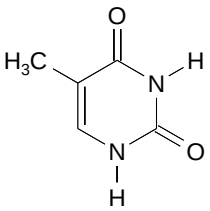
Problem 4-10 DNA, RNA and Amino Acids

The two strands in the DNA structure are held together by hydrogen bonds between specific bases. These heterocyclic bases are:


Adenine (A)


Cytosine (C)


Guanine (G)


Thymine (G)

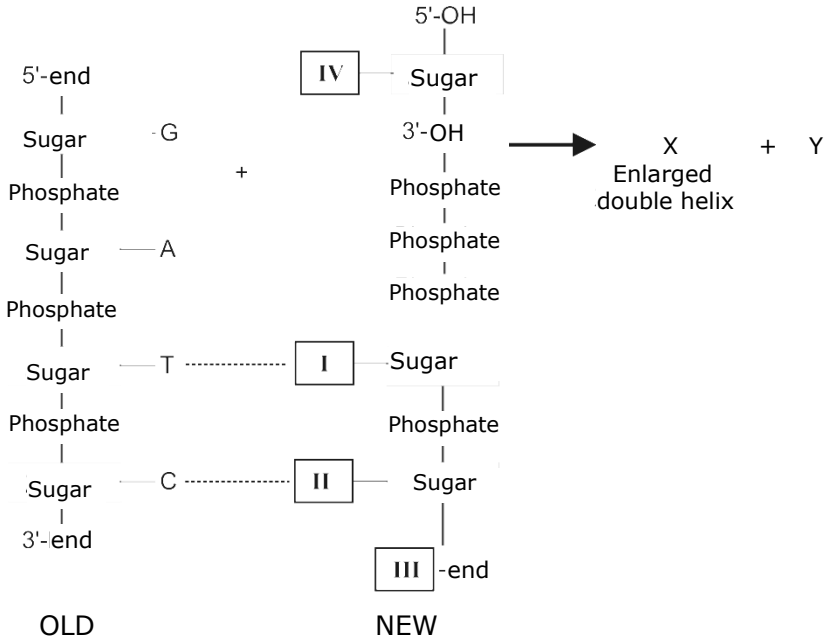
a) Which pairs of bases hold the strands of the double helix together? Insert the relevant hydrogen bonds (---) between the concerning pairs of bases.

There are three fundamental processes which are controlled by the DNA:

- DNA Replication
- DNA Transcription to RNA
- RNA Translation to synthesize proteins.

The first step of the DNA replication is the breaking of the hydrogen bonds between the strands. As the strands separate bases are exposed, new nucleotides line up on each strand in a complimentary manner and two new strands begin to grow. The process is catalyzed by DNA polymerase.

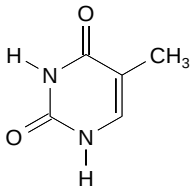
b) Complete the following scheme of a replication of DNA by inserting the relevant bases and the kind of the end, respectively, into the boxes. Insert the given nucleoside triphosphate. Draw the structural formulae of X and Y.



The transcription of DNA leads to RNA which is structurally similar to DNA but contains ribose rather than deoxyribose and uracil (U) rather than thymine (T).

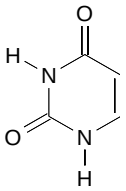
The image shows part of one strand of an unwinded DNA:

DNA:

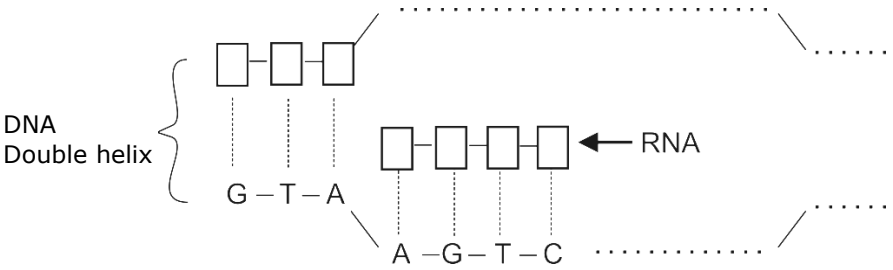


Thymine (G)

RNA:



Uracil (U)



c) Insert the relevant bases into the boxes.

d) Draw the structural formula of the RNA nucleotide with uracil.

e) Characterize the extension of a peptide by the amino acid aspartic acid (Asp) during the translation. Keywords are sufficient.
In doing so use the following terms:
m-RNA (messenger RNA), t-RNA (transfer RNA), genetic code, ribosome, codon and anticodon.
(Aspartic acid (Asp) is coded by GAC).

Fourth Round (practical problems)

Problem 4-11 Quantitative Analysis of Copper and Cobalt

In this problem the unknown content of copper and cobalt in a provided solution have to be determined. The sum of the content of both metals is found by complexometric titration. The content of copper is determined by a redox titration. The difference gives the content of cobalt.

Equipment:

Volumetric flask (250 mL) with the provided solution, pipette (20 mL), 4 Erlenmeyer flasks, graduated pipette (5 mL), 50 mL measuring cylinder, beaker (50 mL), burette (25 mL), stand with boss and clamps, magnetic stirrer plate with stirring bar, spatula, micro spatula, indicator paper.

Substances:

Test solution with Cu^{2+} and Co^{2+}	
Standard solution of Na_2EDTA, $c(Na_2EDTA) = 0.1$ mol/L	
Sodium acetate ($NaOOCCH_3$)	
Trituration of xylenol orange indicator	
Diluted acetic acid	
Sulfuric acid, $w(H_2SO_4) = 25$ %	
Potassium iodide (KI)	
Standard solution of sodium thiosulfate, $c(Na_2S_2O_3) = 0.1$ mol/L	
Solution of starch	
Demineralized water	

Procedure:

The flask with the test solution has to be filled up to 250 mL. The solution has to be mixed well.

<u>Complexometric determination of copper and cobalt</u>

20 mL of the solution are transferred to an Erlenmeyer flask and filled up to approximately 100 mL.

After adding of 3 mL of dil. acetic acid and 4 heaped spatula of sodium acetate the pH of the solution should reach a value between 5 and 6. A micro spatula of the trituration of xylenol orange indicator is added. The solution is titrated with the standard solution of Na_2EDTA until the colour changes from violet to green. Shortly before the end of the titration the addition of Na_2EDTA solution should be done very slowly.

Iodometric determination of copper

20 mL of the solution are transferred to an Erlenmeyer flask and 10 mL of sulfuric acid (w = 25 %) are added. The solution is filled up to approximately 100 mL.
Two spatula of potassium iodide are added. The solution is immediately titrated with the sodium thiosulfate solution until a light yellow colour occurs. Approximately 2 mL of starch solution are added shortly before the end then titrated to the end point of the dark solution. The solution should stay colorless for approximately 1 minute.

Disposal: All solutions have to be poured into the provided disposal

Problems:

a) Write down the label code of your flask with the test solution.

b) Record the mean value of your consumption of Na_2EDTA standard solution.

c) Record the mean value of your consumption of $Na_2S_2O_3$ standard solution and calculate the mass concentration (in mg/L) of copper in the test solution.

d) Calculate the mass concentration (in mg/L) of cobalt in the test solution.

Problem 4-12 Separation of a Mixture of Indicators by Thin-layer Chromatography (TLC)

In this problem you have to find out how many components a provided mixture of indicators contains using TLC. The indicators in the mixture have different colours.

Equipment:

TLC chamber, 3 TLC plates, filter paper for saturation of the chamber, capillary tubes for TLC spotters, measuring cylinder (25 mL), graduated pipette (10 mL), zipper bag to place the TLC plate, tweezers, pencil.

Substances:

Mixture of indicators	
Ethanol	
n-Hexane	

Procedure:

Mark the start on the TLC plate using the pencil. Spot the TLC plate with a bit of the indicator mixture using the capillary tubes provided. Run a TLC in the TLC chamber which is saturated with the solvent. Mark the solvent front as well as the colored spots on the TLC plate. Try different mixing ratios of ethanol and hexane to find the best separation.

Disposal: All solutions have to be poured into the provided disposal.

Problems:

Determine and record the number of components.
Write down which mixing ratio of the solvents you used for the best separation.
Sketch the TLC plate on your answer sheet and give the colours of the different spots.
Dry the TLC plate in air and place it into the zipper bag.

Problem 4-13 Qualitative Analysis of Anions

You find a mixture of salts in the test tubes marked with A, B, C or D. The following anions may be present:
Cl^-, I^-, Br^-, CO_3^{2-}, H_3CCOO^-, $C_2O_4^{2-}$, SO_4^{2-}.
The counter ions are sodium or potassium cations which have not to be determined.

Equipment:

Mortar with pestle, test tubes with rack, test tube holder, Bunsen burner with equipment, fermentation lock, filter paper, funnel, small Erlenmeyer flasks, glass rod, pH paper, spatula, micro spatula, Erlenmeyer flask (250 mL), Pasteur pipette.

Substances:

Mixture of salts	
Dil. hydrochloric acid (HCl)	
Dil. sulfuric acid (H_2SO_4)	
Dil. acetic acid (H_3CCOOH)	
Dil. nitric acid (HNO_3)	
Potassium hydrogensulfate ($KHSO_4$)	
Solution of silver nitrate ($AgNO_3$)	
Solution of barium hydroxide ($Ba(OH)_2$)	
Solution of calcium chloride ($CaCl_2$)	
Solution of potassium permanganate ($KMnO_4$)	
Solution of potassium iodide (KI)	
Solution of potassium bromide (KBr)	
Solution of barium nitrate ($Ba(NO_3)_2$)	
Sat. solution of ammonium carbonate ($(NH_4)_2CO_3$)	
Conc. solution of ammonia(NH_3 (aq))	

Chlorine water (Cl_2 (aq))	
n-Hexane (C_6H_{14})	
Demineralized water	

Problems:

a) Write down the label code of your test mixture.

b) Determine the anions in the test mixture by using the provided equipment. Report your results on the answer sheet.

c) Report the way you found each of your results.

Safety precautions: Wear eye protection and protective clothing.

The following ways of identification are recommended:

First of all mix the provided test substances intensely in the mortar. Acetate and carbonate are detected directly from that mixture. Dissolve a part of the test substances in water to determine the other anions.

<u>Identification of acetate:</u>

A part of the test mixture is triturated in a mortar with potassium hydrogensulfate ($KHSO_4$).

In the presence of H_3CCOO^- a smell of acetic acid is noticed.

There is no interference of other ions.

<u>Identification of carbonate:</u>

A part of the test mixture is filled in a test tube and dil. hydrochloric acid is added. The test tube is immediately closed with a fermentation lock filled with freshly made and filtered solution of barium hydroxide.

In the presence of CO_3^{2-} a turbidity caused by $BaCO_3$ is noticed.

There is no interference of other ions.

<u>Identification of oxalate:</u>

A part of a solution of the test mixture is filled into a test tube and a solution of $CaCl_2$ is added. The following salts may precipitate:

$CaCO_3$ (white), CaC_2O_4 (white). $CaSO_4$ precipitates only when very high concentrations a present. $CaCO_3$ dissolves in dil. H_3CCOOH and is thus separated from oxalate. CaC_2O_4 is then dissolved in dil. H_2SO_4. In boiling heat drops of a potassium permanganate solution are added.

In the presence of oxalate decoloration is noticed.

There is no interference of other ions.

Identification of sulfate:

A part of a solution of the test mixture is filled into a test tube, acidified with dil. nitric acid and a solution of $Ba(NO_3)_2$ is added.

In the presence of sulfate a white precipitate is noticed.

There is no interference of other ions (barium oxalate dissolves in dil. acids).

Identification of chloride, bromide and iodide:

A part of a solution of the test mixture is filled into a test tube, acidified with dil. nitric acid and a solution of $AgNO_3$ is added. The following salts may precipitate:

AgCl (white), AgBr (yellowish), AgI (yellow). The precipitate is treated with a sat. solution of $(NH_4)_2CO_3$. AgCl dissolves but not quantitatively. The filtrate is treated with a solution of KBr.

In the presence of chloride a precipitate is noticed.

The rest of the precipitate of the $AgNO_3$ precipitation is treated with a conc. solution of ammonia. AgCl and AgBr dissolve. A yellow residue indicates iodide. The filtrate is treated with a solution of KI.

In the presence of chloride and/or bromide a precipitate is noticed.

Reaction with chlorine water:

A part of a solution of the test mixture is filled into an Erlenmeyer flask (250 mL) and covered with a small amount of hexane. Then chlorine water is added drop wise and the solution is strongly shaked.

In the presence of iodine and bromine the organic phase turns at first violet (iodide). Adding more chlorine water the organic phase decolors and turns gradually brown (bromide).

Disposal: All solutions have to be poured into the provided disposal.

Part 2

The answers to the problems of the four rounds

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

Answers Round 1

Solution to problem 1-1

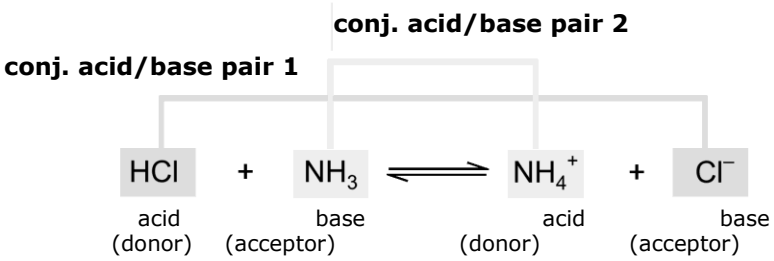
a)

Pure substance	Homogenous mixture	Heterogeneous mixture
α-tin	brass	expanded polystyrene
β-sulfur	aq. solution of sodium chloride	armored concrete
sodium chloride	air	ammonium chloride fumes
ice/water mixture		bath foam

b) NH_3, PH_3, Na_2S, $NaNH_2$, $NaOC_2H_5$, NaOAc etc.

c) The Brønsted definition of an acid is that it is a substance which can give up a proton (H^+) to another species. The species that accepts the proton is a base.

d) Having given up its proton, an acid HA becomes the species A^- which is called the conjugate base of the acid HA. The reason for this name is that A^- can accept a proton to give HA, which means that A^- is itself a base. It is described as the conjugate base of HA since it is the base which derives from the dissociation of AH. In the same way, having accepted a proton the base B becomes the species BH^+, which is described as he conjugate acid of the base B.



e)

Conjugate acid	Conjugate base
NH_4^+	NH_3
NH_3	NH_2^-
H_3O^+	H_2O
H_2O	OH^-
HS^-	S^{2-}
H_2S	HS^-
$H_2PO_4^-$	HPO_4^{2-}
H_3PO_4	$H_2PO_4^-$
HCN	CN^-
HCl	Cl^-
HSO_4^-	SO_4^{2-}
H_3CCOOH	H_3CCOO^-

f)

$Na_2CO_3 + H_2O \rightleftharpoons 2\ Na^+ + HCO_3^- + OH^-$ The solution reacts basic.

$Al_2(SO_4)_3 + 12\ H_2O \rightleftharpoons 2[Al(H_2O)_6]^{3+} + 3\ SO_4^{2-}$

$[Al(H_2O)_6]^{3+} \rightleftharpoons [Al(H_2O)_5(OH)]^{2+} + H^+$ The solution reacts acidic.

$Na_2S + H_2O \rightleftharpoons 2\ Na^+ + OH^- + HS^-$ The solution reacts basic.

$KCl + H_2O \rightleftharpoons K^+ + Cl^- + H_2O$ The solution is neutral.

$Cl_2 + H_2O \rightleftharpoons 2\ H^+ + Cl^- + ClO^-$

$3\ HOCl \rightleftharpoons HClO_3 + 2\ HCl)$ The solution reacts acidic.

g) $pH = -lg\ c(H_3O^+)$ (exactly: $pH = -lg[c(H_3O^+)/c°)]$ with $c° = 1$ mol/L

Note: The pH value is dimensionless. To be exact you should divide $c(H_3O^+)$ by c° before forming the logarithm. However, it is acceptable to write $pH = -lg\ c(H_3O^+)$ provided that you remember that $c(H_3O^+)$ is a shorthand of $c(H_3O^+)/c°$) as c° is 1 mol/L.

In pure water H_3O^+ is produced by the autoprotolysis equilibrium for which $K_w = 1.0 \cdot 10^{-14}$ at 25 °C. Since the formation of one H_3O^+ ion results in the formation of an OH^- ion, it follows that $c(H_3O^+) = c(OH^-)$ and $K_w = c(H_3O^+)^2$. Hence $c(H_3O^+) = 1.0 \cdot 10^{-7}$ mol/L and pH = 7.

h) The autoprotolysis equilibrium of water depends strongly on temperature. $K_w(60\ °C) = 1.0 \cdot 10^{-13.02}$. The number of H_3O^+ and OH^- ion is still equal ($c(H_3O^+)=c(OH^-)=10^{-6.51}$ mol/L), thus water is still neutral and no acid occurs.

i) $\alpha = \frac{c(H_3O^+)}{c_0(HA)} = \frac{10^{-3}\ mol/L)}{0{,}04\ mol/L} \cdot 100\% = 2.5\ \%,$ $\Rightarrow$ weak acid

j) <u>Nitric acid:</u>

$HNO_3 + H_2O \rightleftharpoons H_3O^+ + NO_3^-$

$c_0(HNO_3) = c(H_3O^+) = 0.2$ mol/L $pH = -lg\ 0.2$ $pH = 0.70$

<u>Acetic acid</u>

$HOAc + H_2O \rightleftharpoons H_3O^+ + AcO^-$

$c_0 - x$ x x

$K_a = \frac{c(H_3O^+)\cdot(c(AcO^-)}{c(HA)\cdot 1\ mol/L} = 10^{-4,75} = \frac{x \cdot x}{(0.2-x)}$

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

$x_1 = 1.877 \cdot 10^{-3}$ ($x_2 = -1.895 \cdot 10^{-3}$) $pH = -lg(1.877 \cdot 10^{-3})$ $pH = 2.73$

<u>Sulfuric acid</u>

$H_2SO_4 + H_2O \rightleftharpoons H_3O^+ + HSO_4^-$

1. step of dissociation is quantitatively $c_0(H_2SO_4) = c(H_3O^+) = c(HSO_4^-) = 0.2$ mol/L

2. step of dissociation

	$HSO_4^- + H_2O \rightleftharpoons$	H_3O^+	$+ SO_4^{2-}$
c/(mol/L) at begin	0.2	0.2	0
c/(mol/L) after protolysis	0.2 - x	0.2 + x	x

$K_a = 10^{-1.92} = \frac{(0.2+x)\cdot x}{(0.2-x)}$

$x^2 + (0.2 + 10^{-1.92}) \cdot x - 0.2 \cdot 10^{-1.92} = 0$

$x_1 = 0.0108$ ($x_2 = -0.2228$) $pH = -lg(0.2 + 0.0108) = -lg\ 0.2108$ $pH = 0.68$

Solution to problem 1 - 2

a) <u>Bottle 1</u>: Mass of the solution = 823 g $\triangleq$ 715,7 mL of solution

M(NaOH) = 40.00 g/mol $\frac{123\ g}{40\ g/mol}$ = 3.075 mol in 715.7 mL

c = 4,296 mol/L V = $\frac{2\ mol/L \cdot 1000 mL}{4.296\ mol/L}$ = 465.4 mL have to be filled up to 1 L.

Bottle 2: $M(H_2SO_4)$ = 98.08 g/mol

$\frac{72\ g}{98{,}08\ g/mol}$ = 0.734 mol in 100 g of the solution ≙ 0,734 mol in 60,6 mL of the solution.

c = 0,0121 mol/mL V = $\frac{2\ mol/L \cdot 1000\ mL}{12.1\ mol/L}$ = 165.3 mL have to be filled up to 1 L.

Bottle 3: $M(MgCl_2)$ = 95.21 g/mol

$n(MgCl_2)$= 1.265 mol m(solution) = 720.4 g V(solution) = 631.9 mL

c = $2.001 \cdot 10^{-3}$ mol/mL this is already the wanted concentration.

b) M(NaCl) = 58.44 g/mold = 1.1887 g/cm^3,

100 g of the solution have a volume of 84.13 mL with maximal 0.453 mol of NaCl.

To prepare 2 L of a saturated solution you need n = $\frac{0.453\ mol \cdot 2000\ mL}{84.03\ mL}$ = 10.78 mol of NaCl.

10.78 mol of NaCl ≙ 630.0 g of sodium chloride which have to be filled up to 2 L.

c) $K_{sp} = c_{Ca^{2+}} \cdot c_{OH^-}^2/(1\ mol/L)^3$

$c_{Ca^{2+}} = ½ \cdot c_{OH^-}$ ⇒ $K_L = \cdot\ c_{OH^-}^2 \cdot \frac{1}{2} c_{OH^-} = ½ \cdot c_{OH^-}^3$

$c_{OH^-} = \sqrt[3]{2 \cdot K_{sp}}$ mol/L $c_{Ca^{2+}} = ½ \cdot \sqrt[3]{2 \cdot K_{sp}}$ mol/L = $\sqrt[3]{\frac{1}{4} \cdot K_{sp}}$ mol/L

d) K_{sp} ($Ca(OH)_2$) = $3.89 \cdot 10^{-6}$ K_{sp} ($Ba(OH)_2$) = $4.27 \cdot 10^{-3}$

$M(Ca(OH)_2)$ = 74.09 g/mol. $M(Ba(OH)_2 \cdot 8\ H_2O)$ = 315.46 g/mol

Using the formulae of c):

$c_{Ca^{2+}} = \sqrt[3]{\frac{1}{4} \cdot K_{sp}}$ mol/L = $\sqrt[3]{\frac{1}{4} \cdot 3.89 \cdot 10^{-6}}$ = 0.010 mol/L ≙ 0.74 g $Ca(OH)_2$

$c_{Ba^{2+}} = \sqrt[3]{\frac{1}{4} \cdot K_{sp}}$ mol/L = $\sqrt[3]{\frac{1}{4} \cdot 4.27 \cdot 10^{-3}}$ = 0.102 mol/L ≙ 32.18 g of $Ba(OH)_2 \cdot 8\ H_2O$

0.74 g of $Ca(OH)_2$ and 32.18 g $Ba(OH)_2 \cdot 8\ H_2O$, respectively, have to be filled up to 1 L.

e) Prepare a solution above a solid undissolved solute and filter off from the solid.

Solution of problem 1-3

a) Mass of carbon: m(C) = $\frac{12.01\ g/mol \cdot 1.87\ g}{44.01 g/mol}$ = 0.501 g

mass of hydrogen: m(H) = $\frac{1.008\ g/mol\ 2 \cdot 0.376\ g}{18.02 g/mol}$ = 0.042 g

mass of oxygen: m(O)= 0.766 g – 0.501 g – 0.042 g = 0.223 g

n(C) : n(H) : n(O) = $\frac{0.501}{12.01} : \frac{0.042}{1.008} : \frac{0.223}{16.00}$ = 0.042 : 0.042 : 0.014

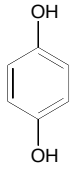
⇒ empirical formula C_3H_3O

b) The ^{13}C-NMR spectrum shows two signals at 149.79 ppm (s) and 115.67 ppm (s) ⇒ two carbon atoms are magnetically equivalent, i.e. there must be a symmetric element, which converts these two carbon atoms into each other.

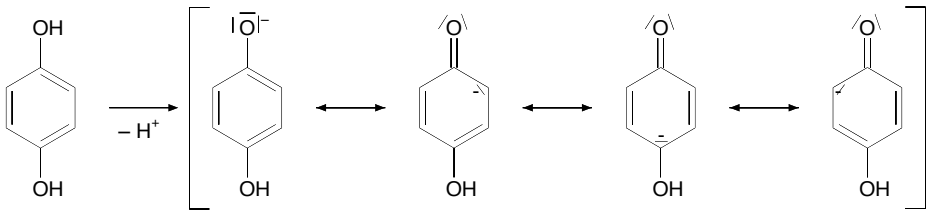
The chemical shifts of these two signals and the singlet at 6.58 ppm in the ^{1}H-NMR spectrum are clues that **A** is an aromatic compound.

The two singlets indicate not-coupling, magnetically equivalent hydrogen atoms.

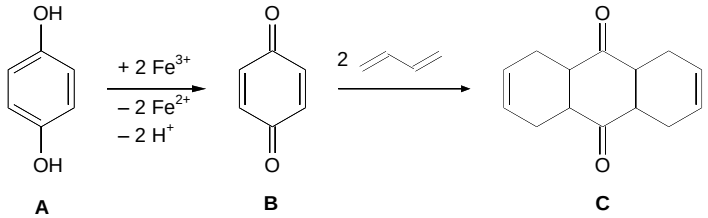
⇒ Compound **A** is hydroquinone, $C_6H_6O_2$



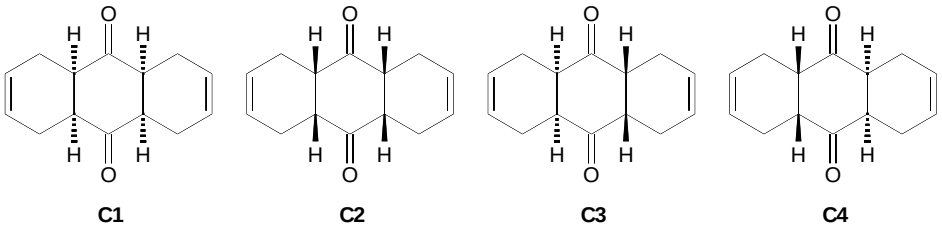
c) The negative charge of the anion is stabilized by the existence resonance structures. Thus the disposal of a proton is favored.



d)

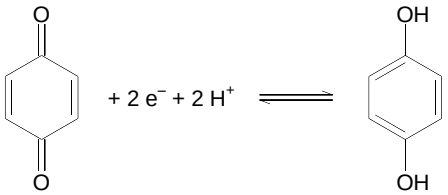


e)



They are stereoisomers. C1/C2 and C3/C4 contain a mirror plane each and are achiral.
C1 = C2, identical (meso compound), C3 = C4 , identical (meso compound).

f)



or

$Q + 2\,e^- + 2\,H^+ \rightleftharpoons HQ$

or

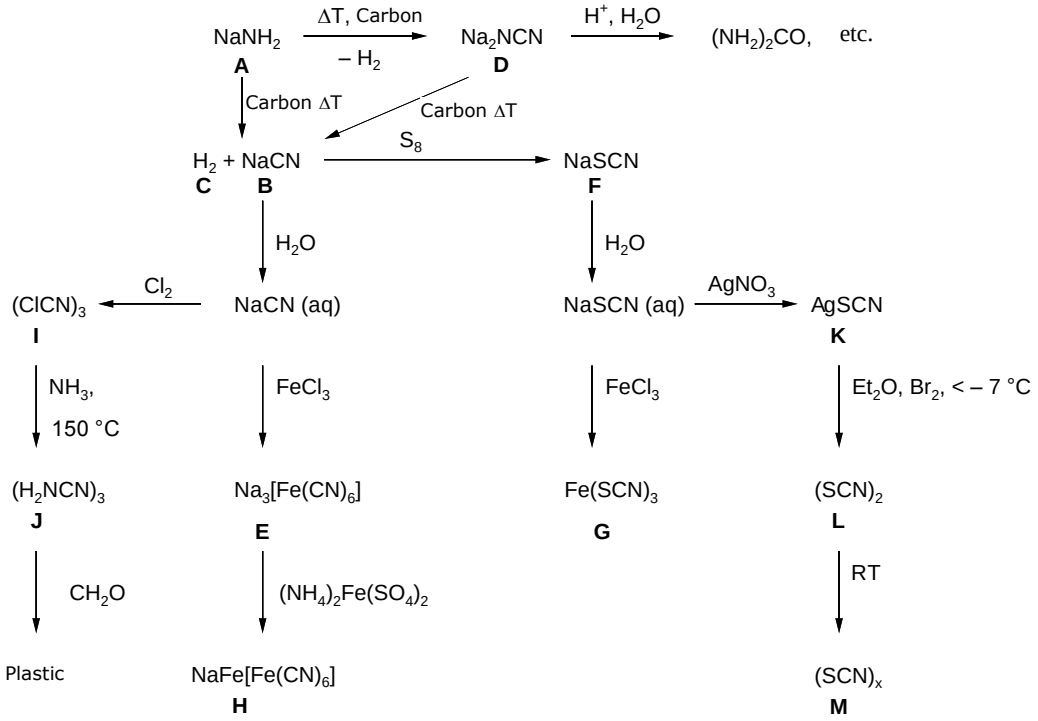
$C_6H_4O_2 + 2\,e^- + 2\,H^+ \rightleftharpoons C_6H_6O_2$

g) $E = E° + \frac{R \cdot T}{n \cdot F} \cdot \ln \frac{c(Ox) \cdot (c°)^{-1} \cdot c^2(H^+) \cdot (c°)^{-2}}{c(Red) \cdot (c°)^{-1}}$ with c° = 1 mol/L

$E = 0.70\ V + \frac{8.314\ J \cdot K^{-1} mol^{-1} \cdot 298.15\ K}{2 \cdot 96485\ C\ mol^{-1}} \cdot \ln \frac{1 \cdot (10^{-5.5})^2}{1} = 0.37\ V$

Answers Round 2

Solution to problem 2-1



a)

A	Sodium amide	$NaNH_2$
B	Sodium cyanide	NaCN
C	Hydrogen	H_2
D	Sodium cyanamide	Na_2NCN bzw. Na_2N_2C
E	Sodium hexacyanoferrate(III)	$Na_3[Fe(CN)_6]$
F	Sodium thiocyanate, sodium rhodanide	NaSCN
G	Iron thiocyanate	$Fe(SCN)_3$ bzw. $[Fe(H_2O)_3(SCN)_3]$
H	Berlin blue	$NaFe[Fe(CN)_6]$
	Remark: $Fe_4(Fe(CN)_6]_3$ is imaginable ,too, but it should not form preferentially with a molar ratio of n(Fe(II)): n(Fe(III)) of 1 : 1.	

b) Comproportionation:

$$\overset{+I\ \ -III}{Na_2N}\overset{+IV-III}{C}\overset{0}{N} + C \rightleftharpoons 2\,\overset{+I\ +II\ -III}{Na\,C\,N}$$

c) $\left[I\underline{\overline{N}}-C\equiv N I\right]^{2-} \leftrightarrow \left[\underline{\overline{N}}=C=\underline{\overline{N}}\right]$

d) 16 electron systems:

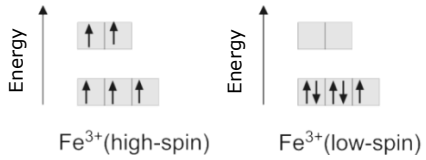
Carbon dioxide: CO_2, azide: N_3^-, cyanate: OCN^-, dinitrogenmonoxide: N_2O,
nitrogendioxide cation: NO_2^+, fulminate: CNO^-, nitridoborate anion$(BN_2)^{3-}$.

e) $NaNH_2 + C \rightleftharpoons NaCN + H_2$ with $M(NaNH_2) = 39.0\ g \cdot mol^{-1}$

19.5 g correlate to 0.5 mol, 1 mol of sodium amide provides 1 mol of hydrogen:

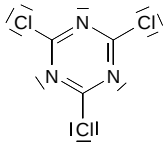
$$V(H_2) = \frac{0.5\ mol \cdot 8.314\ N \cdot m \cdot mol^{-1} \cdot 298\ K}{1.013 \cdot 10^5\ N \cdot m^{-2}} = 0.0122\ m^3 = 12.2\ L$$

f) You may expect a blue colour. The compound should be paramagnetic because of the existing iron(III) ions, independent of the existence of a high-spin (5 unpaired electrons) or a low-spin (1 unpaired electron) configuration.



Remark: In cyanide complexes iron(II) exists always in low-spin configuration which leads to diamagnetic property. Berlin blue contains Fe(III) and Fe(II).

g) I: $C_3Cl_3N_3$, Cyanuric chloride, 2,4,6-trichloro-1,3,5-triazine, cyanuric acid chloride, canuric acid trichloride



J: $C_3H_6N_6$, Melamine, cyanuric acid triamide, 2,4,6-triamino-1,3,5-triazine

h) K: Silver thiocyanate, silver rhodanide, AgSCN
L: Dirhodane, dithiocyanate, dicyanodisulfide, $C_2N_2S_2$
M: Pararhodane: $(SCN)_x$
As pseudo-halogen dirhodane may be correlated to the halogens /group 17.

Solution to problem 2-2

a) Compounds D, E and F have to be looked at first.
Compound D:

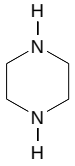
n(C) : n(H) : n(N) = $\frac{55,82}{12,01}$: $\frac{11,71}{1,008}$: $\frac{32,47}{14,01}$ = 4,65 : 11,62 : 2,32 = 2 : 5 : 1 ⇒ D: $(C_2H_5N)_x$

In the same way E: $(C_5H_{12}N_2)_y$ und F: $(C_3H_7N)_z$.
Each of these compounds must have two nitrogen atoms because they react with four equivalents of the N-alkylation agent. These two nitrogen agents have to be 1 x primary and 1 x tertiary or 2 x secondary ⇒ x = 2, y = 1, z = 2.

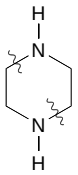
D, E and F are heterocyclic compounds with no other hetero elements than nitrogen
⇒ Each compound contains at least one secondary nitrogen atom in the ring.

D, E and F can be dehydrogenated to form aromatic compounds
⇒ You may assume five/six membered ring systems.

The ^{1}H-NMR spectrum of D shows only two different kinds of protons
⇒ D is a compound with high symmetry.

D: 

Compound D has to be retrosythetically fragmented to fit in the way of the synthesis A ⟶ B ⟶ C :



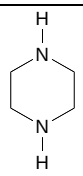
⇒ $CH_2=CH_2$ (**A**) $\xrightarrow{+\ Cl_2}$ $Cl-CH_2-CH_2-Cl$ (**B**) $\xrightarrow{+\ 2\ NH_3}$ $Cl^-\ {}^+NH_3-CH_2-CH_2-NH_3^+\ Cl^-$ (**C**)

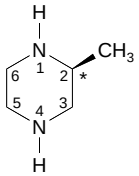
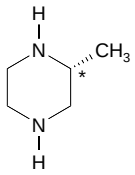
Compound C dimerizes splitting off NH_4Cl when heated to form a heterocyclic dihydrochloride. Basic hydrolysis yields compound D.

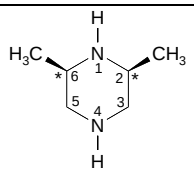
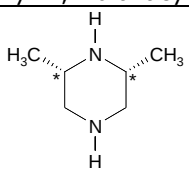
Compound C may react in the same way with C1 to form a heterocyclic dihydrochloride, too, which yields compound E after basic hydrolysis.

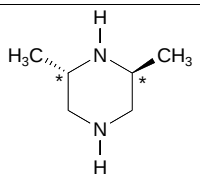
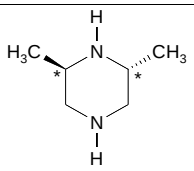
⇒ $CH_3-CH=CH_2$ (**A1**) $\xrightarrow{+\ Cl_2}$ $CH_3-CHCl-CH_2-Cl$ (**B1**) $\xrightarrow{+\ 2\ NH_3}$ $CH_3-CHNH_3^+(Cl^-)-CH_2-NH_3^+\ Cl^-$ (**C1**)

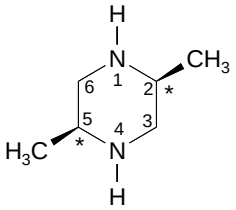
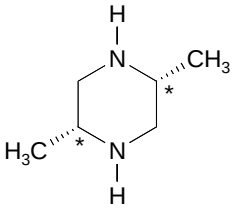
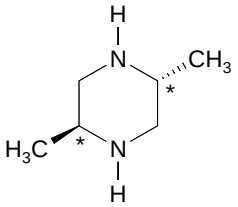
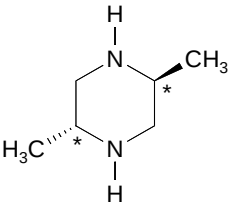
Compound C1 may react in the same way with itself to form a heterocyclic dihydrochloride, too, which yields compound F after basic hydrolysis.

D	$C_4H_{10}N_2$	Piperazine, 1,4-Diazocyclohexane
		
	Percentage of total yield 25 %	
	no stereogenic center	

E	$C_5H_{12}N_2$	2-Methylpiperazine, 2-Methyl-1,4-diazacyclohexane
Enantiomers		
	CIP: 2S	CIP: 2R
	Percentage of total yield 25 %	Percentage of total yield 25 %

F	$C_6H_{14}N_2$	2,6-Dimethylpiperazine, 2,6-Dimethyl-1,4-diazacyclohexane
identical, diastereomeric to the enantiomers		
	CIP: 2S, 6R	CIP: 2R, 6S
	Percentage of total yield 6,25 %	

Enantiomers		
	CIP: 2S, 6S	CIP: 2R, 6R
	Percentage of total yield 3,125 %	Percentage of total yield 3,125 %

F	$C_6H_{14}N_2$	2,5-Dimethylpiperazine, 2,5-Dimethyl-1,4-diazacyclohexane
Enantiomers		
	CIP: 2S, 5S	CIP: 2R, 5R
	Percentage of total yield 3,125 %	Percentage of total yield 3,125 %
identical, diasteromeric to the enantiomers		
	CIP: 2R, 6S	CIP: 2S, 6R
	Percentage of total yield 6,25 %	

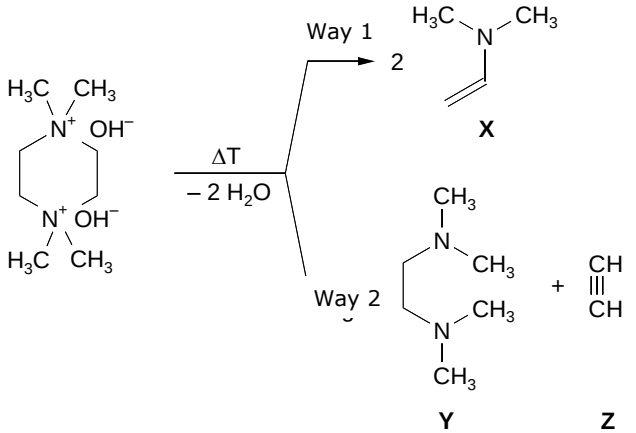
b) $V_m = (1\ mol \cdot 8.314\ JK^{-1}mol^{-1} \cdot 298\ K) / 1.013 \cdot 10^5\ Pa$ $V_m = 24.46 \cdot 10^{-3}\ m^3$

The density of the gas Z generated from D* is $d = m/V \Rightarrow m = d \cdot V$

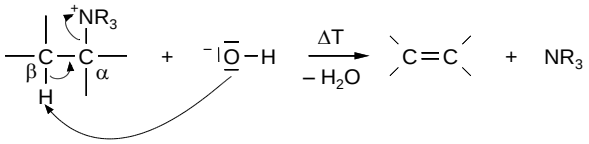
with $m = n \cdot M$ and $n = 1\ mol$: $M = d \cdot V_m / 1\ mol$

$M = 1.064\ kg/m^3 \cdot 24.46 \cdot 10^{-3}\ m^3 / 1\ mol$ $M = 26.03\ g/mol$

this is the molar mass of acetylene:

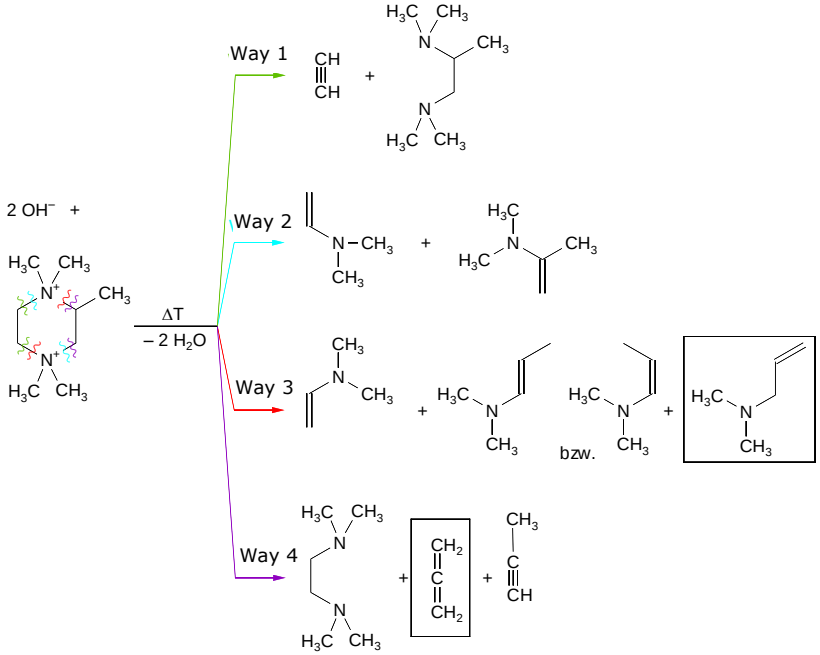


c) Name of the sequence of the reactions: Hofmann elimination. The actual elimination step is an E2 reaction in which the hydroxide ion removes a proton at the same time that the positively charged nitrogen atom leaves. Besides water a trialkylamine and an alkene are generated:



Because of the large size of the trialkylamine leaving group, the base must abstract a hydrogen atom from the most sterically accessible, least hindered position. This is the methyl group ($-CH_3$) in β-position to the nitrogen atom, less favoured is a methylene group ($-RCH_2$) and most difficult at a $-R_2CH$ group.

d) The preferential products are indicated by a box if there are more possibilities.



Solution to problem 2-3

a) $m(S) = \frac{m(SO_3) \cdot M(S)}{M(SO_3) \cdot 0.998}$

$m(S) = \frac{500\ t \cdot 32.1\ g/mol}{80.1\ g/mol \cdot 0.998}$ m(S) = 201 t

$\Delta H = 2 \cdot (-396\ kJ \cdot mol^{-1}) - 2 \cdot (-297\ kJ \cdot mol^{-1}) = -198\ kJ/mol$

$Q = \Delta H/2 \cdot n(SO_3)$

$Q = -99\ kJ/mol \cdot \frac{500\ t}{80.1\ g/mol}$ $Q = 6.18 \cdot 10^8\ kJ$

Mass of sulfur dioxide m_n which did not react:

$m_n(SO_2) = n(S) \cdot 0{,}2\ \% \cdot M(SO_2)$

$m_n(SO_2) = \frac{200.78 \cdot 10^6 g}{32.1\ g/mol} \cdot 0.002 \cdot 64.1\ g/mol$ $m_n(SO_2) = 0.8$ t

b) At standard conditions for equation (1):

$\Delta H = (2 \cdot (-396) - 2 \cdot (-297))\ kJ \cdot mol^{-1}$ $= -198\ kJ \cdot mol^{-1}$

$\Delta S = (2 \cdot 257 - 2 \cdot 249 - 205)\ J \cdot mol^{-1} \cdot K^{-1} = -189\ J \cdot mol^{-1} \cdot K^{-1}$

$\Delta c_p = (2 \cdot 59.0 - 2 \cdot 46.5 - 31.9)\ J \cdot mol^{-1} \cdot K^{-1} = -6.9\ J \cdot mol^{-1} \cdot K^{-1}$

Equations for the conversion to other temperatures:

$\Delta H_{Tx} = \Delta H_{298} + \Delta c_p \cdot \Delta T$ $\Delta S_{Tx} = \Delta S_{298} + \Delta c_p \cdot \ln \frac{T_x}{298\ K}$

$\Rightarrow$

600 °C bzw. 873 K	700 °C bzw. 973 K
ΔT=575 K	ΔT=675 K
$\Delta H_{873} = -202.0\ kJ \cdot mol^{-1}$	$\Delta H_{973} = -202.7\ kJ \cdot mol^{-1}$
$\Delta S_{873} = -196.4\ J \cdot K^{-1} \cdot mol^{-1}$	$\Delta S_{973} = -197.2\ J \cdot K^{-1} \cdot mol^{-1}$
$\Delta G = \Delta H - T\Delta S$	
$\Delta G_{873} = -30.54\ kJ \cdot mol^{-1}$	$\Delta G_{973} = -10.82\ kJ \cdot mol^{-1}$
$\Delta G = -R \cdot T \cdot \ln K$	
$\ln K = -\Delta G / R \cdot T$	
$K_{873} = 67.2$	$K_{973} = 3.81$

As the reacting agents are gaseous the constant is K_p.

c) Van't Hoff equation:

$\ln (K_{p1}/K_{p2}) = \frac{-\Delta H^0}{R} \cdot (T_1^{-1} - T_2^{-1})$ (2)

Using the result of b): $K_{p1} = 67{,}2$ and $\Delta H = -202{,}0\ kJ \cdot mol^{-1}$

$T_1 = 873\ K$ and $T_2 = 973\ K$ $\Rightarrow$

$\ln K_{p2} = \ln 67.2 + \frac{-202000\ J \cdot mol^{-1}}{8.314\ J \cdot mol^{-1} K^{-1}} \cdot (873^{-1} \cdot K^{-1} - 973^{-1} \cdot K^{-1})$ $\Rightarrow K_{p2} = 3.85$

Reasons for the small deviation:
Equation (2) applies for the condition that ΔH is constant i.e. independent of temperature, which here is not the case.

d) With a sufficient amount of air at 1500 °C nitrogen oxides form, simultaneously. Because of the deficit in oxygen only marginal amounts of NO_x form or if formed are reduced by sulfur. There is practically no NO_x formation below 700 °.

e) Assumption: 100 mol of starting mixture

$x = \frac{\text{converted amount of } 0_2}{mol}$ $p_{act} = 1.02\ bar$ $K_p = 65.1$

Total amount of gases in equilibrium = (100 – x) mol

		SO_2	O_2	SO_3	N_2
$\frac{\text{amount}}{\text{mol}}$	before	10	11	0	79
$\frac{\text{amount}}{\text{mol}}$	in equil.	10-2x	11-x	2x	79
mol fraction	in equil.	$\frac{10-2x}{100-x}$	$\frac{11-x}{100-x}$	$\frac{2x}{100-x}$	$\frac{79}{100-x}$
$\frac{\text{partial pressuge}}{\text{bar}}$	in equil.	$\frac{10-2x}{100-x} \cdot 1.02$	$\frac{11-x}{100-x} \cdot 1.02$	$\frac{2x}{100-x} \cdot 1.02$	$\frac{79}{100-x} \cdot 1{,}02$

$$\Rightarrow \quad 65.1 = \frac{(\frac{2x}{100-x} \cdot 1.02)^2}{(\frac{10-2x}{100-x} \cdot 1.02)^2 \cdot (\frac{11-x}{100-x} \cdot 1.02)}$$

$$65.1 = \frac{4x^2 \cdot (100-x)}{(10-2x)^2 \cdot (11-x) \cdot 1.02}$$

$\Rightarrow$ $x^3 - 19.79\, x^2 + 137.06\, x - 279.20 = 0$ $\qquad x \approx 3.47$

$\Rightarrow$ Amount of gases in equilibrium = (100 – x) mol = 96.53 mol

Percentage of volume

SO_2 : $\frac{10-2 \cdot 3.47}{96.53} \cdot 100\ \% = 3.2\ \%$

SO_3 : $\frac{2 \cdot 3.47}{96.53} \cdot 100\ \% = 7.2\ \%$

O_2 : $\frac{11-3.47}{96.53} \cdot 100\ \% = 7.8\ \%$

N_2 : $\frac{79}{96.53} \cdot 100\ \% = 81.8\ \%$

Rel. conversion of sulfur dioxide = (10 mol – 96.53 · 0.032) / 10 mol = 0.6911 ≙ 69.11 %

f) $x_i = \frac{n_i}{n_{gesamt}} = \frac{p_i}{p_{gesamt}}$ mit p_{gesamt} = 1.013 bar

$p_i = x_i \cdot p_{gesamt}$

inserted into the equation for K_p (the pressures are divided by p°):

$K_p = \frac{(x_{SO_3} \cdot 1.1013)^2}{(x_{SO_2} \cdot 1.1013)^2 \cdot x_{O_2} \cdot 1.013}$ $\qquad K_p = \frac{0.338^2}{0.309^2 \cdot 0.353 \cdot 1.013}$

$K_p = 3.35$

$\Delta G = - R \cdot T \cdot \ln K$ $\qquad \Delta G = -8.314\ J \cdot mol^{-1} \cdot K^{-1} \cdot 1000\ K \cdot \ln 3.35$

$\Delta G = -10.05\ kJ \cdot mol^{-1}$

Solution to problem 2-4

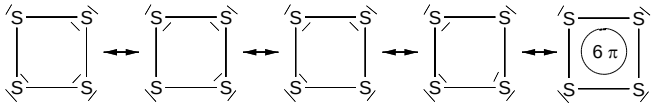
a) $\overset{0}{Se_8} + 3\ \overset{+I+VI-II}{H_2SO_4} \rightleftharpoons \overset{+0,25\ +I+VI-II}{Se_8(HSO_4)_2} + 2\ \overset{+I\ -II}{H_2O} + \overset{+IV-II}{SO_2}$

$4\ \overset{0}{Te} + 3\ \overset{+I+VI-II}{H_2SO_4} \rightleftharpoons \overset{+0,5\ +I+VI-II}{Te_4(HSO_4)_2} + 2\ \overset{+I-II}{H_2O} + \overset{+IV-II}{SO_2}$

(Equations containing ions are correct, too)

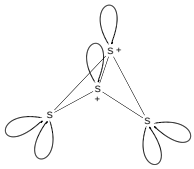
Alternatively the oxidation state +I can be assigned to the two bridging selenium atoms. Then the other ones would get the oxidation state 0.

b) The number of valence electrons amounts to 4 · 6 – 2 = 22. Therefore 11 electron pairs have to be distributed in a way that preferably each atom possesses an electron octet. Double bonds are not possible because of the cyclic structure. Thus four resonance forms with 6 delocalized ions have to be supposed. Following the Hückel rule (4n+2 π electrons, cyclic and planar) this kind of electron distribution is formally the distribution of an aromatic compound.

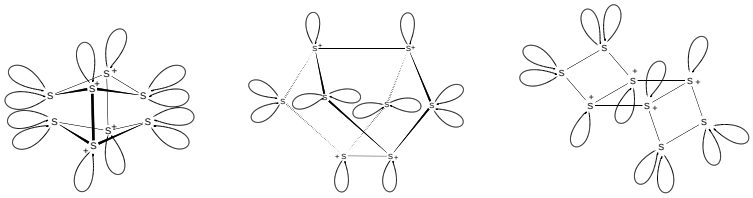


c) Different possibilities are (i) a butterfly structure, (ii) differently connected dimers $(S_4^{2+})_2$, or (iii) a chain

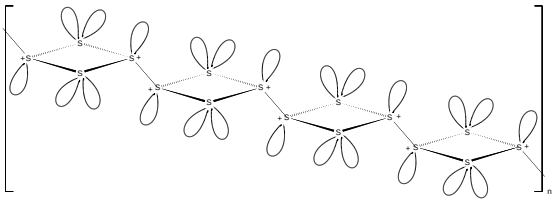
i)



ii)



iii)

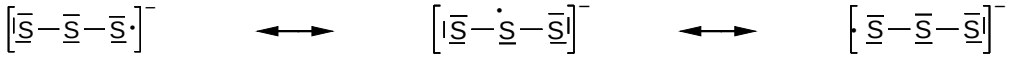


d) Absorption maximum = 17000 cm^{-1}

$\Rightarrow$ wavelength of absorption = $1/(17000 \cdot 10^{-7}\ nm^{-1})$ = 588 nm $\triangleq$ colour yellow

$\Rightarrow$ the molten mass is dark blue.

This colour caused by S_3 anions:



e) The radicals dimerize: $2\ S_3^- \rightleftharpoons S_6^{2-}$

f) Sulfur reacts with (poly-) sulfides forming higher polysulfides:

$S_n^{2-} + {}^1/_8\ S_8 \rightleftharpoons S_{n+1}^{2-}$ (z. B. n = 1 – 5)

Additional information:
In aqueous solutions (poly-) sulfide anions show interionic exchange reactions which lead in very quick equilibrium reactions to a multitude of different polysulfide anions:

$2\ S_2^{2-} \rightleftharpoons S^{2-} + S_3^{2-}$
$S_2^{2-} + S_3^{2-} \rightleftharpoons S^{2-} + S_4^{2-}$
$S_2^{2-} + S_4^{2-} \rightleftharpoons S^{2-} + S_5^{2-}$

Answers Round 3 Test 1

Solution to problem 3-01

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

b)

Element	Li	Na	Be	Mg	B	Al	C	Si	N	P	Cu	Ag	Au
Statement No.	4	8	7	3	2	6	10	1	11	9	13	5	12

Solution to problem 3-02

a) - The solubility of calcium carbonate falls with rising temperature.
- Hydrogen carbonate is in equilibrium with carbon dioxide and carbonate anions:

$$2\ HCO_3^-(aq) \rightleftharpoons CO_2(aq) + CO_3^{2-}(aq) + H_2O$$

The solubility of gases falls with rising temperature. The equilibrium shifts to the right side. This leads to a rising concentration of the carbonate ions and the solubility product is exceeded.

b) Acetic acid is a weak acid. In high concentrations you may use the approximation

$K_a = \frac{(c(H_3O^+) / 1\ mol\cdot L^{-1})^2}{c_0 / 1 mol\cdot L^{-1}}$.

$\Rightarrow$ $c(H_3O^+) = \sqrt{10^{-4.76} \cdot 4.30}$ mol·L^{-1} = 8.64·10^{-3} mol·L^{-1} pH = 2.06

or pH = ½ · (pK_S - lg 4.3) pH = 2.06

$c(OAc^-) = c(H_3O^+)$ = 8.64·10^{-3} mol·L^{-1}

(You get the same values by calculating precisely.)

c) Before dissolving: $c(H_3O^+) = c(OAc^-)_{before}$ = 10$^{-2.30}$ mol·L^{-1}

$K_a = \frac{(10^{-2.3})^2}{c_0(HAc) / 1mol\cdot L^{-1} - 10^{-2.3}}$ $\Rightarrow$ c_0(HOAc) = 1.45 mol·L^{-1}

After dissolving: $K_a = \frac{10^{-5} \cdot c(OAc^-)_{final} / 1mol\cdot L^{-1}}{1.45 - c(OAc^-)_{final} / 1mol\cdot L^{-1}}$ $\Rightarrow$ $c(OAc^-)_{final}$ = 0.92 mol·L^{-1}

Charge equalization: $2\cdot c(Ca^{2+}) + c(H_3O^+) = c(OAc^-)_{final} + c(HCO_3^-) + 2\cdot c(CO_3^{2-}) + c(OH^-)$

Approximation: $c(H_3O^+)$. $c(HCO_3^-)$. $c(CO_3^{2-})$ and $c(OH^-)$ are very small compared with $c(Ca^{2+})$ and $c(OAc^-)_{final}$

$\Rightarrow$ $c(Ca^{2+}) = ½ \cdot c(Ac^-)_{final}$ $c(Ca^{2+})$ = 0.46 mol·L^{-1}

$n(Ca^{2+})$ in 200 mL = 0.46 mol·L^{-1}· 0.2 L = 0.092 mol

$m(CaCO_3)_{dissolved}$ = 0.092 mol·100 g·mol^{-1} $m(CaCO_3)_{dissolved}$ = 9.2 g

Solution to problem 3-03

a) Oxidation state = 2·y/x

b) $Br_xO_y + (x + 2\cdot y)\ I^- + 2\cdot y\ H^+ \longrightarrow x\ Br^- + ½\cdot(x + 2\cdot y)\ I_2 + y\ H_2O$

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

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

d) d) $n(I_2) = ½\cdot n(S_2O_3^{2-}) = ½\cdot c(S_2O_3^{2-})\cdot V(S_2O_3^{2-})$

$n(Br^-) = n(Ag^+) = c(AgNO_3)\cdot V(AgNO_3)$

$\frac{n(I_2)}{n(Br^-)} = \frac{y+x/2}{x}$ $\Rightarrow$ $\frac{y}{x} = \frac{n(I_2)}{n(Br^-)} - 0.5$

Oxide	$n(I_2)$/mol	$n(Br^-)$/mol	y/x	Formula
A	$3{,}35\cdot10^{-4}$	$1{,}34\cdot10^{-4}$	2	**BrO_2**
B	$5{,}75\cdot10^{-4}$	$2{,}88\cdot10^{-4}$	1,5	**Br_2O_3**
C	$2{,}84\cdot10^{-4}$	$2{,}84\cdot10^{-4}$	0,5	**Br_2O**

Reactions

$2\ BrO_2 + 10\ I^- + 8\ H^+ \longrightarrow 2\ Br^- + 5\ I_2 + 4\ H_2O$

$Br_2O_3 + 8\ I^- + 6\ H^+ \longrightarrow 2\ Br^- + 4\ I_2 + 3\ H_2O$

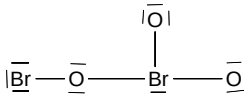
$Br_2O + 4\ I^- + 2\ H^+ \longrightarrow 2\ Br^- + 2\ I_2 + H_2O$

e) $m(BrO_2) = 79.9\ g/mol \cdot 1.34\cdot10^{-4}\ mol + 16.0\ g/mol \cdot 2.68\cdot10^{-4}\ mol$ = **15 mg**

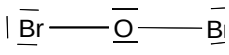
$m(Br_2O_3) = 79.9\ g/mol \cdot 2.88\cdot10^{-4}\ mol + 16.0\ g/mol \cdot 4.31\cdot10^{-4}\ mol$ = **30 mg**

$m(Br_2O) = 79.9\ g/mol \cdot 2.84\cdot10^{-4}\ mol + 16.0\ g/mol \cdot 1.42\cdot10^{-4}\ mol$ = **25 mg**

f)



Corresponding to $HBrO_3$



Corresponding to HBrO

Solution to problem 3-04

a) $HA + H_2O \rightleftharpoons A^- + H_3O^+$ with $K_a = \frac{c(A^-)/1\ mol\cdot L^{-1}\cdot c(H_3O^+)/1\ mol\cdot L^{-1}}{c(HA)/1\ mol\cdot L^{-1}}$.

$c(HA) = 1.00\cdot10^{-3}\ mol\cdot L^{-1}$ and $c(A^-) = 3.00\cdot10^{-2}\ mol\cdot L^{-1}$

$c(H_3O^+)$ can be determined using the Nernst equation:

$E = E° + \frac{R\cdot T}{F} \cdot ln\frac{c(H_3O^+)}{1\ mol\cdot L^{-1}}$ with E = - 0.315 V and E° = 0 V

$-0.315\ V = \frac{8.314\cdot298}{96485}\ V \cdot ln\frac{c(H_3O^+)}{1\ mol\cdot L^{-1}} \Rightarrow c(H_3O^+) = 4.70\cdot10^{-6}\ mol\cdot L^{-1}$

$K_S = \frac{c(A^-)\cdot c(H_3O^+)}{c(HA)\cdot 1\ mol\cdot L^{-1}}$ $K_S = \frac{3.00\cdot10^{-2}\cdot4.70\cdot10^{-6}}{1.00\cdot10^{-3}}$ $K_S = 1.41\cdot10^{-4}$

b) $n(NaOH) = 0.200\ mol\cdot L^{-1} \cdot 34.7\ mL = 6.94\ mmol$

$n(HA) = n(NaOH)$

$n(HA) = m(HA)/M(HA) \Rightarrow M(HA) = 1.36\ g / 6.94\ mmol = 196\ g\cdot mol^{-1}$

c) The pH at the equivalence point equals to the pH of a solution of a salt of this acid. There are (34,7 + 50) mL = 84,7 mL of a solution of sodium gluconate at the equivalence point.

$n(NaOH) = n(Na\text{-gluconate})$

$V(NaOH) \cdot c(NaOH) = V(Na\text{-gluconate}) \cdot c(Na\text{-gluconate})$

$34.7\ mL \cdot 0.200\ mol\cdot L^{-1} = 84.7\ mL \cdot c(Na\text{-gluconate})$

$\Rightarrow c(Na\text{-gluconate}) = 0.082\ mol\cdot L^{-1}$

$A^- + H_2O \rightleftharpoons HA + OH^-$

$K_b = 10^{-14} / K_a \Rightarrow K_b(A^-) = 7.09\cdot10^{-11}$ (weak base)

$c(OH^-) = \sqrt{c(Na-gluconate)\cdot\ K_b\ \cdot 1\ mol\ \cdot L^{-1}}$ $c(OH^-) = \sqrt{0.082\cdot\ 7.09\cdot10^{-11}}\ mol\cdot L^{-1}$

$c(OH^-) = 2.41 \cdot 10^{-6}$ mol·L^{-1} $\Rightarrow$ pOH = 5.62 pH = 8.38

A suitable indicator is phenolphthalein.

Solution to problem 3-05

a) $\frac{1}{2} X_2 \xrightarrow{\text{Dissociation}} X(g) \xrightarrow{\text{Electron acceptance}} X^-(g) \xrightarrow{\text{Hydration}} X^-(aq)$

Cl: $(+\frac{1}{2} \cdot 243 - 349 - 384)$ kJ · mol^{-1} = -611.5 kJ · mol^{-1}

F: $(+\frac{1}{2} \cdot 159 - 328 - 458)$ kJ · mol^{-1} = -706.5 kJ · mol^{-1}

For the oxidation of chloride $\frac{1}{2} F_2 + Cl^-(aq) \longrightarrow F^-(aq) + \frac{1}{2} Cl_2$ you get a negative reaction enthalpy (- 95 kJ/mol) and ,as the entropy change here is not a crucial factor, ΔG is negative, too. So this reaction is favored, not the reverse reaction.

c) Die I-I bond is the weakest as the bond length is the largest. Going to Br_2 and Cl_2 the bond energy raises as the bond length becomes shorter and the bonding electron pair binds more tightly. F_2 has lower bond energy because the free electron pairs interact due to the short bond length and thus weaken the bond strength.

d) Examples are

i) $Cl_2 + Me \rightleftharpoons MeCl_2$

$6\ Cl_2 + P_4 \rightleftharpoons 4\ PCl_3$

$H_2 + Cl_2 \rightleftharpoons 2\ HCl$

$Cl_2 + 2\ I^- \rightleftharpoons 2\ Cl^- + I_2$

ii) $Cl_2 + F_2 \rightleftharpoons 2\ ClF$

$10\ Cl^- + 2\ MnO_4^- + 16\ H^+ \rightleftharpoons 5\ Cl_2 + 2\ Mn^{2+} + 8\ H_2O$

$PbO_2 + 4\ H^+ + 2\ Cl^- \rightleftharpoons Pb^{2+} + Cl_2 + 2\ H_2O$

$MnO_2 + 4\ H^+ + 2\ Cl^- \rightleftharpoons Mn^{2+} + Cl_2 + 2\ H_2O$

$4\ HCl + O_2 \rightleftharpoons 2\ H_2O + 2\ Cl_2$

$4\ CuCl_2 \rightleftharpoons 4\ CuCl + 2\ Cl_2$

$Cr_2O_7^{2-} + 6\ Cl^- + 14\ H^+ \rightleftharpoons 2\ Cr^{3+} + 3\ Cl_2 + 7\ H_2O$

iii) $Cl_2 + H_2O \rightleftharpoons HOCl + HCl$

$3\ HClO \rightleftharpoons 2\ HCl + HClO_3$

$4\ KClO_3 \rightleftharpoons KCl + 3\ KClO_4$

$5\ HClO_2 \rightleftharpoons 4\ ClO_2 + HCl + H_2O$

$CaClOCl + 2\ HCl \rightleftharpoons CaCl_2 + Cl_2 + H_2O$

e) HF < HCl < HBr < HI

Justification using the radius: The atom radius rises from fluorine to iodine. In the same way the bond length of H-X rises and hydrogen is bound less tightly.

Justification using HSAB: The hydrogen cation is a very hard Lewis acid. The hardness of the Lewis base declines from fluoride to. The adduct H-F is a combination hard/hard and following

the HSAB principle very stable while the adduct H-I is a combination hard/soft and thus less stable.

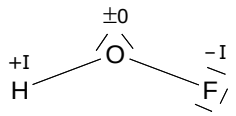
f) c_0 (HA) = c (HA), as HF protolyses only in a small amount, and . c(HA) = c_0(HA)

$10^{-3.19} = \frac{c(H^+)/c_0 \cdot c(A^-)/c_0}{c_0(HA)/c_0} = \frac{c(H^+)^2/(1\ mol/L)^2}{0{,}1} \Rightarrow c(H^+) = \sqrt{10^{-3.19} \cdot 0.1}$ mol/L

$\Rightarrow c(H^+) = 35 \cdot 10^{-3}$ mol/L ≙ 35 % protolysis.

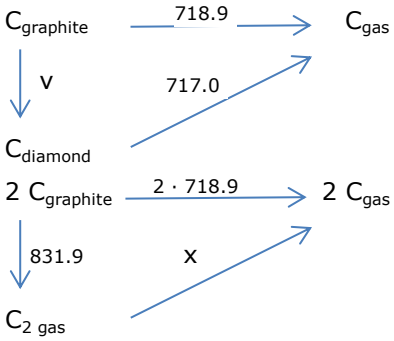
g) Expected shape of the molecule: angular.

h) $HOF + H_2O \rightleftharpoons HF + H_2O_2$



Solution to problem 3-06

a)



u = $\Delta H_f°(C_{graphite})$ = 0 kJ mol^{-1}

v = $\Delta H_f°(C_{diamond})$/kJmol^{-1} = 718.9 - 717.0 = 1.9

w = $\Delta H_f°(C_{gas})$ /kJmol^{-1} = $\Delta H_{at}°$/(kJmol^{-1}) = 718.9

x = $\Delta H_{at}°(C_{2\ gas})$/kJ$mol^{-1}$ = 2 ·718.9 – 831.9

x = 605.9

b) There are 4 · ½ = 2 bonds per atom in a diamond crystal

$\Rightarrow$ y = 717.0 kJmol^{-1} : 2 = 358.5 kJmol^{-1}.

z = x kJmol^{-1} = 605.9 kJmol^{-1}.

c) Bond energy per mol carbon in graphite:

1.5 · ΔH°(C-C, graphite) = 1.5 · 473.3 kJmol^{-1}= 710.0 kJmol^{-1}

Δ = (718.9 – 710.0) kJmol^{-1} = 8.9 kJmol^{-1}

This quantity can be interpreted as bond energy between the layers of graphite.

d) $I_2(g) \rightleftharpoons 2\ I(g)$

in equilibrium $p(I_2)_0 - x$ $2x$

$p_{total} = p(I_2)_0 - x + 2x = p(I_2)_0 + x \Rightarrow x = p_{total} - p(I_2)_0$

$K_p = K = \frac{p^2(I_{equilibtium})/p^{\circ 2}}{p(I_{2,equilibtium})/p^{\circ}}$ with p° = 1 bar

at 1073 K	at 1173 K
x = (0.0760 - 0.0639) bar = 0.0121 bar	x = (0.0930 - 0.0693) bar = 0.0237 bar
$p(I)_{equilibrium}$ = 2x = 0.0242 bar	$p(I)_{equilibrium}$ = 2x = 0.0474 bar
$p(I_2)_{equilibrium}$ = (0.0639 - 0.0121) bar = 0.0518 bar	$p(I_2)_{equilibrium}$ = (0.0693 - 0.0237) bar = 0.0456 bar
$K_{1073} = \frac{0.0242^2}{0.0518}$ K_{1073} = 0.0113	$K_{1173} = \frac{0.0474^2}{0.0456}$ K_{1170} = 0.0493

van't Hoff equation: $\ln (Kp_1/Kp_2) = -\frac{\Delta H^0}{R} \cdot (T_1^{-1} - T_2^{-1})$

$\ln(0.0113/0.0493) = -\Delta H°/(8.314\ J\cdot K^{-1}\cdot mol^{-1}) \cdot (1073^{-1} - 1173^{-1})\ K^{-1}$

$\Rightarrow \Delta H° = 154.2\ kJ\cdot mol^{-1}$

at 1100 K:

$\ln(K_{1100}/0.0113) = -154.2\ kJ\cdot mol^{-1}/(8.314\ J\cdot K^{-1}\cdot mol^{-1}) \cdot (1100^{-1} - 1073^{-1})\ K^{-1}$

$\Rightarrow \ln K_{1100} = -4.059 \quad \Rightarrow K_{1100} = 0.0173$

$\Delta G° = -R \cdot T \cdot \ln K$

$\Delta G° = -8.314\ J\cdot K^{-1}\cdot mol^{-1} \cdot 1100\ K \cdot (-4.059) \quad \Rightarrow \Delta G° = 37.12\ kJ\cdot mol^{-1}$

$\Delta G° = \Delta H° - T \cdot \Delta S°$

$\Delta S° = (154.2\ kJ\cdot mol^{-1} - 37.12\ kJ\cdot mol^{-1})/1100\ K \quad \Rightarrow \Delta S° = 106\ J\cdot mol^{-1}\cdot K^{-1}$

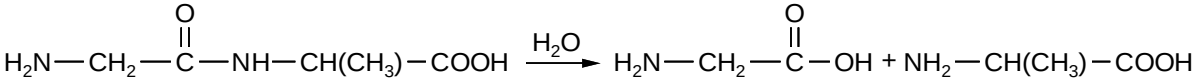
Solution to problem 3-07

a)

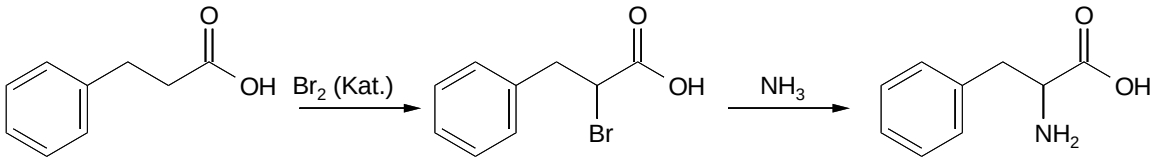
P_1 (pH = 2.35): $H_3N^+CH_2COOH$ (50%) $H_3N^+CH_2COO^-$(50%)	P_2 (pH = 6.07): $H_3N^+CH_2COO^-$(100%)	P_3 (pH= 9.78): $H_3N^+CH_2COO^-$(50%) H_2NCH_2COOH (50%)

b) - The salt like structure based on the zwitterions ($H_3N^+CH_2COO^-$)
- Strong intermolecular (electrostatic) forces between the different charges of the zwitterion.

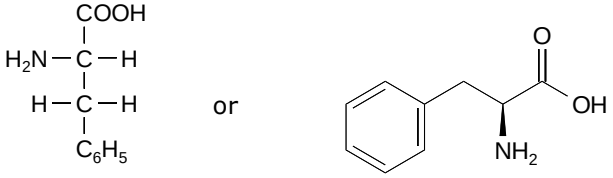
c) Cleavage of the peptide



d) Synthesis of phenylalanine



e) Structure of S-phenylalanine



Solution to problem 3-08

1. $HCHO + CH_3CHO \longrightarrow HO-CH_2-CH_2-CHO$

2. $(CH_3)_2C=CH_2 + Br_2 \longrightarrow (CH_3)_2CBr-CH_2Br$

3. $(CH_3)_2C=CH_2 + HBr \longrightarrow (CH_3)_2CBr-CH_3$

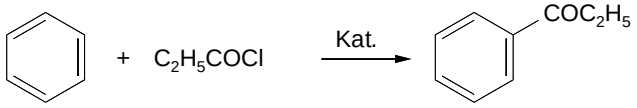
4. $(CH_3)_2C=CH_2 + KMnO_4 \xrightarrow{H_2O} (CH_3)_2COH-H_2COH$

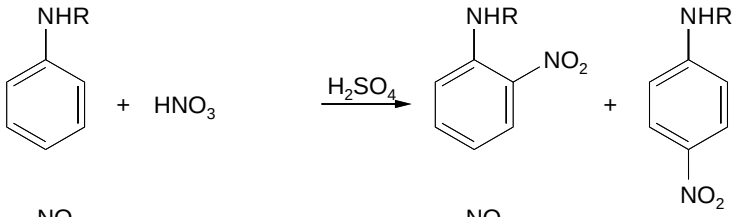
5. $(CH_3)_2C=CH_2 + O_3 \longrightarrow (CH_3)_2CO + HCHO$

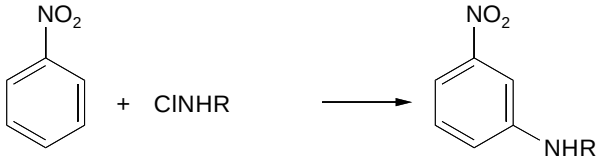
6. $CH_3CH_2C\equiv CH + H_2O \longrightarrow CH_3CH_2C(OH)-CH_2 \longrightarrow CH_3CH_2CO-CH_3$

7. $CH_3CH_2CHO + LiH \longrightarrow CH_3CH_2CH_2OH$

8. $CH_3MgBr + C_2H_5COCH_3 \longrightarrow C_2H_5C(OH)(CH_3)_2$

9.  (+ C_2H_5COCl, Kat.)

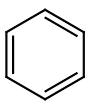
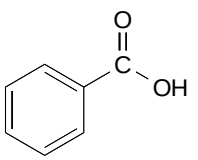
10.  (+ HNO_3, H_2SO_4)

11. 

12. $H_2NCH(CH_3)COOH + H_2NCH_2COOH \longrightarrow H_2NCH(CH_3)CONHCH_2COOH + H_2O$

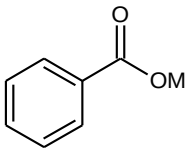
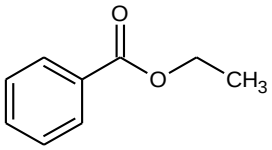
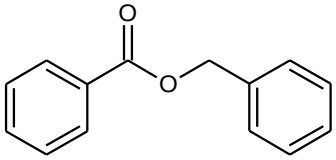
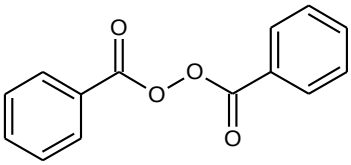
Solution to problem 3-09:

a)

A: 	**B**: 	**R** / **U**: CH_3Cl / $AlCl_3$ **S** / **V**: Br_2 / $FeBr_3$ ($AlBr_3$) **T** / **W**: $COCl_2$ / $AlCl_3$	**X**: $KMnO_4$ or MnO_2 **Y**: Mg or Li or n-BuLi **Z**: H_2O

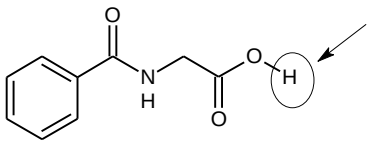
b) Toluene is relatively safe and in great amounts available. Oxidation with Oxygen (at a V_2O_5 catalyst in industry) or $KMnO_4$ or MnO_2 (in this problem) is cost-effective undertaken with chemicals which are not as poisonous as in the two other proposed ways.

c)

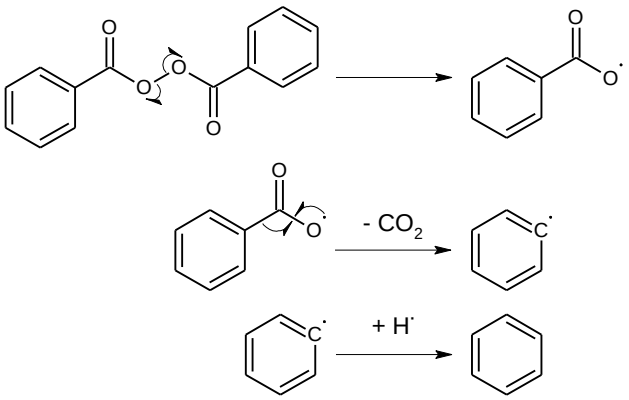
		Name and application
C		Sodium benzoate / Potassium benzoate – Preserving agent for acidic foods – Basic material for organic syntheses
D		Ethyl benzoate – Component of artificial fruit flavors – Aprotic solvent – Agent for denaturation of ethanol – Basic material for organic syntheses
E		Benzyl benzoate – Food additive in artificial flavors – Aprotic solvent – Antiparasitic insecticide – Basic material for organic syntheses
F		Dibenzoyl peroxide – radical initiator to induce polymerizations - Antiseptic and bleaching properties

Compound **I** is benzoic acid chloride.

d)

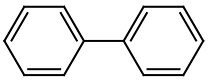


e)



Remark: The hydrogen radical in the scheme may be existent free during the polymerization or can be taken from another hydrocarbon.

$C_{12}H_{10}$ is biphenyl which is formed from two benzene radicals.



Answers of Round 3 Test 2

Solution to problem 3-11

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

Solution to problem 3-12

a) 1. Titration: Boling with acid

$CO_3^{2-} + 2\ H_3O^+ \longrightarrow 3\ H_2O + CO_2$

or $Na_2CO_3 + 2\ HCl \longrightarrow 2\ NaCl + H_2CO_3$

$H_2CO_3 \longrightarrow H_2O + CO_2$

$C_2O_4^{2-} + 2\ H_3O^+ \longrightarrow H_2C_2O_4 + 2\ H_2O$

Titration

$H_3O^+ + OH^- \longrightarrow 2\ H_2O$

or $NaOH + HCl \longrightarrow NaCl + H_2O$

$H_2C_2O_4 + 2\ OH^- \longrightarrow C_2O_4^{2-} + 2\ H_2O$

or $Na_2C_2O_4 + 2\ HCl \longrightarrow 2\ NaCl + H_2C_2O_4$

$H_2C_2O_4 + 2\ NaOH \longrightarrow Na_2C_2O_4 + 2\ H_2O$

2. Titration: Heating at 800 °C $Na_2C_2O_4 \longrightarrow Na_2CO_3 + CO$

Boiling with acid $CO_3^{2-} + 2\ H_3O^+ \longrightarrow 3\ H_2O + CO_2$

Titration $H_3O^+ + OH^- \longrightarrow 2\ H_2O$

b) 1. Titration: $n(HCl, consumed) = 2 \cdot n(Na_2CO_3)$

$0.020\ L \cdot 0.2000\ mol/L - 8.25 \cdot 10^{-3}\ L \cdot 0.1016\ mol/L = 2 \cdot n(Na_2CO_3)$

$n(Na_2CO_3) = 1.5809 \cdot 10^{-3}\ mol$

$m(Na_2CO_3) = 1.5809 \cdot 10^{-3}\ mol \cdot 105.99\ g/mol = 0.1676\ g$

⇒ percentage(**Na_2CO_3**) = 100 % · 0.1676 g/0.7371 g = 22.74 % ≈ **22.7 %**

2. Titration: $n(HCl, consumed) = 2 \cdot [n(Na_2CO_3) + n(Na_2C_2O_4)]$

$n((Na_2CO_3) = 0.2274 \cdot 0.6481\ g / (105.99\ g/mol) = 1.3905 \cdot 10^{-3}\ mol$

⇒ $0.050\ L \cdot 0.2000\ mol/L - 0.01470\ L \cdot 0.1016\ mol/L = 2 \cdot n(Na_2C_2O_4) + 2 \cdot 1.3905 \cdot 10^{-3}\ mol$

$n(Na_2C_2O_4) = (4.2532 \cdot 10^{-3} - 1.3905 \cdot 10^{-3})\ mol = 2.8627 \cdot 10^{-3}\ mol$

$m(Na_2C_2O_4) = 2.8627 \cdot 10^{-3}\ mol \cdot 134.00\ g/mol = 0.3836\ g$

⇒ percentage(**$Na_2C_2O_4$**) = 100 % · 0.3836 g/0.6481 g = 59.19 % ≈ **59.2 %**

⇒ percentage(**NaCl**) = (100 - 22.74 - 59.19) % = 18.07 % ≈ **18.1 %**

(Hint: The results should be given with 3 significant figures)

Solution to problem 3-13

a) There are two solutions to this problem because it's not clear which half cell is the anode, which one the cathode.

$\Delta E = E_{cathode} - E_{anode}$

$E_{known\ half\ cell} = E° + \frac{R \cdot T}{F} \cdot \ln 0.01$ $E_{unknown\ half\ cell} = E° + \frac{R \cdot T}{F} \cdot \ln x$

<u>1. Case:</u> The known half cell is the anode

$\Delta E = \frac{R \cdot T}{F} \cdot (\ln x_1 - \ln 0.01)$

$\ln x_1 = 0.024\ V \cdot \frac{F}{R \cdot T} + \ln 0.01$

$\ln x_1 = -3.67 \qquad x_1 = 0.025$

$c_1 = 25 \cdot 10^{-3}$ mol/L

<u>2. Case:</u> The known half cell is the cathode

$\Delta E = \frac{R \cdot T}{F} \cdot (\ln 0.01 - \ln x_2)$

$\ln x_2 = \ln 0.01 - 0.024\ V \cdot \frac{F}{R \cdot T}$

$\ln x_2 = -5.54 \qquad x_2 = 3.9 \cdot 10^{-3}$

$c_2 = 3.9 \cdot 10^{-3}$ mol/L

b) (1) $Sn^{4+} + 2\ e^- \longrightarrow Sn^{2+}$ $\quad E°_1 = +0.15\ V$ $\quad \Delta G^0_1 = -2 \cdot F \cdot 0.15\ V$

(2) $Sn^{2+} + 2\ e^- \longrightarrow Sn$ $\quad E°_2 = -0.14\ V$ $\quad \Delta G^0_2 = -2 \cdot F \cdot (-0.14\ V)$

(1)-(2) $Sn(s) + Sn^{4+}(aq) \rightleftharpoons 2\ Sn^{2+}(aq)$ $\quad \Delta G^0 = -2 \cdot F \cdot (0.15 + 0.14)\ V$

$\ln K = -\Delta G^0/RT = 2 \cdot F \cdot 0.29\ V / (R \cdot 298\ K)$ $\quad \ln K = 22.59$

$K = e^{22.59} = 6.5 \cdot 10^9$

c) At first the solubility product has to be determined:

(1) $Hg_2^{2+} + 2\ e^- \longrightarrow 2\ Hg$ $\quad E°1 = +0.79\ V$ $\quad \Delta G^0_3 = -2 \cdot F \cdot 0.79\ V$

(2) $Hg_2Cl_2 + 2\ e^- \longrightarrow 2\ Hg + 2\ Cl^-$ $\quad E°_1 = +0.27\ V$ $\quad \Delta G^0_4 = -2 \cdot F \cdot 0.27\ V$

(2)-(1) $Hg_2Cl_2 \longrightarrow Hg_2^{2+} + 2\ Cl^-$ $\quad \Delta G = -2 \cdot F \cdot (-0.52\ V)$

$\ln K = -\Delta G^0/RT = -2 \cdot F \cdot 0.52\ V / (R \cdot 298\ K)$ $\quad \ln K = -40.5 \quad (K = K_{sp})$

$K_{sp} = c(Hg_2^{2+})/1\ mol/L \cdot c(Cl^-)^2/(1\ mol/L)^2$ $\quad K_{sp} = e^{-40.5}$

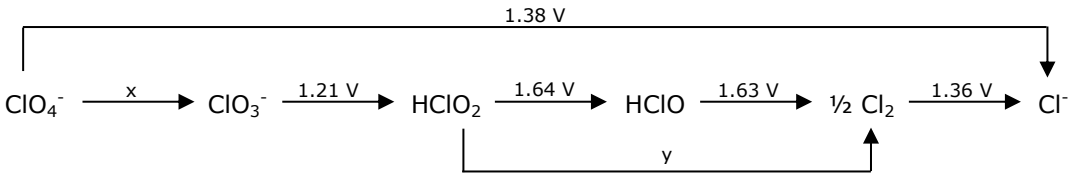
Let $c(Hg_2^{2+})/1\ mol/L = x$ $\quad \Rightarrow \quad c(Cl^-)/1\ mol/L = 2x$

$x \cdot (2x)^2 = e^{-40.5}$ $\quad x^3 = ¼ \cdot e^{-40.5}$ $\quad x = 8.64 \cdot 10^{-7}$

$S = x\ mol/L \cdot M(Hg_2Cl_2)$ $\quad S = 8.64 \cdot 10^{-7}\ mol/L \cdot 472.1\ g/mol$

$S = 0.41\ mg/L$

d)



$8 \cdot 1.38\ V = 2 \cdot x + 2 \cdot 1.21\ V + 2 \cdot 1.64\ V + 1 \cdot 1.63\ V + 1 \cdot 1.36\ V$ $\quad x = 1.18\ V$

$E°(ClO_4^- + 2\ H^+ / ClO_3^- + H_2O) = 1.18\ V$

$3 \cdot y = 2 \cdot 1.64\ V + 1.63\ V$ $\quad y = 1.64\ V$

$E°(HClO_2 + 3\ H^+ / ½\ Cl_2 + 2\ H_2O) = 1.64\ V$

Solution to problem 3-14

a) A: Cu^{2+} or $CuCl_2$, $\quad CuO + 2\ HCl\ (aq) \rightleftharpoons CuCl_2\ (aq) + H_2O\ (l)$

B: $Cu(OH)_2$, $\quad Cu^{2+} + 2\ NaOH \rightleftharpoons Cu(OH)_2 + 2\ Na^+$

C: CuI_2, $\quad Cu^{2+} + 2\ I^- \rightleftharpoons CuI_2$

D: CuI, $\quad CuI_2 \rightleftharpoons CuI + ½\ I_2$

E: $Cu(OH)_2$, $\quad NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-, \quad Cu^{2+} + 2\ OH^- \rightleftharpoons Cu(OH)_2$

F: $[Cu(NH_3)_4]^{2+}$ or $[Cu(H_2O)_2(NH_3)_4]^{2+}$, $\quad Cu(OH)_2 + 4\ NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+} + 2\ OH^-$

G: $[Cu(OH)_4]^{2-}$, $\quad Cu(OH)_2 + 2\ OH^- \rightleftharpoons [Cu(OH)_4]^{2-}$

H: CuO, $Cu(OH)_2 \xrightarrow{\Delta T} CuO + H_2O$

I: Cu, $Cu^{2+} + Mg \rightleftharpoons Cu + Mg^{2+}$

J: Cu, $CuO + CH_3OH \rightleftharpoons Cu + CH_2O + H_2O$

K: Ca_2CuO_3, $2\ CaO + CuO \xrightarrow{\Delta T} Ca_2CuO_3$

b) The combustion of the organic compound with copper oxide gives carbon dioxide and water:

$2\ CuO + C_{\text{of the organic compound}} \rightleftharpoons 2\ Cu + CO_2$

and $CuO + 2\ H_{\text{of the organic compound}} \rightleftharpoons Cu + H_2O$

The tubes are used to absorb the gaseous products. The resulting water is trapped in a tube with hygroscopic material ($CaCl_2$), the carbon dioxide is trapped in the tube with the strong base (NaOH):

$CaCl_2 + H_2O \rightleftharpoons CaCl_2 \cdot H_2O$ and $NaOH + CO_2 \rightleftharpoons NaHCO_3$

You may calculate the mass of carbon and the mass of hydrogen from the difference of the masses of the tubes. The mass of oxygen is found by the following equation

$m_{O_2} = m_{sample} - m_{H_2} - m_C$.

c) Percentage of copper in X: $\frac{0.3997}{1.256} \cdot 100\ \% = 31.84\ \%$

percentage of oxygen in X: (100 – 31.84 – 4.04 – 24.09) % = 40.03 %

$n(Cu) : n(C) : n(H) : n(O) = \frac{31.84}{63.55} : \frac{24.09}{12.01} : \frac{4.04}{1.008} : \frac{40.03}{16} = 0.50 : 2.01 : 4.01 : 2.50$

$\Rightarrow$ Empirical formula of X: $(CuC_4H_8O_5)_n$

d) Loss of mass: $\Delta m = 9.1\% \cdot M(X)$ g/mol $= 1 \cdot M(H_2O) = 1 \cdot 18.02$ g/mol

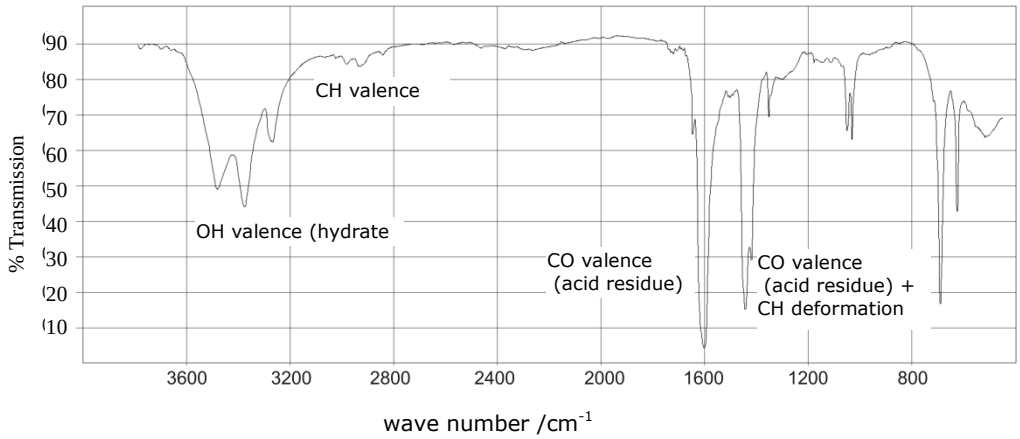
$M(X) = (18.02\ g/mol \cdot 100) / 9.1 \approx 198$ g/mol

$M(CuC_4H_8O_5) = 199.7$ g/mol $\Rightarrow n = 1$

Molecular formula of X: $CuC_4H_8O_5$, as monohydrate: $CuC_4H_6O_4 \cdot H_2O$

e) The IR spectrum shows strong C-O stretching modes at about 1600 and 1400 cm^{-1} which can be assigned to the acid residue $RCOO^-$.

$\Rightarrow$ X = $Cu(CH_3COO)_2 \cdot H_2O$, copper acetate hydrate.



f) Magnetic property: Copper(I) has no unpaired electrons (d^{10}) and is therefore diamagnetic. Copper (II) has one unpaired electron (d^9) and is therefore paramagnetic. By measuring the magnetic properties you can distinguish between Cu(I) and Cu(II).

Possibly colour: Copper(I) and copper(II) compounds may have different colour.

Copper(I) compounds are often colorless because d→d transfers are impossible. Copper(II) compounds are more or less colored depending on their ligands.

Having the same ligands copper(II) compounds are often more intensely colored than the respective copper(I) compounds.

Solution to problem 15

a) Oxygen forms: $2\ MnO_2 + 2\ H_2SO_4 \longrightarrow 2\ MnSO_4 + O_2 + 2\ H_2O$

b) Chlorine instead of oxygen is generated: $MnO_2 + 4\ HCl \longrightarrow MnCl_2 + Cl_2 + 2\ H_2O$

c) Number of formula units = 2

$\rho = \frac{m}{V}$ $\rho = \frac{2\cdot[M(Mn)+2\cdot M(O)]/N_A}{a\cdot b\cdot c} = \frac{2\cdot[54.94\,\frac{g}{mol}+2\cdot 16.00\,\frac{g}{mol}]/6.022\cdot 10^{23}\ mol^{-1}}{(4.4\cdot 10^{-8}\ cm)^2\ \cdot 2.9\cdot 10^{-8}\ cm}$ $\rho = 5.1\ g/cm^3$

d) n(Cs) : n(O) $= \frac{80.61}{132.9} : \frac{19.39}{16} = 1 : 2 \Rightarrow CsO_2$

n(H) : n(O) $= \frac{5.88}{1.008} : \frac{94.12}{16} = 1 : 1 \Rightarrow H_2O_2$

e) $2\ CsO_2 + H_2O_2 \longrightarrow 2\ CsOH + O_2$

f) Pyrolusite is an oxide with oxygen having the oxidation state -2, not a peroxide.

Oxides: such as CrO_2, MnO_2, PbO_2, SnO_2, GeO_2

Peroxides: such as CaO_2, BaO_2, MgO_2

Solution to problem 3-16

a) Manganous sulfate: $MnSO_4$

b) $2\ MnO_4^- + 5\ H_2C_2O_4 + 6\ H^+ \longrightarrow 2\ Mn^{2+} + 10\ CO_2 + 8\ H_2O$

c) $MnO_4^- + 4\ Mn^{2+} + 8\ H^+ \longrightarrow 5\ Mn^{3+} + 4\ H_2O$

Comproportionation

d) If a reaction of 1. order takes place the decrease of concentration in equal time intervals should be the same, e.g. 0 min ⟶ 9 min (Δc = - 4.77 mmol) and 9 min ⟶ 18 min (Δc = - 3.60 mmol). This is not the case ⇒ reaction order ≠ 0.

Reaction of 1. order, graphically: The image of lnc = f(t)) should be a straight line with the slope -k.

Reaction of 1. order by calculation: $c = c_0 \cdot c^{-kt} \Rightarrow \ln c = \ln c_0 - kt \Rightarrow k = \frac{\ln c_0 - \ln c}{t}$

n	0	1	2	3	4	5	6	7
t in min	0	9.0	18.0	25.0	32.0	44.0	50.0	56.0
c(complex) in mmol/L	20.07	15.30	11.70	9.51	7.74	5.34	4.47	3.74
k in 10^{-2} min^{-1}	-	3.015	2.998	2.988	2.978	3.009	3.004	3.000

The values of k match acceptably ⇒ reaction of 1. order.

Mean value k= $3.00\cdot 10^{-2}$ min^{-1} = $5.00\cdot 10^{-4}$ s^{-1}

(There are other possibilities to calculate.)

e) $k = A \cdot e^{-Ea/RT} \quad \Rightarrow \quad k_1 \cdot e^{Ea/RT_1} = k_2 \cdot e^{Ea/RT_2}$

$\ln(k_1/k_2) = \frac{Ea}{R \cdot T_2} - \frac{Ea}{R \cdot T_1}$ $\qquad Ea = \frac{\ln(k_1/k_2) \cdot R}{1/T_2 - 1/T_1}$

$Ea = \frac{\ln(3.80 \cdot 10^{-3} / 5.00 \cdot 10^{-4}) \cdot 8.314\ JK^{-1}mol^{-1}}{1/287\ K - 1/303\ K}$ $\qquad Ea = 91.6\ kJmol^{-1}$

f) $½ \cdot c_0 = c_0 \cdot e^{-kt_{1/2}} \quad \Rightarrow\ t_{1/2} = \ln 2 / k$ und $k = A \cdot e^{-Ea/RT}$

You may use the equation $k_1 \cdot e^{Ea/RT_1} = k_2 \cdot e^{Ea/RT_2}$ to determine k.

$k_{80\ °C} = k_{30\ °C} \cdot e^{Ea/RT_1} / e^{Ea/RT_2}$

$k_{80\ °C} = 3.80 \cdot 10^{-3}\ s^{-1} \cdot e^{(91600\ J/mol)/(8.314\ J/(mol \cdot K) \cdot 303\ K)} / e^{(91600\ J/mol)/(8.314\ J/(mol \cdot K) \cdot 353\ K)}$

$k_{80\ °C} = 0.655\ s^{-1} \quad \Rightarrow \quad t_{1/2.\ 80\ °C} = 1.06\ s$

($Ea = 92{,}0\ kJmol^{-1}$ leads to $k_{80\ °C} = 0.670\ s^{-1}$ and $t_{1/2,\ 80\ °C} = 1.03\ s$)

g) In all cases the reaction rate has the units conc · time^{-1} , e.g. mol·L^{-1}·s^{1}.

i) Reaction order 2, k_i: conc^{-1} · time^{-1}

ii) Reaction order 0, k_{ii}: conc · time^{-1}

iii) Reaction order 1½, k_{iii}: conc$^{-1/2}$ · time^{-1}

h) E.g. $A \longrightarrow B + C$ and $A + B \longrightarrow C$

i) I Activation energy of the reaction $A + B \longrightarrow X$ and
Activation energy of the reaction $A + B \longrightarrow C + D$

II Reaction energy of $A + B \longrightarrow X$

III Activation energy of the reaction $C + D \longrightarrow X$

IV Reaction energy of $A + B \longrightarrow C + D$

V Activation energy of the reaction $X \longrightarrow C + D$

j) Correct answers: i), iv), v), vi), viii)

Solution to problem 3-17

a)

Priority of the substituents	Compound 1	Compound 2
1	$CH_2C_2H_5$	Br
2	CH_2CH_3	Cl
3	CH_3	F
4	H	H

- Let the substituent with the lowest priority (4) point to the back, the remaining substituents now appear to radiate towards us like the spokes on a steering wheel.
- The curved arrow drawn from the highest to the second highest to the third highest priority substituent is clockwise ⇒ R configuration

b) Priorities: Cl > OH > CH_3 > H

i) R configuration ii) S configuration iii) R configuration

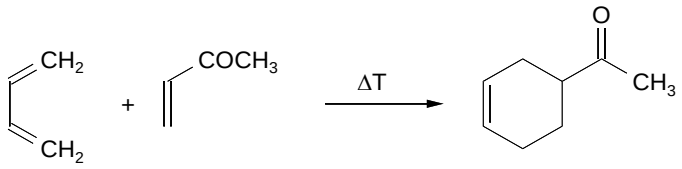
c) Pair 1: identical configurations

Pair 2: different configurations – enantiomerism

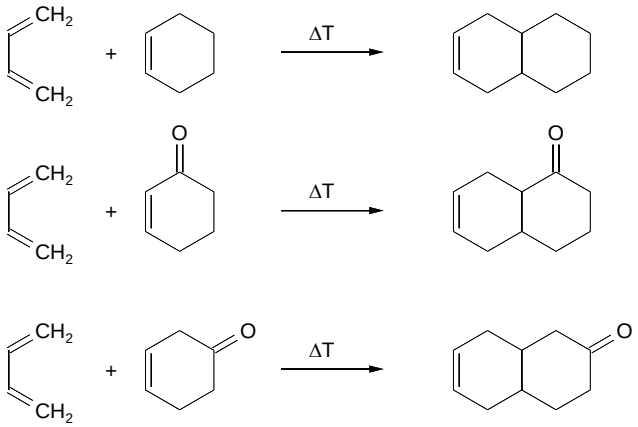
Pair 3: different configurations – enantiomerism

Solution to problem 3-18

a) Compound 2 leads to the product 3-cyclohexenyl methyl ketone:

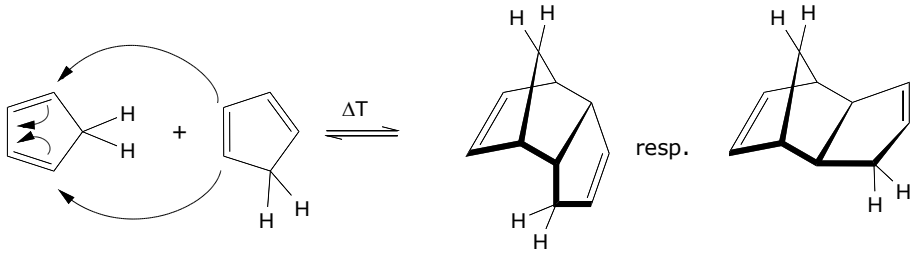


b)



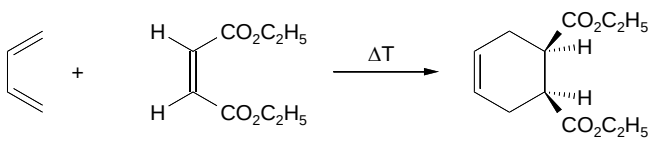
c) The more carbon atoms adjacent to the double bond are polarized the faster the product can form. The polarization is favoured by electron drawing substituents e.g. C=O ⇒ the second reaction is favoured.

d)

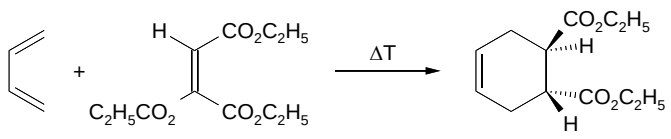


endo-Dicyclopentadiene exo-Dicyclopentadiene

e)



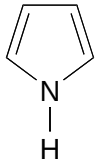
Maleic acid diethylester



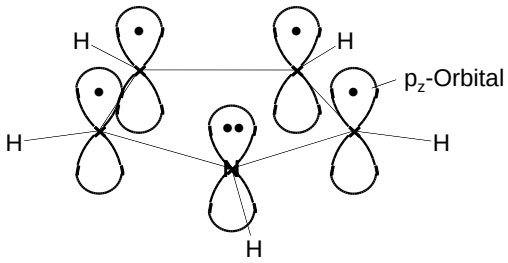
Fumaric acid diethylester

Solution to problem 3-19

a)



b)

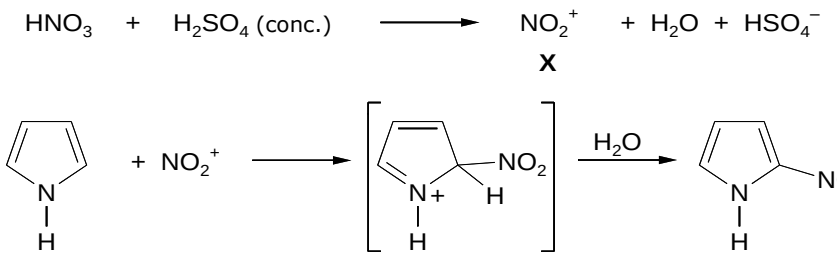


Pyrrole has 6 π electrons and is aromatic. Each of the four carbon atoms contributes one π electron and the sp^2-hybridized nitrogen contributes two more electrons from its lone pair.

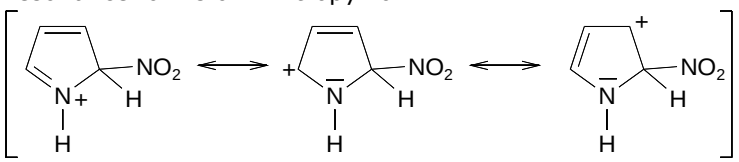
Because the nitrogen lone pair is part of the aromatic sextet, protonation on nitrogen would destroy the aromaticity of the ring. The nitrogen atom in pyrrole is therefore less electron-rich, less basic and less nucleophilic than the nitrogen in an aliphatic amine.

By the same token pyrrole does not react as if having normal double bonds. The carbon atoms of pyrrole are more electron-rich and more nucleophilic than typical double-bond carbons. The pyrrole ring is therefore reactive towards electrophiles.

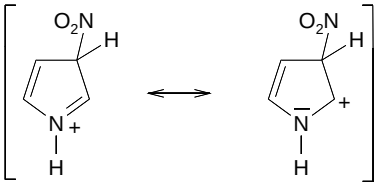
c)



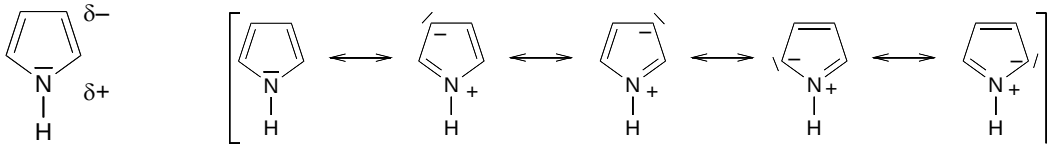
d) Resonance forms of 2-nitropyrro



Resonance forms of 3-nitropyrrole:



e)



Answers Round 4 (theoretical)

Solution to problem 4-01

a) $3\ Ag(s) + NO_3^-(aq) + 4\ H^+(aq) \longrightarrow 3\ Ag^+(aq) + NO(g) + 2\ H_2O(l)$ (1)

b) $\Delta G = 3\cdot\Delta G°_f(Ag^+) + \Delta G°_f(NO) + 2\cdot\Delta G°_f(H_2O) - [3\cdot\Delta G°_f(Ag) + \Delta G°_f(NO_3^-) + 4\cdot\Delta G°_f(H^+)]$
$\Delta G = [3\cdot 77.1 + (90.3 - 0.298\cdot(210.6 - ½\cdot 191.5 - ½\cdot 205.0)) + 2\cdot(-285.9 - 0.298(69.9 - 130.6 - ½\cdot 205.0)) - (-110.5)]$ kJ/mol
$\Delta G = -46.1$ kJ/mol $< 0 \Rightarrow$ The reaction is exergonic.

c) The standard potential of $NO_3^- + 4\ H^+ + 3\ e^- \longrightarrow NO + 2\ H_2O$ is determined and compared with
$E°(Au^{3+} + 3\ e^- \longrightarrow Au)$.
You can get reaction (1) by combining two half-reactions:
(2) $Ag^+(aq) + e^- \longrightarrow Ag(s)$ $E_2° = 0.800$ V $\Delta G_2° = -1\cdot F\cdot 0.800$ V
(3) $NO_3^-(aq) + 4\ H^+(aq) + 3\ e^- \longrightarrow NO(g) + 2\ H_2O(l)$ $E_3° = x$ $\Delta G_3° = -3\cdot F\cdot x$
(1) = (3) − 3·(2) $\Rightarrow \Delta G_1° = \Delta G_3° - 3\cdot\Delta G_2°$
-45000 J/mol = - 3·F·(x − 0.800 V)
$\frac{45000\ J/mol}{3\cdot 96485\ C/mol}$ = x − 0.800 V $\Rightarrow E°(NO_3^- + 4\ H^+ + 3\ e^- \longrightarrow NO + 2\ H_2O) = 0.955$ V
Thus silver with the smaller redox potential (0.8 V) can be oxidized but not gold with a higher potential (1.42 V).
(The standard potentials refer to solutions with the activities 1. Even if you assume a very high activity the redox potential does not exceed 1 V.)

Solution to problem 4-02

a) Step 2 has the smallest activation energy thus the rate constant for $B \longrightarrow C$ (k_2) is very much larger than that for $A \longrightarrow B$ (k_1). Since the moment any B is formed it reacts to C resulting in the concentration of B being very small. This corresponds to plot iii).

b) We can apply the steady state approximation to NH^+, NH_2^+, NH_3^+ und NH_4^+:

$d(NH^+)/dt = 0 = k_1\cdot[N^+]\cdot[H_2] - k_2\cdot[NH^+]\cdot[H_2]$ $\Rightarrow$ $[NH^+] = \frac{k_1\cdot[N^+]}{k_2}$

$d(NH_2^+)/dt = 0 = k_2\cdot[NH^+]\cdot[H_2] - k_3\cdot[NH_2^+]\cdot[H_2]$

$\Rightarrow$ $[NH_2^+] = \frac{k_2\cdot[NH^+]}{k_3} = \frac{k_2\cdot k_1\cdot[N^+]}{k_3\cdot k_2}$ $\Rightarrow$ $[NH_2^+] = \frac{k_1\cdot[N^+]}{k_3}$

$d(NH_3^+)/dt = 0 = k_3\cdot[NH_2^+]\cdot[H_2] - k_4\cdot[NH_3^+]\cdot[H_2]$

$\Rightarrow$ $[NH_3^+] = \frac{k_3\cdot[NH_2^+]}{k_4}$ $\Rightarrow$ $[NH_3^+] = \frac{k_1\cdot[N^+]}{k_4}$

$d(NH_4^+)/dt = 0 = k_4\cdot[NH_3^+]\cdot[H_2] - k_5\cdot[NH_4^+]\cdot[e^-] - k_6\cdot[NH_4^+]\cdot[e^-]$

$\Rightarrow$ $[NH_4^+] = \frac{k_4\cdot[NH_3^+]\cdot[H_2]}{(k_5+k_6)\cdot[e^-]}$ $\Rightarrow$ $[NH_4^+] = \frac{k_1\cdot[N^+]\cdot[H_2]}{(k_5+k_6)\cdot[e^-]}$

c) $d(NH_3)/dt = k_5 \cdot [NH_4^+] \cdot [e^-] = \frac{k_1 \cdot k_5 \cdot [N^+] \cdot [H_2]}{k_5 + k_6} = k \cdot [N^+] \cdot [H_2]$ with $k = \frac{k_1 \cdot k_5}{k_5 + k_6}$

d) The first reaction is the reversible dissociation of methanoic acid to give methanonate and H_3O^+. In the second reaction methanoate is oxidized by bromine:

1) $HCOOH + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} HCOO^- + H_3O^+$ (fast equilibrium)

2) $HCOO^- + Br_2 + H_2O \xrightarrow{k_2} CO_2 + 2\ Br^- + 2\ H_3O^+$ (very slow).

Reaction 2) is rate-limiting $\Rightarrow$ $v = k_2 \cdot [HCOO^-] \cdot [Br_2]$. Due to the great concentration water is included here and in further calculations in k_2 and other constants, respectively. Assuming that the equilibrium between methanoic acid and methanoate is largely undisturbed by the reaction of latter with bromine we can write the usual equilibrium constant K_c as

$K_c = \frac{[HCOO^-] \cdot [H_3O^+]}{[HCOOH]}$ $\Rightarrow [HCOO^-] = K_c \cdot \frac{[HCOOH]}{[H_3O^+]}$.

$v = k_2 \cdot [HCOO^-] \cdot [Br_2] = k_2 \cdot K_c \cdot \frac{[HCOOH]}{[H_3O^+]} \cdot [Br_2]$

$\Rightarrow$ $v = k_{obs} \cdot \frac{[HCOOH] \cdot [Br_2]}{[H_3O^+]}$ with $k_{obs} = k_2 \cdot K_c$.

(Using the steady state approximation for $HCOOH^-$ and including the solvent water into k_1 results in

$v = k_2 \cdot \frac{k_1 \cdot [HCOOH] \cdot [Br_2]}{k_{-1} \cdot [H_3O^+] + k_2 \cdot [Br_2]}$. Following the hint in the problem text you may assume $k_2 \ll k_{-1}$

$\Rightarrow$ $v = k_2 \cdot \frac{k_1 \cdot [HCOOH] \cdot [Br_2]}{k_{-1} \cdot [H_3O^+]}$ with $k_{obs} = \frac{k_1 \cdot k_2}{k_{-1}}$)

Solutions to problem 4-03

a) $[Ar]3d^5 4s^2$

b) The most stable oxidation state is +II because after the removal of two 4s electrons all five 3d orbitals contain a single electron (half occupied d-shell, d^5 electron configuration).

c) i) $MnO_4^- + 8\ H^+ + 5\ e^- \rightleftharpoons Mn^{2+} + 4\ H_2O$

ii) $MnO_4^- + 4\ H^+ + 3\ e^- \rightleftharpoons MnO_2 + 2\ H_2O$

iii) $MnO_4^- + e^- \rightleftharpoons MnO_4^{2-}$

d) Iron as Fe^{2+} in a solution of sulfuric acid. Hydrochloric acid should not be used because permanganate may oxidize chloride ions, too, to form chlorine.

e) At the endpoint there is no longer a decolourization of permanganate and the solution starts to become purple.

f) $MnSO_4 + 2\ KNO_3 + 2\ Na_2CO_3 \rightleftharpoons Na_2MnO_4 + 2\ KNO_2 + Na_2SO_4 + 2\ CO_2$

$3\ Na_2MnO_4 + 4\ H^+ \rightleftharpoons MnO_2 + 2\ NaMnO_4 + 2\ H_2O + 4\ Na^+$

g) $K_L = c(S^{2-}) \cdot c(Mn^{2+})/(c°)^2$ $10^{-13} = c(S^{2-}) \cdot 10^{-5}/c°$ $c(S^{2-})/c° = 10^{-8}$

Calculation of the concentration of sulfide depending on the pH value:

$H_2S \rightleftharpoons H^+ + HS^- \rightleftharpoons 2\ H^+ + S^{2-}$

$K_{a1} = \frac{c(H^+)\cdot c(HS^-)}{c(H_2S)\cdot c^0} = 10^{-6.9}$ $K_{a2} = \frac{c^2(H^+)\cdot c(S^{2-})}{c(H^+)\cdot c(HS^-)\cdot c^0} = \frac{c(H^+)\cdot c(S^{2-})}{\cdot c(HS^-)\cdot c^0} = 10^{-12.9}$

$K_{a1}\cdot K_{a2} = \frac{c^2(H^+)\cdot c(S^{2-})}{c(H_2S)\cdot (c^0)^2} = 10^{-19.8}$

$c(H_2S) = 10^{-1}$ mol/L:

$c^2(H^+)\cdot c(S^{2-}) = 10^{-20,8}\cdot (c°)^3$, $c(S^{2-}) = 10^{-20,8}\cdot (c°)^3 / c^2(H^+)$

$\Rightarrow$ $c(H^+) = \sqrt{\frac{10^{-5}\cdot 10^{-20.8}}{10^{-13}}}$ mol/L $\approx 4\cdot 10^{-7}$ mol/L $\Rightarrow$ pH = 6,4

h) $Mn^{2+} + 2\ OH^- \rightleftharpoons Mn(OH)_2$

$2\ Mn(OH)_2 + ½\ O_2 \rightleftharpoons 2\ MnO(OH) + H_2O$ (resp. $Mn_2O_3 \cdot H_2O + H_2O$)

$Mn_2O_3 + 6\ H^+ + 9\ H_2O \rightleftharpoons 2\ [Mn(H_2O)_6]^{3+}$

The oxidation may partly end up in Mn(IV):

$Mn(OH)_2 + ½\ O_2 \rightleftharpoons MnO(OH)_2$ (resp. $MnO_2 \cdot H_2O$)

i) A mixture of manganese(II) hydroxide and the hexammincomplex forms:
$Mn(OH)_2$ / $[Mn(NH_3)_6]^{2+}$

j)

Anion	MnO_4^{4-}	MnO_4^{3-}	MnO_4^{2-}	MnO_4^-
Oxidation state	+IV	+V	+VI	+VII
Name	Manganite	Hypomanganate	Manganate	Permanganate

k) The possible sodium tetraoxomanganates are Na_4MnO_4, Na_3MnO_4, Na_2MnO_4 and $NaMnO_4$. The manganese content of a compound $4X \cdot NaOH \cdot 48\ H_2O$ is

X	Na_4MnO_4	Na_3MnO_4	Na_2MnO_4	$NaMnO_4$
m-% Manganese	12.6	13.3	14.1	14.9

Solid X should look blue due to its content of Mn(V).

l) $2\ Na_3MnO_4 + 2\ H_2O \rightleftharpoons Na_2MnO_4 + MnO_2 + 4\ NaOH$

Solution to problem 4-04

a) $[Cr(H_2O)_6]^{3+} \rightleftharpoons [Cr(H_2O)_5(OH)]^{2+} + H^+$

b) i) $Ba^{2+} + SO_4^{2-} \rightleftharpoons BaSO_4$

ii) $K^+ + ClO_4^- \rightleftharpoons KClO_4$

iii) $Cr^{3+} + 3\ OH^- \rightleftharpoons Cr(OH)_3$ bzw.
$[Cr(H_2O)_6]^{3+} + 3\ OH^- \rightleftharpoons Cr(OH)_3 + 6\ H_2O$

c) $[Cr(H_2O)_3Cl_3] \cdot 3\ H_2O \rightleftharpoons [Cr(H_2O)_4Cl_2]Cl \cdot 2\ H_2O \rightleftharpoons [Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$
(green) $\rightleftharpoons [Cr(H_2O)_6]Cl_3$ (violet)

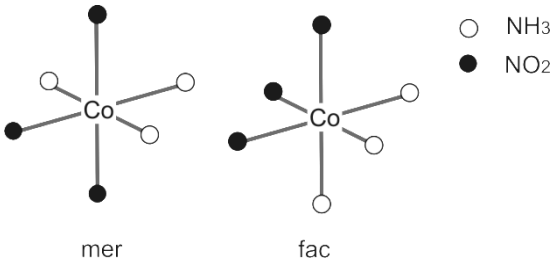
d) $[Co(H_2O)_6]^{2+} + 4\ Cl^- \overset{\Delta T}{\rightleftharpoons} [CoCl_4]^{2-} + 6\ H_2O$

e) i) $Cl^- + Ag^+ \rightleftharpoons AgCl$

ii) There is no reaction with sodium hydroxide solution.

f) $CoCl_3 \cdot (NH_3)_5$ should show the smallest conductivity. In an aqueous solution there are three ions: $[Co(NH_3)_5Cl]^{2+} + 2\ Cl^-$. The other two salts dissociate in water forming four ions.
In the case of $[Co(NH_3)_5H_2O]Cl_3$ you may expect that by and by the ligand water is substituted by chloride – then there would be only three ions – but this should not be considered here.

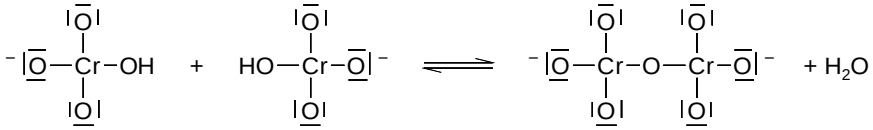
g) In an aqueous solution this complex does not form ions: $[Co(NH_3)_3(NO_2)_3]$
Isomers:



Solution to problem 4-05

a) $2\ CrO_4^{2-} + 2\ H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$
Alkaline solution: predominantly chromate
Acidic solution: predominantly dichromate
An intermediate stage is a hydrogenchromate ion:

$2\ CrO_4^{2-} + 2\ H^+ \rightleftharpoons 2\ HCrO_4^-$
$2\ HCrO_4^- \rightleftharpoons Cr_2O_7^{2-} + H_2O$



b) A/B/C: Dimethyl chlorosilane, Trimethyl chlorosilane, Methyl trichlorosilane
$2\ CH_3Cl + Si \rightleftharpoons (H_3C)_2SiCl_2$
$2\ (H_3C)_2SiCl_2 \rightleftharpoons (H_3C)_3SiCl + (H_3C)SiCl_3$ and
$4\ CH_3Cl + 2\ Si \rightleftharpoons (H_3C)_3SiCl + (H_3C)SiCl_3$, resp.

c) and d)
$(H_3C)_2SiCl_2 + 2\ H_2O \rightleftharpoons (H_3C)_2Si(OH)_2 + 2\ HCl$
$2\ (H_3C)_2Si(OH)_2 \rightleftharpoons (H_3C)_2(OH)Si\text{-}O\text{-}Si(OH)(CH_3)_2 + H_2O$ and higher condensation products.

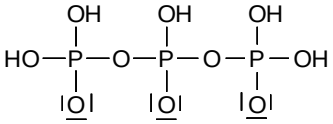
$(H_3C)_3SiCl + H_2O \rightleftharpoons (H_3C)_3Si(OH) + HCl$
$2\ (H_3C)_3Si(OH) \rightleftharpoons (H_3C)_3Si\text{-}O\text{-}Si(CH_3)_3$ no further condensation possible.

$(H_3C)SiCl_3 + 3\ H_2O \rightleftharpoons (H_3C)Si(OH)_3 + 3\ HCl$
$2\ (H_3C)Si(OH)_3 \rightleftharpoons (H_3C)(OH)_2Si\text{-}O\text{-}Si(OH)_2(CH_3)$ and higher condensation products, highest degree of cross linking.

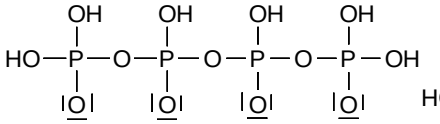
The reactions are almost quantitative because

- hydrogenchloride forms which escapes and is no longer relevant for the equilibrium.
- silanols react to form polysiloxanes (silcones) which are no longer relevant for the equilibrium, too.

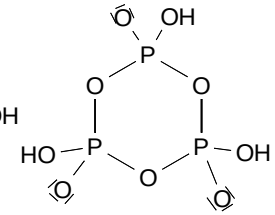
e) The acidity of the protons in the polyphosphoric acids is different. In the case of a chain-like molecule the hydrogen atoms in the chain react strongly acidic the ones at the ends only weakly. In the case of an annular molecule all hydrogen atoms have the same acidity.



$H_5P_3O_{10}$



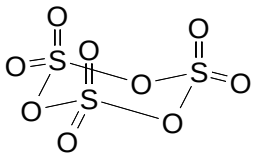
$H_6P_4O_{13}$

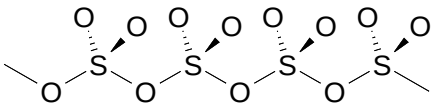


$H_3P_3O_9$

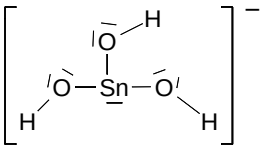
f) Solid SO_3 exists in three modifications,

γ-SO_3 forms trimeric molecules, α- and ß-SO_3 exist in chains:

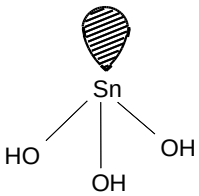




g) Lewis structure



VSEPR: trigonal pyramid



For example

$2\ [Sn(OH)_3]^- \rightleftharpoons [Sn(OH)_2OSn(OH)_2]^{2-} + H_2O$

h) $2\ H_3AsS_3 \rightleftharpoons 3\ H_2S + As_2S_3$

$2\ H_3AsS_4 \rightleftharpoons 3\ H_2S + As_2S_5$

Solution to problem 4-06

a) -80 °C: Gas $\longrightarrow$ solid CO_2

0 °C: Gas $\longrightarrow$ fluid CO_2 $\longrightarrow$ solid CO_2

100 °C: Only gas (at high pressure it is called "supercritical fluid"), no phase transition

b) There is no way. All states at 1.013 bar at any temperature lie outside the region in which fluid CO_2 is stable.

c) CO_2 in steel gas bottles is liquid.

The vertical axis is logarithmical. By interpolation you get ~ 60 bar (exactly 57.5 bar).

Even when the content of the bottle comes to an end the vapor pressure of the liquid stays at 57.5 bar. You can find the remaining content of CO_2 by weighing the bottle and comparing the weight with that of the empty bottle.

d) In phase diagrams boundaries separate the regions of stable phases. At the conditions on these boundary lines both phases are in equilibrium. You may consider these lines as a function: p = f(T).
The expression $\frac{dp}{dT}$ denotes the slope of these functions.

e) In the equation $\frac{dp}{dT} = \frac{\Delta H}{T \cdot \Delta V}$ are T = 350.73 K and

$\Delta V = (163.3 - 161.0)\ cm^3/mol = 2.3 \cdot 10^{-6}\ m^3/mol$.

If you approximate the boundary by an straight line you may calculate the slope:

$\frac{dp}{dT} = \frac{(101.3-1.013)\cdot 10^5 Pa}{(351.26-350.75)K}$ $\frac{dp}{dT} = 19.66 \cdot 10^6$ Pa/K

$\Rightarrow$ $\Delta H = 19.66 \cdot 10^6$ Pa/K $\cdot$ 350.73 K $\cdot$ $2.3 \cdot 10^{-6}$ m^3/mol

$\Delta H = 15.9 \cdot 10^3$ m^3·Pa/mol = 15.9 kJ/mol (1 Pa = 1 N/m^2 = 1 Nm/m^3 = 1 J/m^3)

It is only an approximation because the function p = f(T) is not necessarily a straight line. Thus the slope can be determined only approximately.

f) In the equation $\frac{dp}{dT} = \frac{\Delta H}{T \cdot \Delta V}$ the slope of the boundary line is $\frac{dp}{dT}$. The slope of the boundary between the solid and the fluid phase is negative. ΔH, being the heat of fusion as well as the temperature, is positive

$\Rightarrow \Delta V = V_{fluid} - V_{solid} < 0$ $\Rightarrow$ $V_{fluid} < V_{solid}$

The ratio of the molar volume is reciprocally proportional (**?**) to the densities: $\Rightarrow \rho_{fluid} > \rho_{solid}$

or by calculation

$\rho_{fluid} = \frac{M}{V_{fluid}}$ $\Rightarrow$ $V_{fluid} = \frac{M}{\rho_{fluid}}$

$\rho_{solid} = \frac{M}{V_{solid}}$ $\Rightarrow$ $V_{solid} = \frac{M}{\rho_{solid}}$

$\frac{M}{\rho_{fluid}} < \frac{M}{\rho_{solid}}$ $\Rightarrow$ $\frac{1}{\rho_{luid}} < \frac{1}{\rho_{solid}}$ $\Rightarrow \rho_{solid} < \rho_{fluid}$

Solution to problem 4-07

a) $E^{\circ\prime} = E^\circ + R \cdot T/(n \cdot F) \cdot \ln (1 \cdot 10^{-7})^m$

(i) m = 1: $E^{\circ\prime} = -0.11\ V + \frac{8.314 \cdot 298.15}{2 \cdot 96485}\ V \cdot \ln 1 \cdot 10^{-7}$ $E^{\circ\prime} = -0.32$ V

(ii) m = 4: $E^{\circ\prime} = 1.23\ V + \frac{8.314 \cdot 298.15}{4 \cdot 96485}\ V \cdot \ln (1 \cdot 10^{-7})^4$ $E^{\circ\prime} = +0.82$ V

b) $\Delta G' = \Delta G^{\circ\prime} + RT \ln Q$

$\Delta G' = -30.5$ kJ/mol + RT $\ln \frac{c(ADP)\cdot(1\ mol/L)^{-1} \cdot c(P_i)\cdot(1\ mol/L)^{-1}}{c(ATP)\cdot(1\ mol/L)^{-1}}$

$\Delta G' = -30500\ J/mol + (8.314 \cdot 298.15)\ J/mol \cdot \ln(0.00025 \cdot 0.00165/0.00225)$

$\Delta G' = -30.5\ kJ\ mol^{-1} - 21.3\ kJ\ mol^{-1}$ $\Delta G' = -51.8\ kJ/mol$

c) $\Delta G^{o\prime} = -RT \cdot \ln K_2'$ $K_2' = e^{-\Delta G°'/RT}$

$K_2' = e^{-13800\ J/mol\ /\ (8.314\ J/(mol\ K) \cdot 298.15\ K)}$ $K_2' = 0.0038$

$\frac{c(glucose-6-phosphate^{2-})}{c(Glucose)} = K_2' \cdot c(P_i)/(1\ mol/L)$

$\frac{c(glucose-6-phosphate^{2-})}{c(Glucose)} = 0.0038 \cdot 0.00165 = 6.3 \cdot 10^{-6}$

d) $\Delta G°'(3) = \Delta G°'(1) + \Delta G°'(2)$

$\Delta G°'(3) = -30.5\ kJ\ mol^{-1} + 13.8\ kJ\ mol^{-1}$ $\Delta G°'(3) = -16.7\ kJ\ mol^{-1}$

$\Delta G^{o\prime} = -RT \cdot \ln K_3'$ $K_3' = e^{-\Delta G°'/RT}$

$K_3' = e^{16700\ J/mol\ /\ (8.314\ J/(mol\ K) \cdot 298.15\ K)}$ $K_3' = 843$

$K_3' = \frac{c(glucose-6-phosphate^{2-}) \cdot c(ADP)}{c(glucose) \cdot c(ATP)}$

$\frac{c(glucose-6-phosphate^{2-})}{c(glucose)} = K_3' \cdot \frac{c(ATP)}{\cdot c(ADP)} = 843 \cdot 2.25/0.25 = 7587$

e) The overall reaction is the sum of two reactions

(iii) $ADP + P_i + H^+ \longrightarrow ATP + H_2O$ $\Delta G°'(iii) = +30.5\ kJ\ mol^{-1}$

(iv) $H_2O + NADP^+ \longrightarrow ½\ O_2 + NADPH + H^+$ $\Delta G°'(iv)$

$\Delta G°'(iv)$ can be determined from the standard biochemical redox potentials:

$NADP^+ + 2\ H^+ + 2\ e^- \longrightarrow NADPH$ $E°' = -0.32\ V$ $\Delta G°' = 2 \cdot F \cdot 0.32\ V$

$O_2 + 4\ H^+ + 4\ e^- \longrightarrow 2\ H_2O$ $E°' = +0.82\ V$ $\Delta G°' = -4 \cdot F \cdot 0.82\ V$

$\Delta G°'(iv) = 2 \cdot F \cdot 0.32\ V - ½ \cdot (-4 \cdot F \cdot 0.82\ V)$ $\Delta G°'(iv) = 220\ kJ/mol$

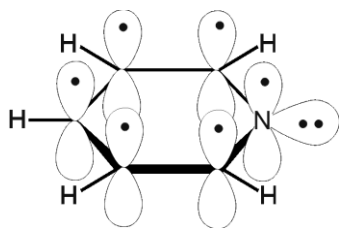
$\Rightarrow \Delta G°'(overall) = \Delta G°'(iii) + \Delta G°'(iv)$ $\Delta G°'(overall) = 250.5\ kJ/mol$

The overall light reaction does not contain any protons hence the concentration of H^+ does not occur in the expression for the equivalent $\Rightarrow \Delta G° = \Delta G°'$.

f) $E_{Photon} = h \cdot c/\lambda$

$\frac{8800 \cdot 10^3\ J/mol}{N_A} = n \cdot \frac{6.63 \cdot 10^{-34}\ J \cdot s \cdot 3 \cdot 10^8\ m/s}{680 \cdot 10^{-9}\ m}$ $\Rightarrow n = \frac{8800 \cdot 10^3 \cdot 680 \cdot 10^{-9}}{6.023 \cdot 10^{23} \cdot 6.63 \cdot 10^{-34} \cdot 3 \cdot 10^8}$ $n \approx 50$

Solution to problem 4-08



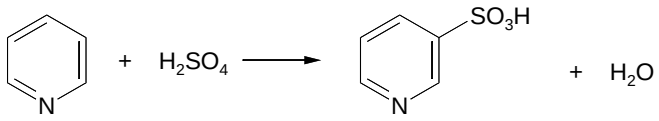
a)

6 π electrons in the ring ⇒ pyridine is an aromatic compound.

The lone electron pair does not take part in the aromatic system and occupies an sp^2 orbital in the plane of the ring. Thus it may function as an electron acceptor (base).

The electron density of the ring is decreased by the electron-withdrawing inductive effect of the electronegative nitrogen atom. Thus the ring acts as positive, the nitrogen as negative end of the dipole.

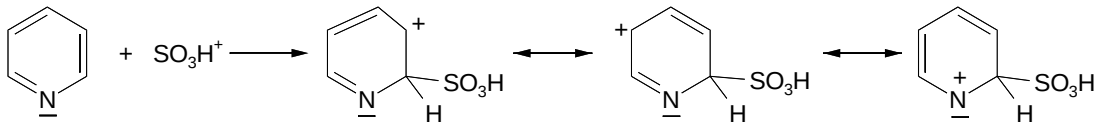
b)



3-Pyridine sulfonic acid

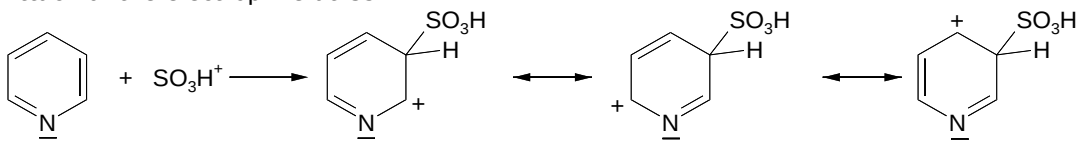
Pyridine undergoes electrophilic aromatic substitution.

c) Attack of the electrophile at C2:



Unfavorable

Attack of the electrophile at C3:

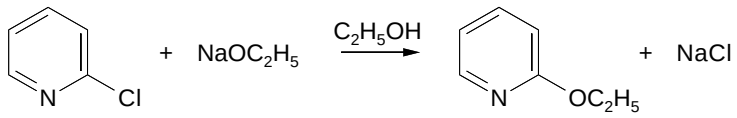


The attack of the electrophilic at C3 leads to an intermediate where the positive charge is distributed over three C atoms of the ring.

The attack of the electrophilic at C2 leads to an intermediate where the positive charge is distributed over two C atoms of the ring and the nitrogen atom which is energetically more unstable.

Thus the yield of the C3 product is higher than that of the C2 product.

d)



Nucleophilic aromatic substitution.

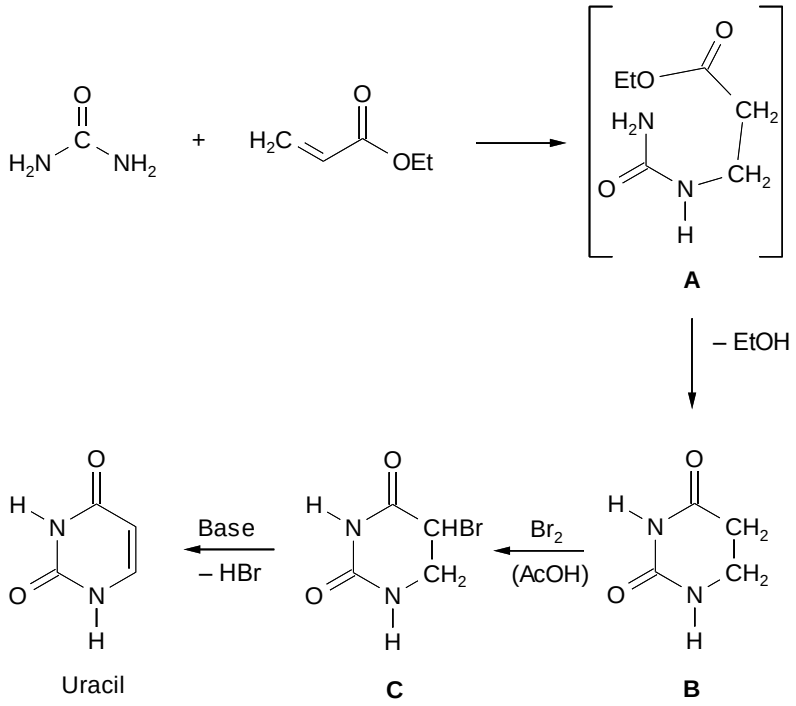
e)

Substitution	Benzene	Pyridine
Electrophilic aromatic substitution (b)	A lot of substitutions with many applications of products high yield	Inhibited, possible only under drastic conditions low yield
Nucleophilic aromatic substitution (d)	Possible only under special conditions (Reduced charge density in the ring e.g. by Cl substituents), low yield	High reactivity with a lot of substitutions and many applications of the products, high yield

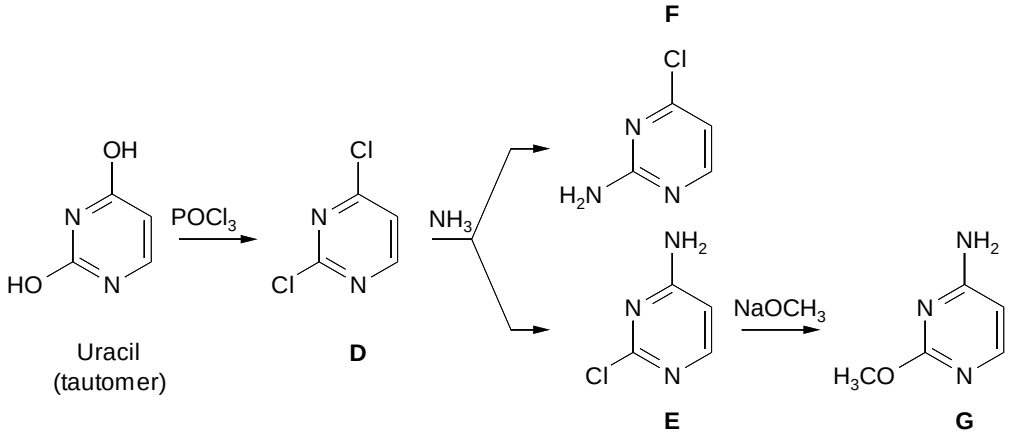
Nucleophilic substitutions are facilitated by the nitrogen atom in the pyridine ring. The stronger electronegative nitrogen atom decreases the electron density of the ring (compared to benzene) and thus stabilizes the intermediate anion and increases the yield.

Reaction of an electrophilic with the positively polarized carbon atoms is difficult and thus pyridine shows a low reactivity (compared to benzene) towards electrophilic substitution and a low yield.

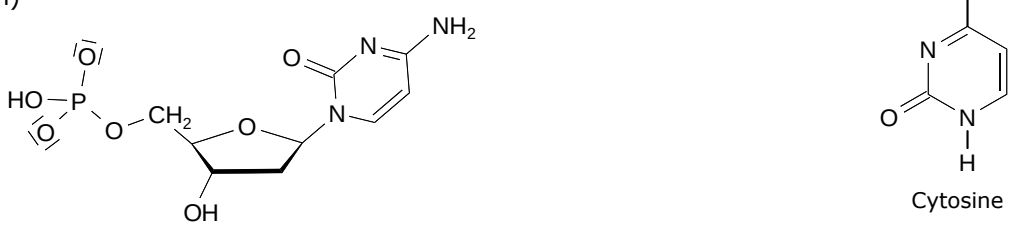
f) Formation of uracil:



g) Formation of Cytosine

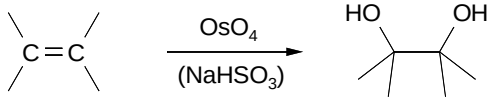
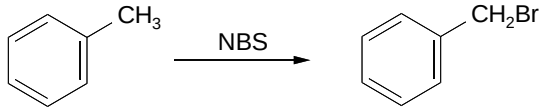
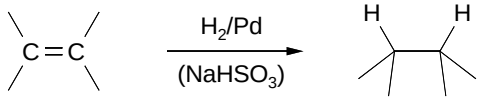
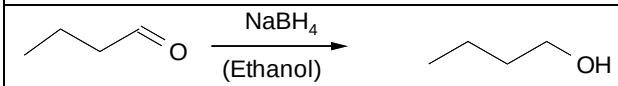
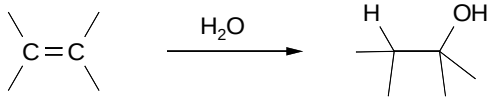
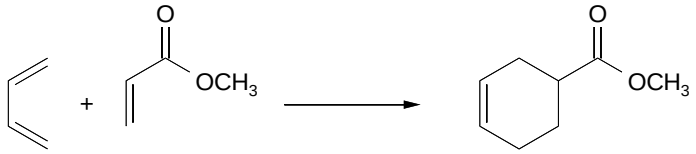


h)



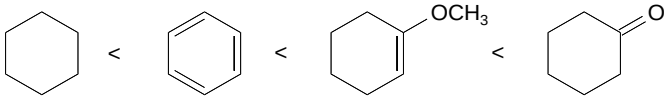
Solution to problem 4-09

a)

	Oxidation
	Oxidation
	Reduction
	Reduction
	no redox reaction
	no redox reaction

b)

i) $CH_3OH < H_2C{=}O < HCO_2H < CO_2$

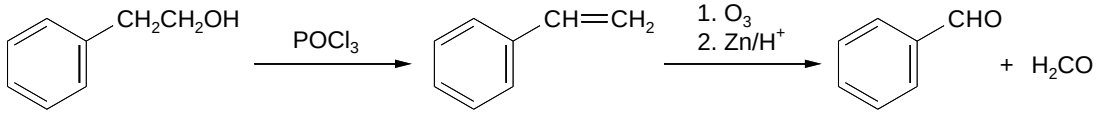
ii) 

iii) $CH_3CH_2NH_2 < NH_2CH_2CH_2NH_2 < CH_3CN$

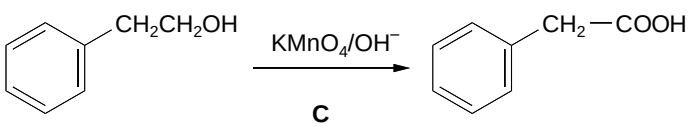
c) X = Lithium aluminum hydride reduces carbonyl groups but not double bonds.

Y = Palladium/Hydrogen reduces only double bonds but does not attack carbonyl groups.

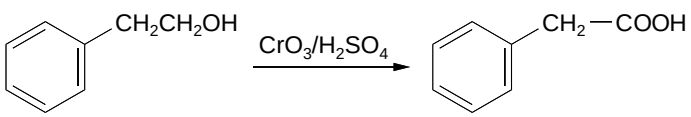
d)



A **B**

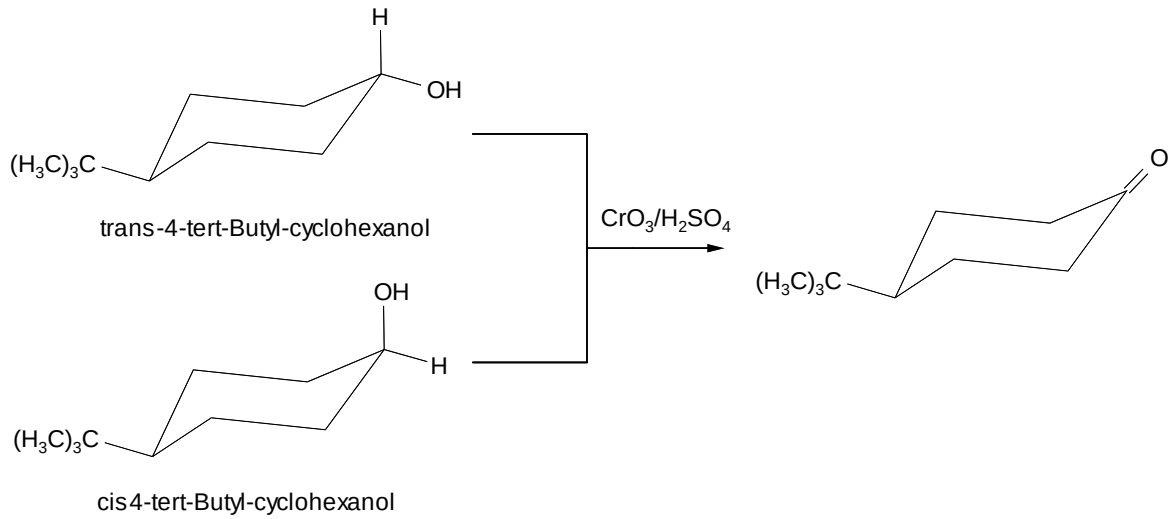


C



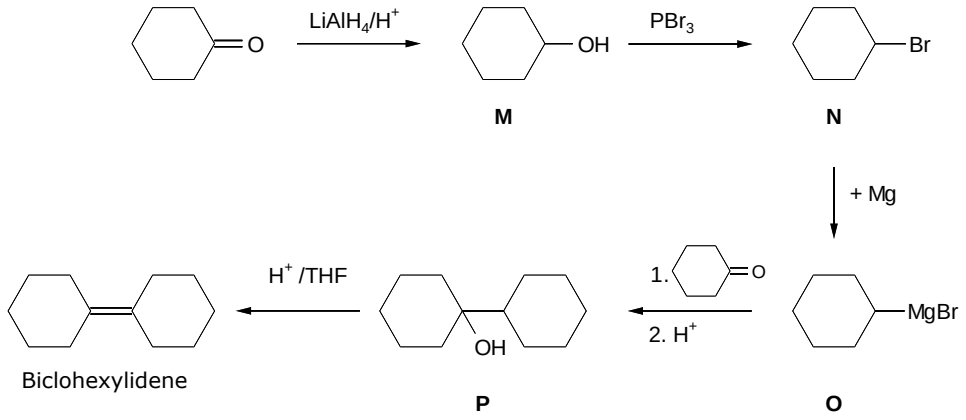
D

e)



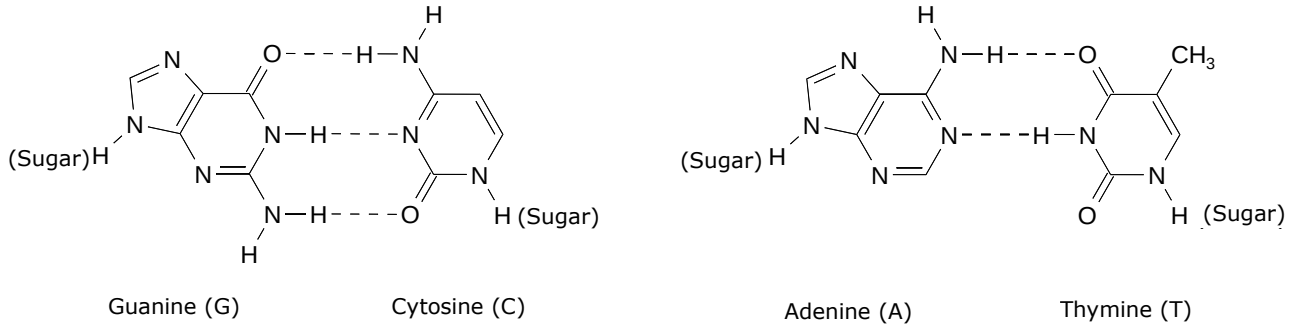
The space demanding t-butyl group takes the equatorial position.

f)



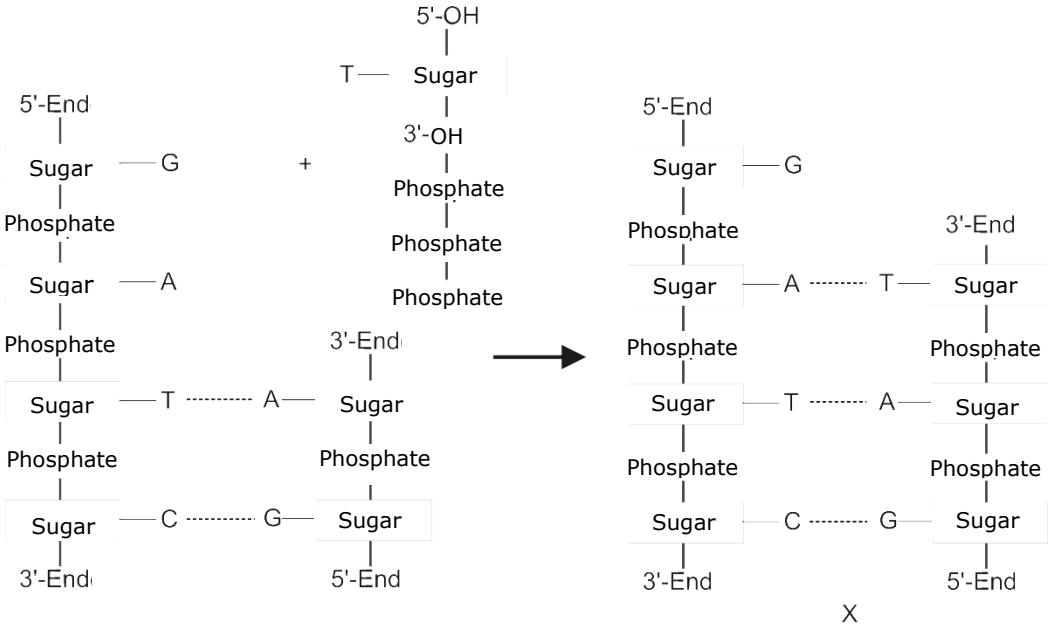
Solution to problem 4-10

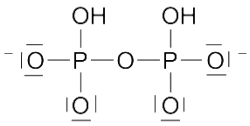
a) Complementary base pairing: A---T and G---C



Guanine (G) Cytosine (C) Adenine (A) Thymine (T)

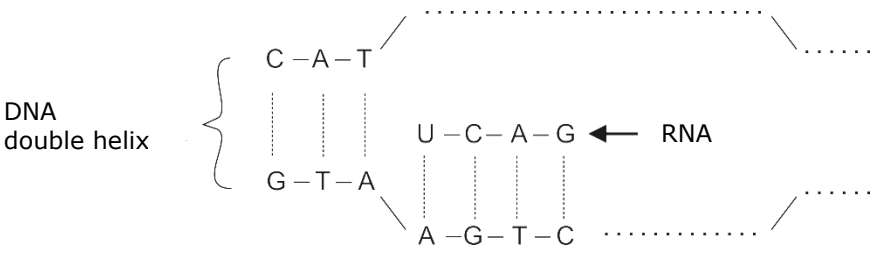
b)


5'-OH
T
Sugar
5'-End
3'-OH
Sugar
G
+
Phosphate
Phosphate
Phosphate
Sugar
A
Phosphate
3'-End
Sugar
T
A
Sugar
Phosphate
Phosphate
Sugar
C
G
Sugar
3'-End
5'-End
5'-End
Sugar
G
Phosphate
3'-End
Sugar
A
T
Sugar
Phosphate
Phosphate
Sugar
T
A
Sugar
Phosphate
Phosphate
Sugar
C
G
Sugar
3'-End
5'-End
X

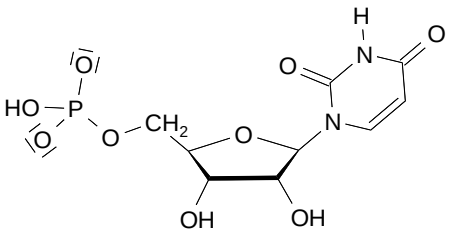

OH
OH
O
P
O
P
O
O
O

Y = $[H_2P_2O_7]^{2-}$

c)


DNA
double helix
C – A – T
G – T – A
U – C – A – G
RNA
A – G – T – C

d)


HO
P
O
O
O
CH2
O
H
N
O
O
N
OH
OH

e)

- mRNA binds to the ribosome,
- three bases of mRNA (codon) code for a specific amino acid (= genetic code of the specific amino acid), e.g. GAC for Asp,
- $tRNA_{Asp}$ has the anticodon GUC and the amino acid attached to its end,
- $tRNA_{Asp}$ binds with its anticodon to the codon of the mRNA,
- the amino acid Asp is transferred to the growing peptide.

Face your challenge,
Be smart

EXAMINATIONS

JULY 2013
MOSCOW, RUSSIA

Theoretical Test

Physical Constants, Units, Formulas and Equations

Avogadro's constant	$N_A = 6.0221 \times 10^{23}$ mol^{-1}
Universal gas constant	$R = 8.3145$ J·K^{-1}·mol^{-1}
Speed of light	$c = 2.9979 \times 10^8$ m·s^{-1}
Planck's constant	$h = 6.6261 \times 10^{-34}$ J·s
Faraday constant	$F = 96485$ C·mol^{-1}
Gravity of Earth	$g = 9.81$ m·s^{-2}
Standard pressure	$p^\circ = 1$ bar $= 10^5$ Pa $= 750$ mmHg
Atmospheric pressure	1 atm $= 1.013 \times 10^5$ Pa $= 760$ mmHg
Zero of the Celsius scale	273.15 K

1 nanometer (nm) = 10^{-9} m
1 Da = 1 atomic mass unit
1 electron volt (eV) = $1.6022 \cdot 10^{-19}$ J = 96485 J·mol^{-1}

Energy of a light quantum with wavelength λ	$E = hc / \lambda$
Energy of one mole of photons	$E_m = hcN_A / \lambda$
Gibbs energy	$G = H - TS$
Relation between equilibrium constant and standard Gibbs energy	$K = e^{\frac{\Delta G^\circ}{RT}}$
Relation between standard Gibbs energy and standard emf	$\Delta G^o = -nF\Delta E^o$
Clapeyron equation for phase transitions	$\frac{dp}{dT} = \frac{\Delta H}{T\,\Delta V}$
Integrated Clausius-Clapeyron equation for phase transitions involving vapor	$\ln\frac{p_2}{p_1} = \frac{\Delta H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$
Dependence of Gibbs energy of reaction on concentration or pressure	$\Delta G = \Delta G^\circ + RT\ln\frac{a_{\text{prod}}}{a_{\text{reag}}}$, $a = c$ / (1 mol/L) for the substances in solution, $a = p$ / (1 bar) for gases
Volume of a sphere of radius R	$V = \frac{4}{3}\pi R^3$
Surface area of a sphere of radius R	$S = 4\pi R^2$
Hydrostatic pressure	$p = \rho g h$

Problem 1 Clathrate gun

The only gun that is able to kill all living people in one shot

On the floors of oceans and seas there are vast reserves of methane in the form of clathrate compounds called methane hydrates. These reserves can be mined and serve as a source of energy or of raw materials for organic synthesis. However, scientists are seriously worried about the possibility of spontaneous decomposition of hydrates caused by the raising ocean temperature. It is believed that if a sufficient amount of methane is released into the atmosphere, then the oceans will warm up quicker due to the greenhouse effect, further accelerating the decomposition of clathrates. Due to the explosion of the resulting methane-air mixture and/or changes in the composition of the atmosphere, all living creatures may become extinct. This apocalyptic scenario is called a clathrate gun.

Upon decomposition of 1.00 g of a methane hydrate with a fixed composition at 25 °C and atmospheric (101.3 kPa) pressure, 205 mL of methane is released.

1. *Determine n (not necessarily integer) in the formula of methane hydrate, $CH_4 \cdot nH_2O$.*

Real methane hydrate has a non-stoichiometric composition close to $CH_4 \cdot 6H_2O$. At atmospheric pressure, methane hydrate decomposes at –81 °C. However, under high pressures (e.g. on the ocean floor) it is stable at much higher temperatures. Decomposition of methane hydrate produces gaseous methane and solid or liquid water depending on temperature.

2. *Write down the equation of the decomposition of 1 mole of $CH_4 \cdot 6H_2O$ producing solid water (ice) $H_2O(s)$.*

The enthalpy of this process equals 17.47 $kJ \cdot mol^{-1}$. Assume that the enthalpies do not depend on temperature and pressure. The volume change upon decomposition of hydrate is equal to the volume of released methane. Methane is an ideal gas.

3. *At what external pressure does the decomposition of methane hydrate into methane and ice take place at –5 °C?*
4. *What is the minimum possible depth of pure liquid water at which methane hydrates can be stable?*

   To answer this question, you should first deduce at which minimum temperature methane hydrate can coexist with liquid water. Choose the correct answer.

   ☐ 272.9 K ☐ 273.15 K ☐ 273.4 K

Large methane hydrate stocks on the floor of the Baikal lake, the largest freshwater lake in the world, have been discovered in July 2009 by the crew of the deep-submergence

vehicle «Mir-2». During the ascent from the depth of 1400 m methane hydrate samples started to decompose at the depth of 372 m.

5. *Determine the temperature in the Baikal lake at the depth of 372 m. The enthalpy of fusion of ice is 6.01 kJ·mol^{-1}.*

The total amount of methane in hydrates on Earth is not less than $5 \cdot 10^{11}$ tons.

6. *By how many degrees would the Earth atmosphere heat up, if such an amount of methane is burned by reacting with atmospheric oxygen?*
   The enthalpy of combustion of methane is –889 kJ·mol^{-1}, the total heat capacity of the Earth's atmosphere is about $4 \cdot 10^{21}$ J·K^{-1}.

Problem 2 Break down photosynthesis – the Hill reaction

In the history of photosynthesis research there were some breakthrough experiments which added much to our knowledge of this very complex process. One of such experiments was performed in 1930s by an English biochemist Robert Hill. In this problem, we consider some of his data together with the data of more recent experiments.

1. *In plants under illumination carbon dioxide is reduced to carbohydrates (denoted as {CH_2O}) and oxygen is produced. Write the overall equation of photosynthesis in plants.*

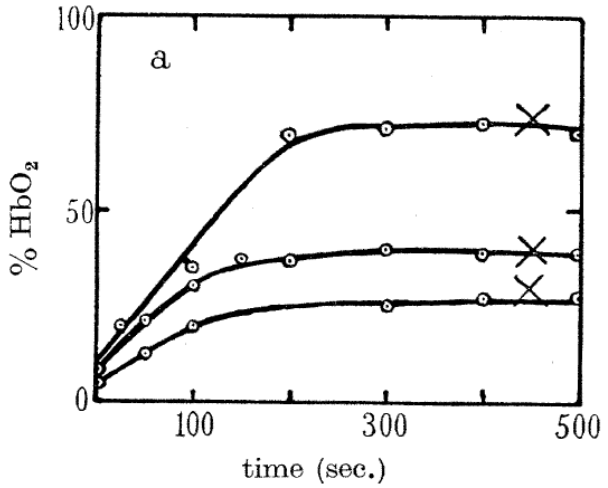
Much of the photosynthesis takes place in chloroplasts – organelles found in plant cells and containing chlorophyll – the light-absorbing substance. Hill isolated chloroplasts from the cells by grinding the leaves in the sucrose solutions. The cell-free chloroplasts did not produce oxygen under illumination even in the presence of CO_2. However, upon adding potassium ferrioxalate $K_3[Fe(C_2O_4)_3]$ (with an excess of potassium oxalate) to the chloroplast suspension Hill observed oxygen liberation under illumination even without CO_2. Hill's experiment enabled to determine the source of oxygen during photosynthesis.

2. *Write the formulas of the oxidant and the reducing agent in the photosynthesis inside the plant cells and in the cell-free chloroplasts (Hill reaction).*

Hill measured the amount of evolved oxygen using muscle haemoglobin (denoted it Hb) which binds all molecular oxygen in a 1:1 ratio to form HbO_2. The initial concentration of Hb was $0.6 \cdot 10^{-4}$ M. Kinetic curves corresponding to different ferrioxalate concentrations are shown in the figure (the upper curve corresponds to $2.0 \cdot 10^{-4}$ M).

3a. From the figure, estimate the Fe / O_2 mole ratio at the end of reaction. Do not take the iron from Hb into account.

3b. Write the equation of Hill reaction assuming that it proceeds with a high yield.



The fraction of bound haemoglobin HbO_2 (with respect to the initial amount of Hb) as function of time. Crosses denote the end of reaction.
(Figure 2a from the original Hill's paper: *R. Hill. Oxygen produced by isolated chloroplasts. – Proc. R. Soc. B, 1939, v. 127, pp. 192-210*)

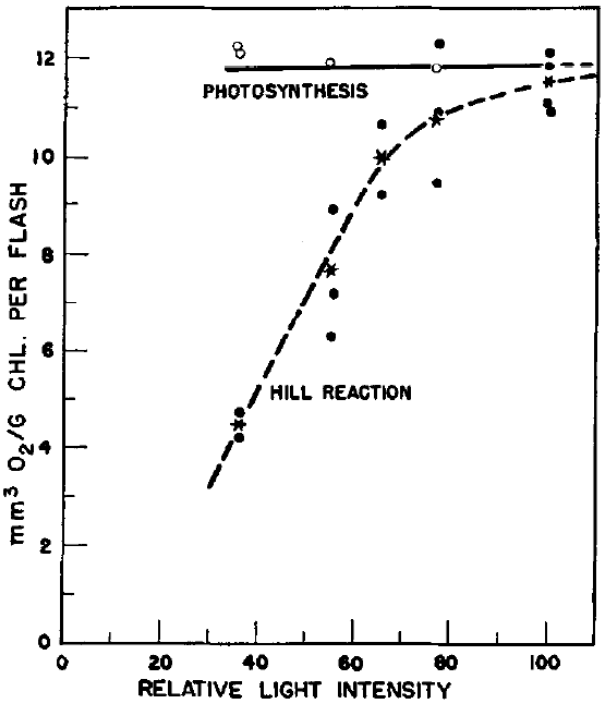
3c. Using the table of standard electrode potentials, determine the Gibbs energy of the Hill reaction at T = 298 K, oxygen pressure 1 mm Hg, pH = 8 and standard concentrations of other species. Is this reaction spontaneous at such conditions?

Half-reaction	E°, V
$O_2 + 4H^+ + 4e \rightarrow 2H_2O$	+1.23
$CO_2 + 4H^+ + 8e \rightarrow \{CH_2O\} + H_2O$	–0.01
$Fe^{3+} + e \rightarrow Fe^{2+}$	+0.77
$Fe^{3+} + 3e \rightarrow Fe^0$	–0.04
$[Fe(C_2O_4)_3]^{3-} + e \rightarrow [Fe(C_2O_4)_3]^{4-}$	+0.05
$[Fe(C_2O_4)_3]^{4-} + 2e \rightarrow Fe + 3C_2O_4^{2-}$	–0.59

Now, the name "Hill reaction" denotes photochemical oxidation of water by any oxidant other than carbon dioxide which is sensitized by plant cells or isolated chloroplasts.

In another experiment (1952), quinone in an acid solution was used as an oxidant in the Hill reaction initiated by light flashes in the *Chlorella* algae. Experimental data are shown in the figure below. The volume of oxygen (in mm^3, at 10 ^oC and p = 740 mmHg) per one gram of chlorophyll per one flash was determined as a function of light intensity for natural photosynthesis and for isolated chloroplasts. It was found that the maximum yield of oxygen is the same for natural photosynthesis and the Hill reaction.

4a. Determine the reaction order of a photochemical Hill reaction with respect to the light intensity at low and high intensity. For each case choose one of three values on the answer sheet.



(Figure 1 from: *H. Ehrmantraut, E. Rabinovitch. Kinetics of Hill reaction. – Archives of Biochemistry and Biophysics, 1952, v. 38, pp. 67-84*)

4b. How many chlorophyll molecules participate in the formation of one oxygen molecule in the saturation limit of the Hill reaction? (The molecular mass of chlorophyll is about 900 Da).

The quantum requirement of the light redox reactions is defined as the average number of light photons (not necessarily integer) needed for the transfer of one electron from a reducing agent to an oxidant. The isolated chloroplasts were irradiated during 2 hours by a monochromatic light (wavelength 672 nm) with the energy input 0.503 mJ/s, and the total volume of oxygen formed was 47.6 mm^3 (under the conditions of question 4).

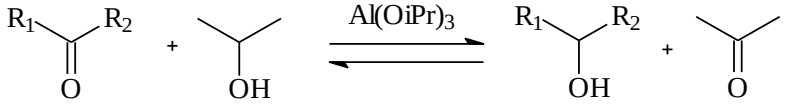
5. Calculate the quantum requirement for the Hill reaction.

6. Try to make conclusions from the above experiments (questions 2-5). For each of the following statements choose either "Yes" or "No".

	Yes	No
In natural photosynthesis, water oxidation and CO_2 reduction are separated in space.		
In chloroplasts, O_2 is produced from CO_2.		
Oxidation of water in chloroplasts requires light illumination.		
Most of chlorophylls in chloroplasts participate directly in the photochemical O_2 production.		
In isolated chloroplasts, every absorbed photon causes transfer of one electron.		

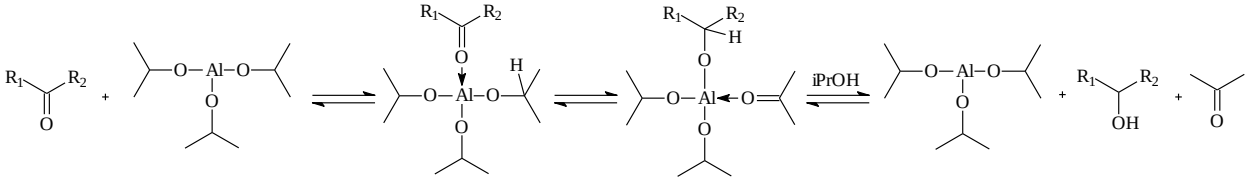
Problem 3. Meerwein-Schmidt-Ponndorf-Verley reaction

The Meerwein-Schmidt-Ponndorf-Verley (MSPV) reaction is a useful tool for the reduction of carbonyl compounds to alcohols. It is the reduction of carbonyl compounds by low molecular weight alcohols in the presence of alkoxides of aluminium or other metals:



(1)

The mechanism of the reaction includes thecoordination of carbonyl compound by aluminium alkoxide, hydride transfer in the inner sphere of the complex and subsequent transalkoxylation. It can be schematically represented as follows (transalkoxylation is shown as a one-step process for brevity):



(2)

The reaction is reversible and shifting the equilibrium to the desired product. It requires some excess of the reductant. In some cases (e.g. in the case of reduction of aromatic aldehydes and ketones) the equilibrium constant is so large that the reverse reaction can be neglected.

The table below contains standard entropies and standard enthalpies of formation of liquid substances at 298 K. The boiling points of the substances at 1 bar are also given.

Substance	$\Delta_f H^\circ_{298}$, kJ/mol	S°_{298}, J/(mol·K)	t_{vap}, °C
Acetone	–248.4	200.4	56
Isopropanol	–318.1	180.6	82
Cyclohexanone	–271.2	229.0	156
Cyclohexanol	–348.2	203.4	161

1a. Calculate the minimum isopropanol:cyclohexanone mass ratio which is required to reach a 99% yield of the reaction at 298 K. Assume that a) the reaction mixture eventually gets to equilibrium and b) no products are initially present.

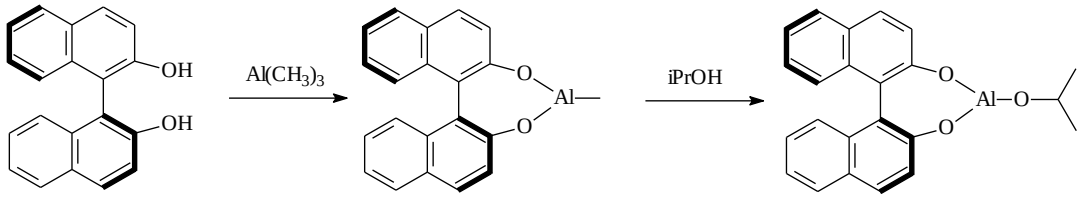
1b. Choose the appropriate way(s) to increase the cyclohexanol yield.

Increase the temperature up to 50°C using a reflux	
Increase the temperature up to 60°C, evaporating (distilling) the acetone	
Add some ethanol to the reaction mixture	
Add some ethanal to the reaction mixture	

Often the rate-limiting step in the MSPV reaction is the hydride transfer or the alcoholysis of the alkoxide after hydride transfer.

2. *For these two cases, using the above mechanism (2), derive an expression for the rate of reaction as a function of current concentrations of a carbonyl compound, isopropanol and a catalyst.*
   In both cases determine the rate orders in the reactants and the catalyst. Assume that all reaction steps before the limiting step are fast and reversible. Use equilibrium approximation, if necessary. For brevity use the following notation: ***A*** *for carbonyl compound,* ***B*** *for isopropanol,* ***C*** *for catalyst. Denote intermediates as you wish.*

The MSPV reaction can be used to obtain chiral alcohols, if the chiral catalyst is employed. For instance, Campbell et al. used the catalyst based on the chiral 2,2'-dihydroxy-1,1'-binaphtyl (BINOL), which is synthesized *in situ* from binaphtol and trimethylaluminium:

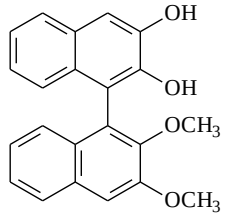
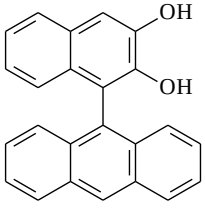
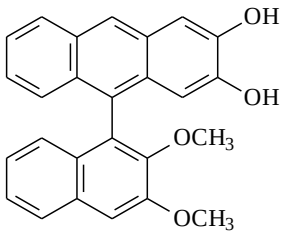
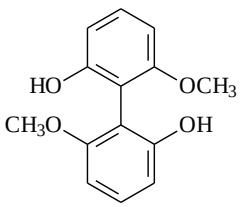


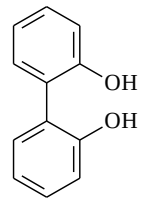
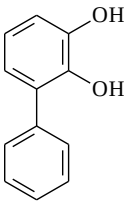
(BINOL)Al(OiPr)

(3)

The chirality of BINOL is due to the sterically hindered rotation around the C-C bond. Though perfectly stable at room temperature, BINOL may racemize when heated.

3. *Which of the phenols below can form stable (at room temperature) enantiomers so that they can be used in the same fashion to produce a chiral catalyst?*

Substance	Can be used	Substance	Can be used
			
			

Enantiomeric excess, *ee*, is used to characterize the enantiomeric purity of the substance. This quantity equals ratio of the difference of concentrations of enantiomers *R* and *S* to their sum:

$$ee = \frac{|[R] - [S]|}{[R] + [S]}$$

Enantiomeric excess of the pure *R* isomer is unity, *ee* of the racemic mixture is zero.

When using the enantiomerically pure (BINOL)Al(OiPr) as a catalyst for reduction of α-bromoacetophenone, the *ee* of the product equals 81%.

4. *What is the ee of the product if the catalyst ee equals 50%? Provide your calculation with an illustration or derivation of the final formula.*

Problem 4 A simple inorganic experiment

Compound **A** which contains the metal **X** is a colorless crystalline solid and highly soluble in water. It is used as a reagent in analysis and gives in alkali media a binary compound **B** containing 6.9 % (mass) of oxygen. Under heating **A** decomposes with a mass loss of 36.5%.

1. *Determine the metal **X** and compounds **A**, **B**.*

Upon adding some amount of sodium thiosulphate to the solution of **A** the color immediately becomes red, then changes to reddish-brown, and after some minutes a dark-brown precipitate **C** forms (reaction 1). The solution over it is colorless. Being heated on air at 600ºC, **C** gives a grey powder **X** (reaction 2), so as 0.90 g of residue can be obtained from 1.10 g of **C**. A gas, evolved by heating **C** in vacuum (reaction 3), can be absorbed by calcium hydroxide suspension (reaction 4). Being stored for a long time under saturated solution of barium perchlorate in 0.1 M $HClO_4$, the color of the precipitate becomes lighter, while the use of magnesium perchlorate doesn't give such effect.

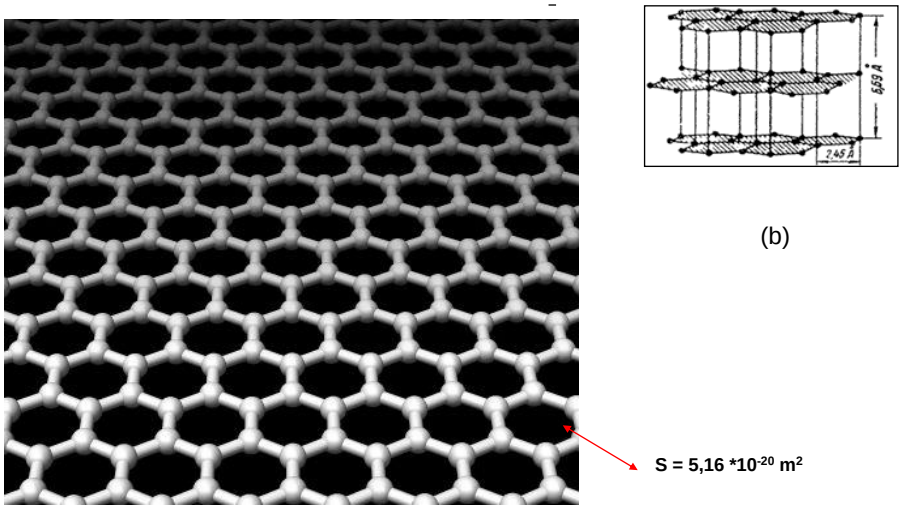
2. *What is **C**? Write the equations of the reactions (1 – 4).*

The compound **C** being stored under the mother liquor (containing an excess of **A**). Its color changes to yellow due to the transformation into **D**. If barium ions are added to the suspension of **C** in the mother liquor, a mixture of **D** and of a white precipitate forms.

3. *Propose the formula of **D**, taking into account that it contains 77.5% (mass) of **X**. Give the equation of **D** formation.*

Problem 5 Simple estimates of graphene properties

Graphene is a two-dimensional, one atom thick carbon material (Fig.1 a). Many layers of graphene stack together to form graphite (Fig. 1b).



(a) (b)

Fig. 1. (a) The structure of graphene. Spheres are carbon atoms. They are arranged in hexagons. The area of one carbon hexagon is $5.16 \cdot 10^{-20}$ m^2.
(b) Crystal lattice of graphite. Three graphene layers are shown.

Such atomic structure was long considered to be unstable. However, in 2004 Andrey Geim and Konstantin Novoselov have reported the production of the first samples of this unusual material. This groundbreaking invention was awarded by Nobel prize in 2010.
Experimental studies of graphene are still restricted. Production of massive portions of the new substance is still a challenging synthetic problem. Many properties of graphene were *estimated*. Usually, there is not enough information for rigorous calculations, so we have to make assumptions and neglect unimportant factors. In this problem, you will estimate the adsorption properties of graphene.

1a. Estimate the specific surface of graphene open for adsorption in units m^2 /g. Consider that graphene plane is separated from any other solid or liquid substance.

The single layer of nitrogen molecules adsorbed on the outer surface of graphite is shown in Fig. 2. Assume that the same arrangement of nitrogen molecules is formed on a graphene surface.

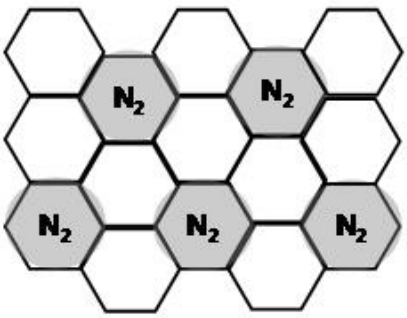


Fig. 2. Nitrogen molecules N_2 (grey circles) on the outer surface of graphite

1b. How many grams of nitrogen can be adsorbed on 1 gram of graphene assuming that the graphene layer is placed onto the surface of a solid support? Estimate the volume occupied by these nitrogen molecules after the complete desorption from 1 g of graphene (pressure 1 bar, temperature 298 K).

Let us consider adsorption as a common chemical equilibrium

$$A_{gas} \rightleftarrows A_{ads}, \qquad (1)$$

(A_{gas} are molecules A in the gaseous state, A_{ads} are the same molecules on the surface) with the equilibrium constant *K*:

$$K_{ads} = \frac{n_{A_{ads}}\,(\mathrm{mol}\cdot\mathrm{m}^{-2})}{p_{A_{ads}}\,(\mathrm{bar})}$$

(such assumption holds if a small number of molecules is adsorbed on the surface)

Adsorption properties of graphene can be estimated from the data for adsorption on regular three-dimensional graphite. The enthalpy of adsorption (ΔH^o of reaction (1)) of any molecule A on graphene is on average by 10% less negative compared to that on graphite. On graphite, the adsorbed molecule is bound more strongly due to the interaction with the lower graphene layers in the lattice (Fig. 1b) and hence the enthalpy of adsorption is more negative. The standard entropies of adsorption on graphene and graphite are assumed to be the same.

2. How many moles, n, of CCl_4 are adsorbed on 1 g of graphene at $p(CCl_4) = 10^{-4}$ bar if $2.0\cdot10^{-7}$ mol of CCl_4 are adsorbed on 1 m^2 of graphite at $p(CCl_4) = 6.6\cdot10^{-5}$ bar? Assume that graphene is placed onto the surface of a solid support and the interaction of CCl_4 with the support does not change the enthalpy of adsorption of CCl_4 on graphene.The temperature in both cases is 293 K. ΔH^o of adsorption of CCl_4 on graphite is –35.1 kJ/mol.

The graphene films are expected to be sensitive gas detectors. If 10^9 particles of a gas are adsorbed on 1 cm^2 of a graphene surface this is enough to measure an electrical resistivity change of the graphene layer and to detect the presence of a gas in the environment.

3. Determine the minimal content of ethane, C_2H_6, in the air (in mol.%) at atmospheric pressure (T = 293K) at which a graphene sensor will detect this gas. The known data for the adsorption of alkanes on graphite are shown in Fig 3. Assume that air doesn't affect the adsorption properties of ethane.

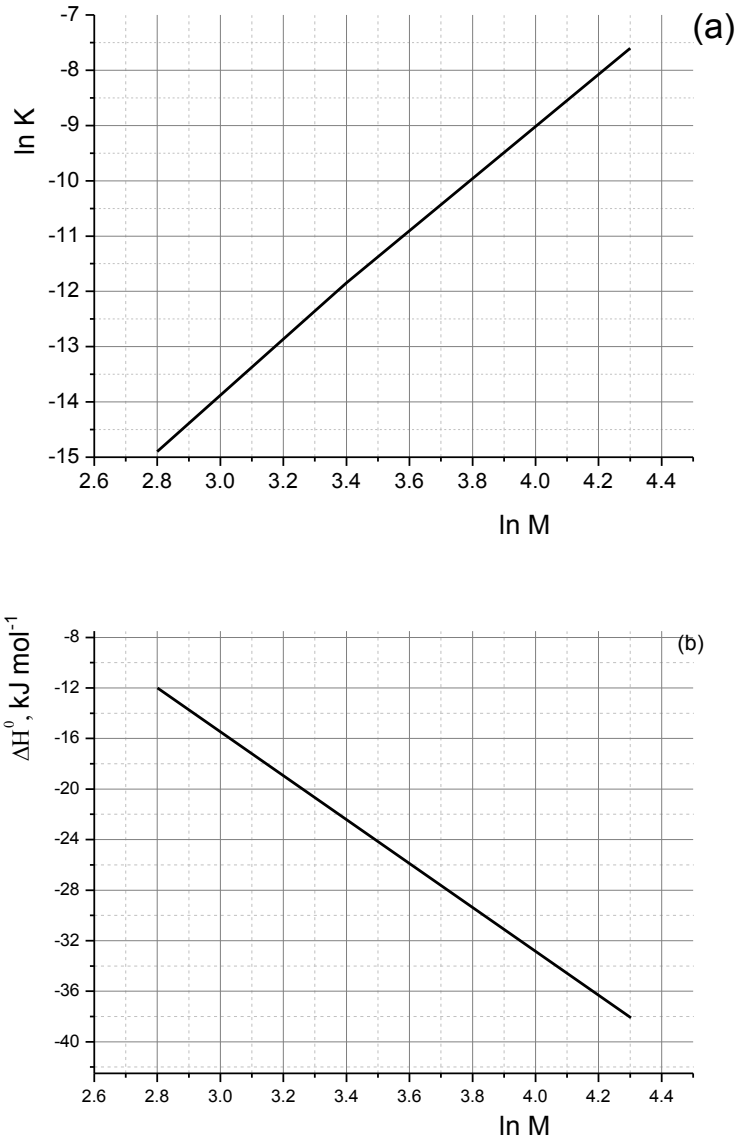


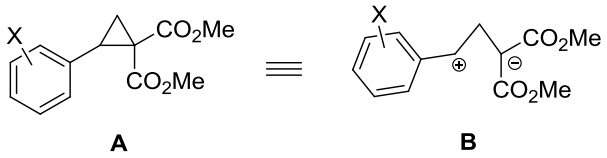
Fig. 3. Thermodynamic properties for the adsorption of alkanes on a graphite surface.

(a) ln *K* {mol/m^2/bar} as a function of ln *M* (*M* – molecular mass of alkane in g/mol);

(b) ΔH^o of adsorption as a function of ln *M*. Linear dependences are assumed in both cases

Problem 6. Cyclopropanes. So simple. So fancy…

Cyclopropanes bearing donor and acceptor substituents at the neighboring C-atoms, for example, **A**, demonstrate high reactivity behaving similar to 1,3-zwitterion **B**.



A **B**

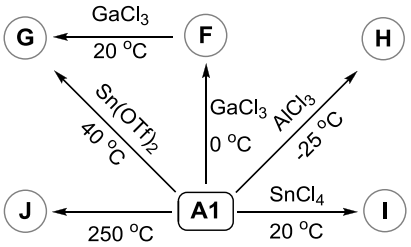
Thus, **A1** (X = 4-OMe) undergoes the three-membered ring opening in the Lewis acid catalyzed reaction with 1,3-dimethoxybenzene as a nucleophile to give product **C**.

1. *Write down structural formula of **C**.*

A1 participates in cycloadditions, annulations, oligomerizations, and other processes. Thus, [3+2]-cycloaddition between **A1** and 4-methoxybenzaldehyde leads to a five-membered ring in **D**. Complete decarboxylation of **D** produces **E** ($C_{18}H_{20}O_3$), the molecule of the latter having a plane of symmetry.

2. *Write down structural formulae of **D** and **E** indicating their stereochemistry.*

A can undergo various transformations in the absence of any reaction partners except catalysts, too. Some transformations typical of **A1** are shown in the Scheme below.



OTf = OSO_2CF_3

To determine the structures of **F-J**, a set of physico-chemical data was obtained (see Table below for some results). It was found that:

a) **F** and **G** are structural isomers of **A1**;
b) **G** is formed as the most stable stereoisomer;
c) **H** and **I** are structural isomers;
d) **H** is formed as a single diastereomer with C_2 axis of symmetry (the molecule looks the same after rotation through the angle of 180°);
e) **I** is formed as a mixture of two diastereomers;
f) **J** is naphthalene derivative.

In the process leading to **I**, one molecule of **A1** demonstrates the described above common reactivity (analogous to that of **B**). The other molecule of **A1** behaves differently. Also, the latter behavior is demonstrated by cyclopropane **A2** (dimethyl 2-(3,4,5-

trimethoxyphenyl)cylopropane-1,1-dicarboxylate) when treated with $SnCl_4$ in CH_3NO_2 giving **K** as a mixture of two diastereomers. The major isomer has the center of symmetry. Similar reactivity is shown by **A2** in $Sn(OTf)_2$-catalyzed reaction with **G** leading to **L**.

*3. Write down the structural formulae of **F-J, L**, and of the major isomer of **K**.*

	Ratio of the number of hydrogen-containing groups					**Composition**
	Non-aromatic				Aromatic	
	CH	CH_2	CH_3	OH		
F	1	1	1+1+1	0	4 in total	C 63.62%, H 6.11%
G	1+1+1	0	2+1	0	4 in total	C 63.62%, H 6.11%
H	1	1	1+1+1	0	4 in total	C 63.62%, H 6.11%
I	1+1+1	1+1	2+1+1+1+1	0	7 in total	C 63.62%, H 6.11%
J	0	0	1+1	1	5 in total	C 67.22%, H 5.22%
K	1+1	1	2+1+1+1	0	1	C 59.24%, H 6.23%
L	1+1+1+1+1	1	2+2+1+1+1+1	0	5 in total	C 61.21%, H 6.18%

Problem 7 Diverse Permanganatometry

The amount of many reducing agents can be determined by permanganatometric titration in alkaline medium allowing permanganate ion reduction to manganate.

1. Write down the ionic reaction equation for formate titration with permanganate in an aqueous solution containing ~0.5 M NaOH.

Titration with permanganate in alkaline medium is often supplemented by addition of a barium salt, which leads to precipitation of manganate as $BaMnO_4$.

2. Which side reaction of the redox processes involving manganate is suppressed by the barium salt? Write down an example of equation of the corresponding reaction.

10.00 mL (V_{Mn}) of 0.0400 M (c_{Mn}) $KMnO_4$ solution was placed in each of flasks **A**, **B**, and **C** and different reactions were conducted in each flask.

To flask **A**, a sample solution containing crotonic acid (CA) CH_3–CH=CH–COOH, an alkali and barium nitrate (both in an excess) were added, and the reaction mixture was incubated for 45 min. It is known that crotonic acid loses 10 electrons under the experiment conditions.

3a. Write down the total ionic reaction equation.

8.00 mL (V_{CN}) of 0.0100 M (c_{CN}) potassium cyanide solution was further added to the incubated mixture. This resulted in completion of the following reaction:

$$2\ Ba^{2+} + 2\ MnO_4^- + CN^- + 2\ OH^- \longrightarrow 2\ BaMnO_4 + CNO^- + H_2O$$

$BaMnO_4$ precipitate was then filtered off and the excess of cyanide in the filtrate was titrated with 0.0050 M (c_{Ag}) $AgNO_3$ solution till detectable precipitation was observed.
Note that both CN^- and CNO^- are analogs of halide ions, but CNO^- has soluble silver salt.

3b. Give the formula for the complex formed when Ag^+ ions were initially added to the cyanide solution (until the precipitate was formed).

3c. Give the formula of the precipitate formed.

3d. Derive the formula for calculating the amount of crotonic acid in the sample solution. Calculate the mass of crotonic acid (in mg) if 5.40 mL (V_{Ag}) of the silver salt solution was consumed for the titration to the endpoint.

Another sample of crotonic acid and alkali (in excess) were added to flask **B**, this mixture lacking barium salt. An excess of KI (instead of cyanide) was added as a reducing agent. The mixture was further acidified, and the iodine evolved was titrated with 0.1000 M (c_S) thiosulfate solution. 4.90 mL (V_{S1}) of the titrant was used to reach the endpoint.

4. Derive the formula for calculating the amount of crotonic acid in this experiment. Calculate the mass of crotonic acid (in mg).

A sample containing tin(II) was added to flask **C**, and the medium was adjusted to weak alkaline. Tin(II) was quantitatively oxidized to $Sn(OH)_6^{2-}$, whereas a precipitate formed as a result of permanganate reduction. The precipitate was isolated, washed off, dried at 250°C, weighed (the mass of the water-free precipitate (m_{prec}), representing a binary compound, was of 28.6 mg), and dissolved in H_2SO_4 in the presence of an excess of potassium iodide. The evolved iodine was titrated with 0.1000 M thiosulfate solution. 2.5 mL (V_{S2}) of the latter was consumed to attain the endpoint.

5a. Write down the reaction of precipitation. Confirm it wih calculations.

5b. Calculate the mass of tin in the sample (in mg) referred to the metal.

Problem 8 Unique life of archaea

Archaea (or archaebacteria) are single-celled microorganisms. They significantly differ from bacteria and eukaryotes at the molecular level.
An enzymatic reaction of methylamine with water is the major energy source for some archaea. In a particular experiment an archaea strain was cultivated at pH 7 under anaerobic (oxygen free) conditions with the nutrient medium containing $^{13}CH_3NH_2$ as the

only energy source. After a certain incubation period, the gas over the archaea culture was sampled and analyzed. It was found that the gas contains two substances **A** and **B** in the molar ratio of 1.00:3.00 correspondingly (the sample density rel. H_2 is of 12.0).

1. *Calculate the volume fractions (in %) of **A** and **B** in the mixture.*
2. *Determine **A** and **B** if there is no nitrogen atoms in gas collected.*
3. *Write down the equation of the enzymatic reaction of methylamine with water described in the above experiment using the predominant form of each species.*

Enzymes containing the residue of α-amino acid **X** are found in many archaea capable of methylamine utilization. It is known that

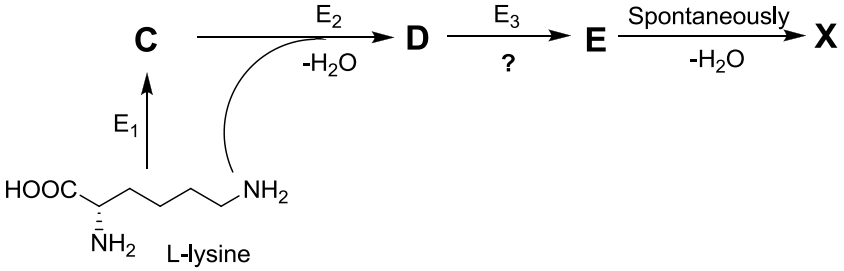
- **X** is composed of atoms of 4 elements;
- **X** is 18.8 % oxygen by mass;
- **X** possesses the single individual tRNA and is incorporated into proteins of archaea during translation.

Amino acid *L*-lysine (see the structure in scheme below) was identified as the **X** precursor in archaea. All carbon and nitrogen atoms found in **X** originate from two starting lysine molecules. Different isotope-labeled *L*-lysines were introduced into a model system to clarify the biosynthetic pathways of **X**. The results are summarized in the table.

Isotope composition of *L*-lysine	Molecular mass (rounded to integer) of the **X** residue [$RCH(NH_2)CO$], bound to tRNA, g/mol
Normal	238
All carbons ^{13}C, all nitrogens ^{15}N	253
ε-Amino group with ^{15}N	239

4. *Determine the molecular formula of **X**.*

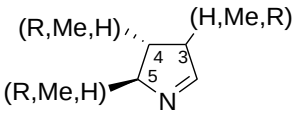
X is biosynthesized in archaea according to the following scheme (E_1–E_3 – enzymes):



At the first step, lysine is transformed into its structural isomer (α–amino acid, **C**), whereas **D** contains a peptide bond, and **E** a formyl group [-CHO]. All reaction coefficients in the above scheme equal 1.

5. *Give the chemical formula of **C**, **D** and **E**. From the reaction types given hereunder, choose (tick) **only one** corresponding to the enzyme E_3 catalyzed reaction.*

X contains the following fragment:

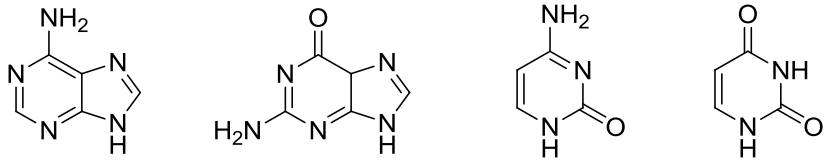


R is a massive substituent (M>100 g/mol). The 3rd carbon atom is non-asymmetric, the 4th and 5th carbon atoms are stereogenic centers. All carbon atoms in the cycle are bound with at least one hydrogen atom. Each substituent (H, Me and R) is found only once.

6. *Determine the positions of the substituents H, Me, and R.*

7. *Draw structural formulae of **C** and **X** with stereochemical details. Mark every stereocenter of **X** with either R or S.*

Only one codon is responsible for the incorporation of **X** residues into proteins in archaea. The nitrogen bases forming this codon contain two exocyclic amino groups and three exocyclic oxygen atoms in total.



8. *Determine the nucleotide composition of the codon by filling in the table on the answer sheet. Write down the number of each nitrogen base in the codon encoding **X**. Tick only one box in each line.*

The fragment of mRNA coding sequence given below contains the codons encoding **X** residue incorporation into an archaea enzyme:

5′…AAUAGAAUUAGCGGAACAGAGGGUGAC…3′

9a. Using the table of the genetic code, decide how many amino acid residues are incorporated into the enzyme chain due to this fragment translation.

9b. Write down the amino acid sequence translated from this fragment. Note that more than one **X** residue is found in the fragment.

See table next page

RNA Codons for the 20 Amino Acids

First base	Second base: U	C	A	G	Third base
U	Phe	Ser	Tyr	Cys	**U**
	Phe	Ser	Tyr	Cys	**C**
	Leu	Ser	STOP	STOP	**A**
	Leu	Ser	STOP	Trp	**G**
C	Leu	Pro	His	Arg	**U**
	Leu	Pro	His	Arg	**C**
	Leu	Pro	Gln	Arg	**A**
	Leu	Pro	Gln	Arg	**G**
A	Ile	Thr	Asn	Ser	**U**
	Ile	Thr	Asn	Ser	**C**
	Ile	Thr	Lys	Arg	**A**
	Met(start)	Thr	Lys	Arg	**G**
G	Val	Ala	Asp	Gly	**U**
	Val	Ala	Asp	Gly	**C**
	Val	Ala	Glu	Gly	**A**
	Val	Ala	Glu	Gly	**G**

Amino-acid abbreviators

Ala = Alanine	Trp = Tryptophan
Arg = Arginine	Tyr = Tyrosine
Asn = Asparagine	Val = Valine
Asp = Aspartic acid	
Cys = Cysteine	
Glu = Glutamic acid	
Gln = Glutamine	
Gly = Glycine	
His = Histidine	
Ile = Isoleucine	
Leu = Leucine	
Lys = Lysine	
Met = Methionine	
Phe = Phenylalanin	
Pro = Proline	
Ser = Serine	
Thr = Threonine	

Practical Test
18. July 2013

List of Chemicals

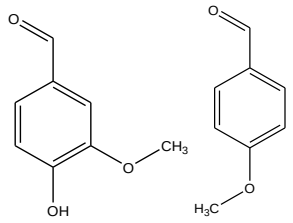
Reagent	Quantity	Placed in	Labeled	Safety
Problem 1				
2,4-Dinitrophenylhydrazine	200 mg each, 2 vials	small screw neck vial	2,4-dinitrophenylhydrazine	H228, H302
Sulfuric acid, concentrated	1 mL each, 2 tubes	Plastic tube with screw neck	H_2SO_4 concentrated	H314
Aldehyde solution 1 mmol in ethanol	4 mL each, 2 bottles	30 mL small glass-stoppered bottle	Aldehyde 1 and Aldehyde2	H319 and H302
Ethanol	30 mL	glass-stoppered bottle	Ethanol	H225
NaOH solution (used in problems 1 and 2)	27 mL	60 mL glass-stoppered bottle	NaOH 2M	H314
Acetone	30 mL	amber glass screw neck vial	Acetone	H225, H319, H336
Problem 2				
EDTA, 0.0443M* standard solution	70 mL	125 mL glass-stoppered bottle	EDTA 0.05M	H319
HCl, 0.0535M* standard solution	70 mL	125 mL glass-stoppered bottle	HCl	H314, H335
Methyl orange, 0.1% in water	25 mL	dropping bottle	Methyl orange	H301
Murexide indicator, solid mix with NaCl (1:250 by mass)	in 10 mL bottle	small screw neck vial	Murexide	
Sample of water	500 mL	0.5 L plastic can	Water sample	
Problem 3				
Poly(vinyl) alcohol	40 mL each, 5 vials	amber glass screw neck vial	P1, P2, P3, P4 and X	
To be used in all problems				
Distilled water	500 mL	Plastic wash bottle	H_2O	
To be shared by students, on the common table				
Sodium hydrocarbonate	800 mL	800 mL beaker	$NaHCO_3$	

Labware and equipment

Item	Quantity
On every working place	
5 mL Plastic tube with screw neck labeled "1" with your student code	1
5 mL Plastic tube with screw neck labeled "2" with your student code	1
Lab stand	1
50 mL beaker	2
25 mL beaker	2
25 or 50 mL beaker	1
Magnetic stirrer	1
Stirring bar	2
Glass filter	2
Adapter	1
50 mL round bottom flask	1
Water-jet pump	1
2 mL pipette	2
5 mL pipette	2
Pipette filler	1
Spatula	2
500 mL plastic washer bottle	1
800 mL beaker for waste	1
10 mL measuring cylinder	1
Filter paper, round	2
Scissors	1
Filter paper	2
Glass rod	1
pH indicator papers (in a zipper-bag)	3
Viscometer	1
Stop-watch	1
30 mL rubber bulb	1
Ruler	1
Marker	1
25 mL burette	1
25 mL pipette	1
Plastic funnel	1
Erlenmeyer flask	2
Test strips for determining total dissolved solids content in zipper bag	1
Paper tissues (on the corner of each table, to be shared between 3 students)	1 package
Plastic basket	1
Graph paper	4 sheets
pH scale (in zipper bag)	1
On the tables for the common use	
Filter paper, round	
Filter paper	
Gloves	
Balances	
Bottle labeled "H_2O dist."	
Thermometer immersed in H_2O	
Measuring cylinder 100 mL	
pH-meter	

Problem 1 Synthesis of 2,4-dinitrophenylhydrazones

Hydrazones belong to the class of *imines*, which contain a nitrogen-nitrogen single bond adjacent to a carbon-nitrogen double bond. Hydrazones are formed when NH_2-containing hydrazine reacts with aldehydes or ketones under appropriate conditions. Because the hydrazone derivatives of the carbonyl compounds are often stable, crystalline, highly colored solids, they are used to confirm the identity of aldehydes and ketones.
In this task you will have to identify two substituted benzaldehydes (shown below) by studying the products of their reactions with 2,4-dinitrophenylhydrazine.



Procedure

Preparation of 2,4-dinitrophenylhydrazones

Equip one 50 mL beaker with a magnetic bar. Fix the beaker on the stirrer using the metal ring attached to the stand. Place the content of vial (200 mg of 2,4-dinitrophenylhydrazine) into the beaker and start stirring carefully. Only in the presence of your lab assistant, carefully pour one sample of concentrated sulfuric acid (1 mL) onto the solid. Using pipettes add 1.6 mL of water and 4 mL of ethanol to the reaction mixture. Then using a pipette add dropwise the content of the aldehyde solution bottle (either "aldehyde 1" or "aldehyde 2", each contains 1.00 mmol of the aldehyde). Bright precipitate starts forming at once. Continue stirring for 10 min, then add 10 mL of water and stir for another 3 min.

Separation and purification of the product

Using scissors carefully cut out a filter paper circle, *ca.* 1 cm bigger in diameter than that of the glass filter. Wet the filter circle with water, and carefully put it on the filtering surface. The paper filter should fit evenly and tightly. If you fail to cut out an even circle, take a new filter from the table of common use and repeat cutting out. Assemble the apparatus. Remove the stirring bar from the beaker using the spatula and transfer the reaction product onto the filter. Turn on the water-jet pump (seek for help from your lab assistant if you experience difficulties) and filter out the precipitate. Put a little amount of water in the beaker and transfer the leftover product onto the filter. Wash the solid on the filter with water until the pH of the drops coming out the funnel are neutral. (Use the WASTE beaker to pour the round-bottom flask). Then wash the solid twice with ethanol using no more than 3 mL each time (Note: Hydrazone is slightly soluble in ethanol). Dry out the solid on the filter with working water-jet pump, loosening and squeezing the

product with a glass rod from time to time. After *ca.* 20-30 min carefully transfer the dried powder into the self-made filter paper box for the final drying in the air. Put the box with the product in a safe place (e.g. on the shelf). Turn off the water-jet pump when you do not use it! As soon as your products seem dry, we advise you weigh them to avoid queuing at the balances. To collect the products, use the plastic tubes with your student code. Fill in the answer box below. Note: The products you synthesized will be further re-examined by lab staff.

Repeat the above procedures with the other aldehyde**.**

1.1. Write down the structures of 2,4-dinitrophenylhydrazine and both products.

1.2. What kind of stereoisomerism (if any) is possible for these hydrazones? Tick the appropriate box!

☐ R/S ☐ E/Z ☐ threo/erythro ☐ manno/gluco ☐ D/L

2.1. What is the role of sulfuric acid in 2,4-dinitrophenylhydrazone formation? Tick the appropriate box.

☐ stoichiometric reagent ☐ catalyst ☐ reducing agent ☐ oxidizing agent

2.2. How would the rate of the reaction change, if the synthesis is carried out in neutral medium? Tick the appropriate box.

☐ highly increase	☐ slightly increase
☐ not change	☐ the reaction would proceed very slow

2.3. How would the rate of the reaction change, if it is carried out in alkaline medium? Tick the appropriate box.

☐ highly increase	☐ slightly increase
☐ not change	☐ the reaction would not proceed

Characterization

Place small amount ("on the tip of a spatula") of each product in an individual 25 mL beaker. Add 10 mL of acetone to each beaker. The best result will be obtained if the color and color intensity in each beaker are similarly yellow. Pour 5 mL of $NaHCO_3$ solution into each beaker. Stir the resulting mixtures with the glass rod using different ends.

3.1. Record your observations of the solutions color change in the box.

☐ The color does not change in either beaker ☐ Color changes significantly in both beakers ☐ Color changes significantly only in one beaker

Add 2 mL of NaOH solution to each of the resultant mixtures from the question 3.1. Stir the reaction mixtures with the glass rod.

3.2. Record your observations of the solutions color change in the box.

☐ The color does not change in either beaker ☐ Color changes significantly in both beakers ☐ Color changes significantly only in one beaker

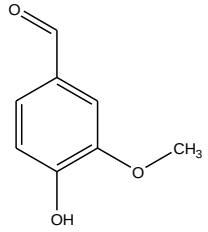
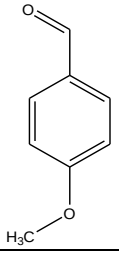
4.1. What structural features of your products explain the color change in the reaction with $NaHCO_3$? Tick the appropriate box.

☐ presence of MeO group at position 4 in the benzene ring; ☐ presence of MeO group at position 3 in the benzene ring; ☐ presence of the OH group at position 4 in the benzene ring; ☐ presence of both MeO and OH groups.

4.2. Which of the listed processes is responsible for the color change observed in the reaction of 2,4-dinitrophenylhydrazones with aqueous NaOH?

☐ alkaline hydrolysis ☐ dehydration ☐ hydration ☐ deprotonation ☐ dehydrogenation

4.3. Draw the structures of the main organic species present in each test reaction medium in the answer box below.

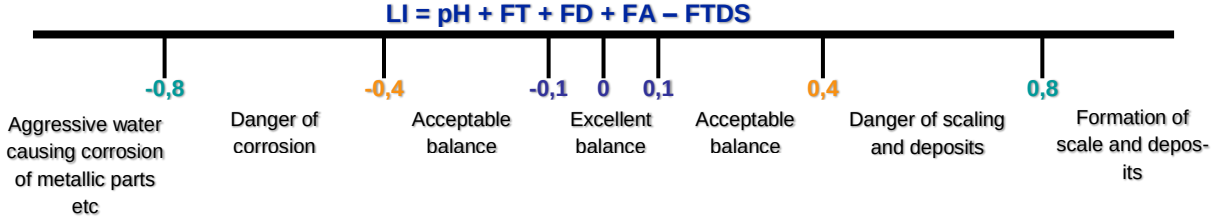
Initial aldehyde:  	Initial aldehyde: 
Solution of $NaHCO_3$ ...	Solution of $NaHCO_3$ ...
Solution of NaOH ...	Solution of NaOH ...

5. Put the numbers 1 or 2 under each structure. Calculate the percent yields of both hydrazones.

Problem 2. Determination of the Langelier Saturation Index of a pool water

The Langelier Saturation Index (LI) is a measure of a swimming pool water corrosivity as well as its ability to dissolve or deposit calcium carbonate. If LI is approximately zero, the water is considered "balanced". If the LI is a positive number, the water tends to deposit calcium carbonate and is scale-forming. If the LI is a negative number, the water is corrosive and dissolves calcium carbonate. The LI is a combination of the physical values factors taken from Table 1 and can be calculated by the formula:

$$LI = pH + FT + FD + FA - FTDS$$



pH : pH value

FT : Temperature factor

FD : Calcium hardness (CH) factor

FA : Total alkalinity (TA) factor

FTDS : Total dissolved solids (TDS) factor

Table 1. Values and corresponding factors

Temperature, °C	FT	Calcium hardness (CH), mg/L $CaCO_3$	FD	Total alkalinity (TA), mg/L $CaCO_3$	FA	Total dissolved solids (TDS), mg/L NaCl	FTDS
0	0.0	5	0.3	5	0.7	0	12.0
3	0.1	25	1.0	25	1.4	-	-
8	0.2	50	1.3	50	1.7	1000	12.1
12	0.3	75	1.5	75	1.9	-	-
16	0.4	100	1.6	100	2.0	2000	12.2
19	0.5	150	1.8	125	2.1	-	-
24	0.6	200	1.9	150	2.2	3000	12.25
29	0.7	250	2.0	200	2.3	-	-
34	0.8	300	2.1	300	2.5	4000	12.3
41	0.9	400	2.2	400	2.6	-	-
53	1.0	600	2.35	800	2.9	5000	12.35
-	-	800	2.5	1000	3.0	-	-
-	-	1000	2.6	-	-	6000	12.4

In this task you will have to determine the LI value of the given water sample. Note that hardness is expressed as the equivalent to the concentration of $CaCO_3$ (expressed in

mg/L). Total alkalinity being the acid equivalent to the total amount of carbonate and hydrocarbonate, also expressed in mg/L of $CaCO_3$, whereas TDS is recalculated as NaCl concentration (mg/L).

Procedures

Calcium hardness is determined by complexometric titration with EDTA (Na_2H_2Y). This is performed in a strongly alkaline medium to mask magnesium (large amounts of Mg^{2+} interfere due to the co-precipitation of calcium with $Mg(OH)_2$; moreover, the complexometric indicator is also adsorbed on $Mg(OH)_2$, which impairs the observation of its color change). When the alkali is added, titration should be carried out immediately to avoid the deposition of $CaCO_3$.

1.1. Write down equation of the reaction occurring during titration with Na_2H_2Y:

Procedure for calcium determination

a) Put the standard solution of **EDTA** (exact concentration of 0.0443 M) in the burette.
b) Pipette a 20 mL aliquot of the **Water sample** into an Erlenmeyer flask.
c) Add 3 mL of 2M NaOH solution with the 10-mL measuring cylinder.
d) Add murexide indicator with spatula to obtain noticeably pink solution.
e) Within few minutes titrate the mixture with EDTA until the indicator color changes from pink to purple.

1.2. Do the determination as described.

2. Calculate the hardness of the water sample in mg/L $CaCO_3$. Write down the result in Table 4 (see question 7).

3.1. Write down the pH value in Table 4 (see question 7).

3.2. Which form of carbonic acid predominates in your water sample?

Note. The dissociation constants of carbonic acid are: $K_1 = 4.5 \cdot 10^{-7}$; $K_2 = 4.8 \cdot 10^{-11}$.

3.3. Write down the ionic equation of the predominant reaction of titration of the water sample with HCl.

To obtain the value of the total alkalinity the water sample should be titrated to H_2CO_3. An acid-base indicator used is methyl orange, which starts changing its color from yellow to orange at pH of about 4.5.

a) Rinse the burette with distilled water and fill it with the standard HCl solution (exact concentration of 0.0535 M).
b) Pipette a 50.0 mL aliquot of water sample into an Erlenmeyer flask and add 3 drops of methyl orange solution.

c) If the sample is orange prior to addition of the acid the total alkalinity is zero. If the solution is yellow titrate it with the standard acid solution until the first noticeable color change towards orange is observed. Record the volume of the titrant used.

4.1. Do the determination as described.

4.2. Calculate the total alkalinity (in mg/L $CaCO_3$). Write down the result in Table 4 (see question 7).

5. Temperature measurement. Read the thermometer located at the table of common use and write down the value into Table 4 (see question 7).

6. TDS determination in the water sample with the test strip.

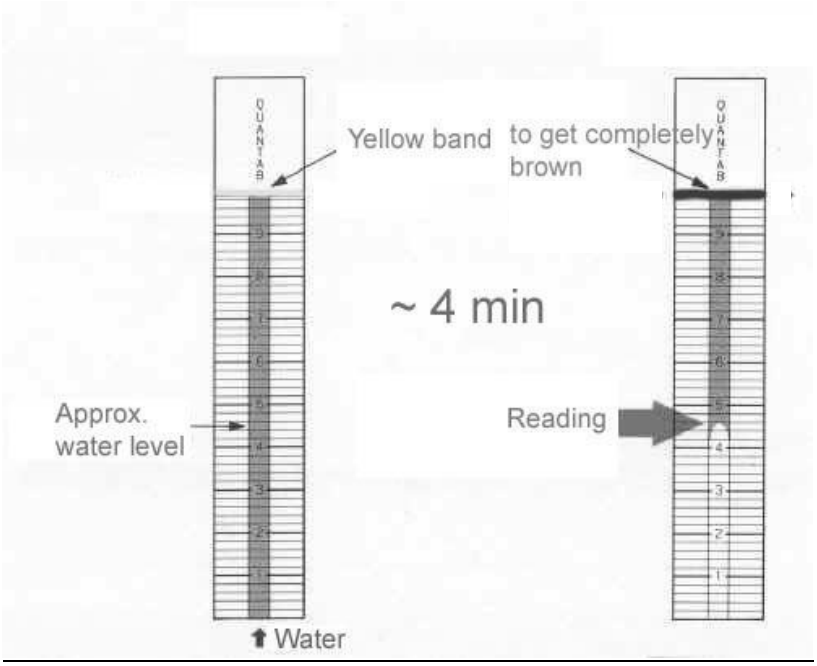
a) Fill a beaker with the water sample to a level of about 3 cm of height. Immerse the strip into water; be sure that the yellow band on the top of the strip does not touch the liquid.

b) Wait for 3–4 min until the yellow band turns completely brown. Take the reading as shown in the picture hereunder, reading result to one decimal digit.

c) Report the reading.

d) Find your TDS concentration as that of NaCl, mg/L in the table to the right of the picture.

e) Write down the concentration of NaCl in Table 4 (see question 7).



Reading	NaCl conc., mg/L
1.4	360
1.6	370
1.8	420
2.0	430
2.2	470
2.4	530
2.6	590
2.8	660
3.0	730
3.2	800
3.4	880
3.6	960
3.8	1050
4.0	1140
4.2	1240
4.4	1340
4.6	1450
4.8	1570
5.0	1700

7. *Fill in all the blank boxes in the Table 4. Calculate LI and write down the result in Table 4. Take the values of the factors to the accuracy of two decimal digits.*

Table 4. Calculation of LI of the water sample

Water sample Number _____					
CH, mg/L $CaCO_3$	TA, mg/L $CaCO_3$	*t*, °C	pH	TDS, mg/L NaCl	LI
FD	FA	FT		FTDS	

Theoretical questions. Water balance correction.

If LI significantly deviates from zero, it is needed to be adjusted to zero.

Imagine you are given a sample of pool water analyzed as you have done above. The results of the analysis are: CH = 550 mg/L, FD = 2.31, TA = 180 mg/L, FA=2.26, t° = 24°C, FT = 0.6; TDS = 1000 mg/L , FTDS = 12.1, pH = 7.9, LI = 0.97.

The pool serviceman added 10 mL of 0.0100 M solutions of reagents ($NaHCO_3$, NaOH, $NaHSO_4$, $CaCl_2$, EDTA (disodium salt dihydrate) and HCl) to different pool water samples 200 mL each (one reagent for one sample).

8. *Decide whether $CaSO_4$ is deposited upon addition of $NaHSO_4$.*

Note: $CaSO_4$ solubility product is $5 \cdot 10^{-5}$. Assume no precipitate of $CaCO_3$ is formed upon addition of any of the above reagents

9. *Fill in the hereunder table by showing the trends of changes resulting from addition of each reagent to this particular water sample (use "+" if the factor increases, "−" if it decreases, and "0" if it does not change).*

Table 5

Reagent	pH	FA	FD	FTDS	LI
$NaHCO_3$					
NaOH					
$NaHSO_4$					
$CaCl_2$					
Na_2H_2Y					
HCl					

Problem 3 Determination of molecular mass by viscometry

Viscosity coefficient is a measure of fluid resistance to flow. It can be determined by measuring the rate of liquid flow through a thin capillary. Polymer solution viscosity grows with increasing concentration. At constant concentration, stronger solvent-

polymer interactions result in more expanded polymer coils, and therefore, in higher viscosity.

Provided the density of the diluted solution of a polymer is equal to that of the solvent, the reduced viscosity η_{red} of the polymer solution with concentration c (g/mL) is defined as follows:

$$\eta_{red} = \frac{t - t_0}{t_0 c}$$

where t and t_0 are the flow times of the solution and pure solvent, respectively.

Reduced viscosity for dilute polymer solutions depends on concentration as follows:

$$\eta_{red}(c) = [\eta] + kc,$$

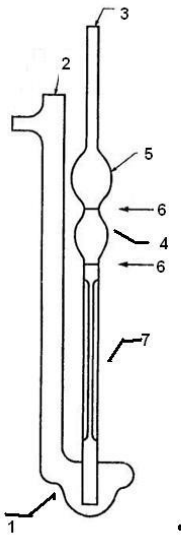
with k, a parameter (mL^2/g^2) and [η], intrinsic viscosity (mL/g). The intrinsic viscosity *[η]* is determined by extrapolation of the reduced viscosity to zero polymer concentration. In general, the intrinsic viscosity is related to the molecular mass M of the polymer according to the Mark-Kuhn-Houwink equation:

$$[\eta] = KM^{\alpha},$$

where K and α are the constants for a particular solvent-polymer pair at a certain temperature.

Thus, M can be derived from the Mark-Kuhn-Houwink equation using experimentally determined *[η]* and reference data for K and α.

How to work with viscometer



1 – Collection vessel
2, 3 – Supplementary tubing
4 – Measurement vessel
5 – Collection vessel
6 – The match marks
7 - Capillary

a) Mount the viscometer so that its tubing (3) is vertical, and the collection vessel (1) stands on the lab stand basement. Adjust the fixing clamp as low as possible.

b) Put 10 mL of the liquid to be analyzed into the collection vessel (1) through the tubing (2) using a pipette.

c) Place the pipette filler or rubber bulb on top of the tubing (3) and suck the liquid into the measurement vessel (4) so that the liquid is drawn into the collection vessel (5). When sucking the liquid, avoid the air bubbles in the capillary (7) and the vessels (4, 5), as these can cause significant experimental errors. The liquid meniscus should be about 10 mm above the upper mark (6).

d) Zero the stopwatch, and remove the pipette filler or bulb out of the tube (3). The liquid starts flowing down to the collection vessel (1).

e) Measure the **flow time**: start the stopwatch when the liquid meniscus passes the upper match mark (6) and stop the stopwatch when the liquid meniscus passes the lower match mark (6).

Clean the viscometer three times with tap water and once with distilled water before you pass over to a new polymer sample. To do this, first wash it with tap water, and then rinse with distilled water. There is no need to wash it with the polymer solution, the error can occur but it is negligible.

Procedure

You are provided with a set of aqueous solutions of polymers (0.01 g/mL, stock solutions). Three of P1-P4 are solutions of poly(vinyl alcohol), whereas the fourth one is that of a partially hydrolyzed poly(vinyl acetate) containing *ca*. 10% of non-hydrolyzed units. It is unknown which of the P1-P4 solutions is partially hydrolyzed poly(vinyl acetate). Molecular masses of the polymers P1-P4 are given in the Table.

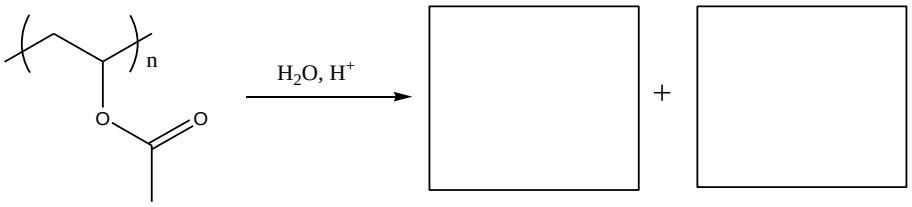
Approximate molecular mass	Sample code
26650	P2
50850	P1
65300	P4
91900	P3

Sample X is poly(vinyl alcohol) of an unknown molecular mass.

In this task you will have to identify which of P1-P4 is the solution of partially hydrolyzed poly(vinyl acetate) and determine the molecular mass of polymer X.

1. *Write down the reaction scheme of poly(vinyl alcohol) preparation by hydrolysis of poly(vinyl acetate).*

Reaction scheme:



2. *Choose (tick appropriate box) which polymer shows the stronger interaction with water and compare the viscosities of aqueous solutions of fully and partially hydrolyzed poly(vinyl acetates). Assume that the concentration of the solutions and the molecular masses of the polymers are the same.*

   Poly(vinyl alcohol) ☐

   Partially hydrolyzed poly(vinyl acetate) ☐

   Compare the viscosities:

   $\eta_{\text{poly(vinyl alcohol)}}$ _____ $\eta_{\text{partially hydrolyzed poly(vinyl acetate)}}$ (put either <. >, or ≈)

3. *Measure the flow time of the pure solvent (distilled water). You are not requested to fill all the boxes below.*

4. *Measure the flow times of the stock solutions of P1-P4, and that of X. Calculate the reduced viscosities. You are NOT requested to fill in all table cells in the Answer Boxes. Perform as many measurements as you prefer for accurate averaging.*

Sample→	**P2** (26650)	**P1** (50850)	**P4** (65300)	**P3** (91900)	**X**
Flow time, s					
Accepted flow time:	_____ s	_____ s	_____ s	_____ s	_____ s

Sample→	**P2** (26650)	**P1** (50850)	**P4** (65300)	**P3** (91900)	**X**
Reduced viscosity of the stock solutions, mL/g					

5. *Encircle the solution out of P1-P2-P3-P4 which is the sample of partially hydrolyzed poly(vinyl acetate).*

   Hint: Take into account the given molecular masses of the polymers P1-P4.

P1	P2	P3	P4

DO NOT USE THIS POLYMER IN THE NEXT PART OF THE EXPERIMENT.

6. *To determine the parameters of the Mark-Kuhn-Houwink equation and calculate the unknown molecular mass of X choose and encircle two most appropriate solutions of poly(vinyl alcohol) with different molecular masses. Assume that the absolute error of intrinsic viscosity determination does not depend on the sample molecular mass.*

P1	P2	P3	P4

7. Using appropriate measuring glassware to prepare the solutions, measure the flow time of a number of diluted solutions of three poly(vinyl alcohol) samples: that of unknown molecular mass (X), and the pair of poly(vinyl alcohols) chosen in i. 6, and calculate the corresponding reduced viscosities. When calculating the diluted solutions concentration, assume density of the polymer solutions is equal to that of water.

   Determine the intrinsic viscosities for each of the examined samples. Submit the graph paper with your plots together with the booklet. Note: if you would like to plot the data referring to different samples on the same plot, make sure you use clearly distinguishable symbols for each dataset. You are NOT requested to fill in all table cells in the Answer Boxes.

   The following table for each sample:

Concentration, g/mL:					
Stock solution, mL					
Water, mL					
Flow time, s:					
Accepted flow time, s					
Reduced viscosity, mL/g					
Intrinsic viscosity [☐], mL/g					

Summary of experimental results (only fill in the measured values)

Sample→	P__	P__	X
Concentration (c), g/mL:	0.01	0.01	0.01
Reduced viscosity (η_{red}), mL/g			
c (1st dilution), g/mL:			
η_{red}, mL/g			
c (2nd dilution), g/mL:			
η_{red}, mL/g			
c (3rd dilution), g/mL:			
η_{red}, mL/g			
c (4th dilution), g/mL:			
η_{red}, mL/g			
c (5th dilution), g/mL:			
η_{red}, mL/g			

8. *Write down the form of equation you would use to determine K and α.*
   Derive the K and a values for the aqueous solution of poly(vinyl alcohol).

9. *By using the obtained K and α values, as well as the intrinsic viscosity of the X solution, calculate the molecular mass of the polymer X. If you have failed to determine K and a, use K = 0.1 mL/g and a = 0.5.*

Solutions to the theoretical problems

Solutions to problem 1

1. n(methane) = $\frac{p \cdot V}{R \cdot T}$ n(Methane) = $\frac{101300\ \text{Pa} \cdot 205 \cdot 10^{-6}\ \text{m}^3}{8.313\ \text{JK}^{-1}\text{mol}^{-1} \cdot 298.15\ \text{K}}$ = $8.38 \cdot 10^{-3}$ mol

   n(water) = $\frac{1\ \text{g} - 8.38 \cdot 10^{-3}\ \text{s mol} \cdot 16\ \text{g/mol}}{18\ \text{g/mol}}$ = $48.1 \cdot 10^{-3}$ mol

   n(water) / n(Methane) = 48.1 / 8.38 = 5.74 Formula: $CH_4 \cdot 5.75\ H_2O$

2. $CH_4 \cdot 6H_2O \longrightarrow CH_4 + 6H_2O$

3. Decomposition of methane hydrate can be viewed as a phase transition, which obeys the Clausius-Clapeyron equation:

   $\frac{dp}{dT} = \frac{\Delta H}{T \cdot \Delta V}$ $\Delta V = \frac{R \cdot T}{p} + \frac{6 \cdot M(H_2O_{(s)})}{p(H_2O_{(s)})} - \frac{M(CH_4 \cdot 6\ H_2O)}{p(CH_4 \cdot 6\ H_2O)}$

   The difference between two last terms is negligibly small in comparison with the first term.

   $\Rightarrow \quad \frac{1}{p}\,dp = \frac{\Delta H}{R \cdot T^2}\,dT \qquad \Rightarrow \quad \ln p = -\frac{\Delta H}{R} \cdot \frac{1}{T} + C$

   $p = p_0 \cdot e^{\left(\frac{\Delta H}{R} \cdot \left(\frac{1}{T_0} - \frac{1}{T}\right)\right)}$ mit T_0 = 192.15 K. T = 268.15 K p_0 = 101300 Pa

   $\Rightarrow$ p = 2.2 MPa

4. At the minimum possible depth, the sum of pressures of atmosphere and water column is equal to the dissociation pressure of methane hydrate. The temperature should be as low as possible, but it cannot be less than the melting point of water at the corresponding pressure. Thus, the temperature and pressure should correspond to the point of coexistence of water, ice, methane hydrate and gaseous methane. Since the melting point of water decreases with increasing pressure, the correct answer is 272.9 K.

   ☑ 272.9 K ☐ 273.15 K ☐ 273.4 K

   Substituting T = 272.9 K into the relevant equation above, we obtain p = 2.58 MPa.
   The height of the water column:, h = $\frac{p - p_{atm}}{g \cdot \rho(H_2O)}$ with g = 9.8 $m \cdot s^{-2}$ $\Rightarrow$ h = 250 m

5. From the Hess's law, the enthalpy of the process $CH_4 \cdot 6H_2O \longrightarrow CH_4 + 6H_2O(l)$ is
   ΔH = (17,47 + 6·6,01) kJ/mol = 53,53 kJ/mol.
   From question 4 we know that at T_0 = 272.9 K and p_0 = 2.58 MPa there is an equilibrium between methane, water and methane hydrate.
   Since that we can calculate the temperature of decomposition T at pressure
   p = (9.8·1000·372 + 101000) Pa = 3746600 Pa using the equation $\frac{1}{T} = \frac{1}{T_0} + \frac{R}{\Delta H} \cdot \ln\frac{p_0}{p}$.
   T = 277.3 K ≈ 4°C (which is in agreement with the measured temperature of Baikal water at such depth).

6. $M(CH_4)$ = 16 g/mol $\Rightarrow$ $5 \cdot 10^{11}$ t CH_4 ≙ $5 \cdot 10^{17}$ g /16 $g \cdot mol^{-1}$ = $3.125 \cdot 10^{16}$ mol CH_4
   released heat = $3.125 \cdot 10^{16}$ mol · 889 $kJ \cdot mol^{-1}$ = $2.78 \cdot 10^{22}$ J
   ΔT = $2{,}78 \cdot 10^{22}$ J / $4 \cdot 10^{21}$ $J \cdot K^{-1}$ ≈ 7 K

Solution to problem 2.

1. $H_2O + CO_2 = \{CH_2O\} + O_2$

2.

Natural photosynthesis		Hill reaction	
Oxidant	Reducing agent	Oxidant	Reducing agent
CO_2	H_2O	$K_3[Fe(C_2O_4)_3]$	H_2O

3a. The upper curve in the saturation limit gives ~ 75% of HbO_2

$n(Fe) / n(O_2) = c(Fe) / c(HbO_2) = 2.0\cdot10^{-4} / (0.75\cdot0.6\cdot10^{-4}) = 4.4 : 1$

3b. Ratio ~ 4:1 shows that Fe(III) is reduced to Fe(II), which in the presence of excess oxalate exists as a complex:

$2\ H_2O + 4\ [Fe(C_2O_4)_3]^{3-} \longrightarrow O_2 + 4\ [Fe(C_2O_4)_3]^{4-} + 4\ H^+$

3c. $[Fe(C_2O_4)_3]^{3-} + e \longrightarrow [Fe(C_2O_4)_3]^{4-}$ $E_1^\circ = 0.05$ V

$O_2 + 4\ H^+ + 4\ e \longrightarrow 2H_2O$ $E_1^\circ = 1.23$ V

emf: $E^\circ = E_1^\circ - E_2^\circ = -1.18$ V

$\Delta G = \Delta G^\circ + R\cdot T\cdot\ln(p_{O_2}\cdot[H^+]^4 = [- 4\cdot96500\cdot(-1.18) + 8.314\cdot298\cdot\ln(\frac{1}{750}\cdot(10^{-8})^4)]$ J/mol

$\Delta G = 257$ kJ/mol

$\Delta G = \Delta G^\circ + R\cdot T\cdot\ln(p_{O_2}\cdot[H^+]^4 = [- 4\cdot96500\cdot(-1,18) + 8,314\cdot298\cdot\ln(\frac{1}{750}\cdot(10^{-8})^4)]$ J/mol

$\Delta G = 257$ kJ/mol

The reaction is not spontaneous, highly endergonic.

4a.

Low intensity			High intensity		
0 ☐	1 ☑	2 ☐	0 ☑	1 ☐	2 ☐

4b. $n(Chl) / n(O_2) = 1/900 / [(12\cdot10^{-6}\cdot(740/760)\cdot101.3)/(8.314\cdot283)] = 2200$

5. Total energy absorbed: $E = 0.503\cdot10^{-3}\cdot 3600\cdot2$ J = 3.62 J

Energy of one mole of photons: $E_m = hcN_A / \lambda$

$E_m = [6.63\cdot10^{-34}\cdot3.00\cdot10^8\cdot6.02\cdot10^{23} / (672\cdot10^{-9})]$ J/mol = $1.78\cdot10^5$ J/mol

$n(phot) = E / E_m = 2.03\cdot10^{-5}$ mol

$n(O_2) = PV / RT = (740/760)\cdot101.3\cdot47.6\cdot10^{-6} / (8.314\cdot283) = 2.00\cdot10^{-6}$ mol.

Formation of one O_2 molecules requires the transfer of 4 electrons:

$n(e) = 8.00\cdot10^{-6}$ mol $n(phot) / n(e) = 2.5$.

6.

	Yes	No
In natural photosynthesis, water oxidation and CO_2 reduction are separated in space.	√	
In chloroplasts, O_2 is produced from CO_2.		√
Oxidation of water in chloroplasts requires light illumination.	√	
Most of chlorophylls in chloroplasts participate directly in the photochemical O_2 production.		√
In isolated chloroplasts, every absorbed photon causes transfer of one electron.		√

Solution to problem 3

1a. $\Delta_r H^o_{298} = \Delta_f H^o_{298}(C_3H_6O) + \Delta_f H^o_{298}(C_6H_{12}O) - \Delta_f H^o_{298}(C_3H_8O) - \Delta_f H^o_{298}(C_6H_{10}O)$

$\Delta_r H^o_{298} = [(-248.4) + (-348.2) - (-318.1) - (-271.2)]$ kJ/mol = – 7.3 kJ/mol,

$\Delta_r S^o_{298} = S^o_{298}(C_3H_6O) + S^o_{298}(C_6H_{12}O) - S^o_{298}(C_3H_8O) - S^o_{298}(C_6H_{10}O)$

$\Delta_r S^o_{298} = [200.4 + 203.4 - 180.6 - 229.0]$ J/(mol·K) = –5.8 J/(mol·K)

$\Rightarrow \quad \Delta_r G^o_{298} = \Delta_r H^o_{298} - T\,\Delta_r S^o_{298} = -5.6$ kJ/mol

$\Rightarrow \quad K = e^{-\Delta_r G^0_{298}/RT} = 9.6$

$$K = \frac{x(C_3H_6O)\cdot x(C_6H_{12}O)}{x(C_3H_8O)\cdot x(C_6H_{10}O)} = \frac{n(C_3H_6O)\cdot n(C_6H_{12}O)}{n(C_3H_8O)\cdot n(C_6H_{10}O)}$$

where x is the molar fraction of a substance in the equilibrium mixture, v is an amount of a substance in the mixture. Denote the initial amount of cyclohexanone as y. 99% of cyclohexanone must react. Hence, in equilibrium the amounts of $C_6H_{10}O$ and $C_6H_{12}O$ are $0.01y$ and $0.99y$, respectively. Denote the initial amount of isopropanol z. Due to the reaction stoichiometry the amounts of C_3H_6O and C_3H_8O in equilibrium are $0.99y$ and $(z - 0.99y)$, respectively. Substituting these amount into the expression for equilibrium constant one gets:

$$K = 9{,}6 = \frac{0{,}99y\cdot 0{,}99y}{0{,}01z\cdot(z-0{,}99y)} = \frac{98{,}01}{\frac{z}{y}-0{,}99} \qquad \Rightarrow \frac{z}{y} = n(C_3H_8O) : n(C_6H_{10}O) = 11{,}2$$

$\Rightarrow \quad m(C_3H_8O) : m(C_6H_{10}O) = v(C_3H_8O)\cdot M(C_3H_8O) / (v(C_6H_{10}O)\cdot M(C_6H_{10}O))$

$\Rightarrow \quad m(C_3H_8O) : m(C_6H_{10}O) = 11.2 \cdot 60 / 98 = 6.9$

1b.

Increase the temperature up to 50°C using a reflux	
Increase the temperature up to 60°C, evaporating (distilling) the acetone	**V**
Add some ethanol to the reaction mixture	**V**
Add some ethanal to the reaction mixture	

2. Rate-limiting step is the hydride transfer

$A + C \rightleftarrows A{\cdot}C$ FAST, K

$A{\cdot}C \longrightarrow A'{\cdot}C'$ rate-determining, k

$$K = \frac{[A\cdot C]}{[A]\cdot[C]}$$

$r = k\cdot[A\cdot C] \quad \Rightarrow \quad r = k\cdot K\cdot[A]\cdot[C]$

Rate-limiting step is the transalkoxylation of the alcoholate by isopropanol

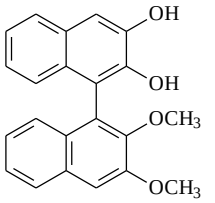
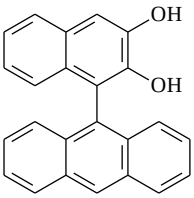
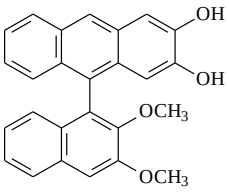
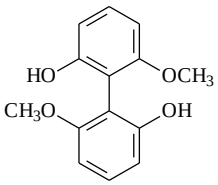
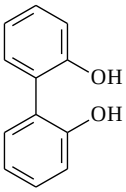
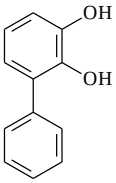
$A + C \rightleftarrows A{\cdot}C$ fast, K_1

$A{\cdot}C \rightleftarrows A'{\cdot}C'$ fast, K_2

$A'{\cdot}C' + B \rightarrow P$ rate-determining, k

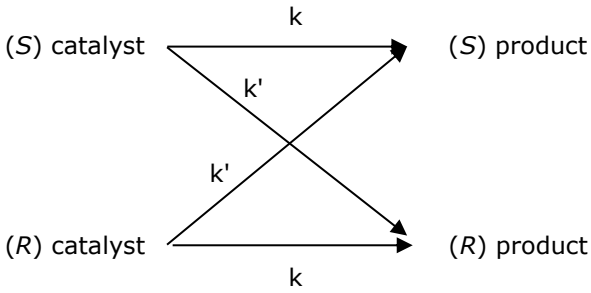
$r = k\cdot[A'{\cdot}C']\cdot[B] \quad \Rightarrow \quad r = k\cdot K_1\cdot K_2\cdot[A]\cdot[B]\cdot[C]$

3.

Substance	Can be used	Substance	Can be used
	V		
	V		V
			

4. Solution 1

The total kinetic scheme is:



According to the scheme, the *R*:*S* ratio is

$$\frac{[(R)-product]}{[(S)-product]} = \frac{k\cdot[(R)-Katalysator]+ k'\cdot[(S)-Kataöysator]}{k\cdot[(S)-Kataöysator]+ k'\cdot[(R)-Katalysator]}$$

After inserting this expression into *ee* definition one gets:

$$ee_{product} = \frac{[(R)-product]- [(S)-product]}{[(R)-product]+ [(S)-product]} = \left(\frac{[(R)-product]}{[(S)-product]} - 1\right) / \left(\frac{[(R)-product]}{[(S)-product]} + 1\right)$$

$$ee_{product} = \frac{k\cdot[(R)-catalyst]+ k'\cdot[(S)-catalyst]-k\cdot[(S)-catalyst]+ k'\cdot[(R)-catalyst]}{k\cdot[(R)-catalyst]+ k'\cdot[(S)-catalyst]+ k\cdot[(S)-catalyst]+ k'\cdot[(R)-catalyst]}$$

$$ee_{product} = \frac{[(R)-catalyst]- [(S)-catalyst]}{[(R)-catalyst]+ [(S)-catalyst]+} \cdot \frac{k-k'}{k+k'} = ee_{catalyst} \cdot \frac{k-k'}{k+k'}$$

That is, the *ee* of the product is proportional to the *ee* of the catalyst:

$ee_{Produkt} = ee_{Katalysator} \cdot \frac{k-k'}{k+k'}$, applying numbertst: $ee_{Produkt} = 0.50 \cdot 0.81 = 0.41$

Solution 2

R-catalyst ⟶ 90.5% R + 9.5% S

Rac- catalyst ⟶ 50% R + 50% S

% of R-product = 0.5 · 0.905 + 0.5 · 0.5 = 0.7025

% of R-product = 0.5 · 0.095 + 0.5 · 0.5 = 0.2975

ee-product = 0.7025 - 0.2975 = 0.405

Solution to problem 4

1. (a) The general formula of a binary compound is XO_n. The molar ration of **X** and O should be 93.1/*X* : 6.9/16 = 1 : *n*, where *X* is a molar mass of metal **X** and *n* = n ∈ {0,5; 1; 1,5; 2...}. *n* = 0.5 gives *X* = 107.9 g/mol that is of silver. **X** – Ag, **B** – Ag_2O.
   (b) The heating of silver salts generally results in reduction of the metal. According to the mass loss, the molar mass of **A** is 170 g/mol, that is silver nitrate: **A**` – $AgNO_3$.

2. (a) The residue formed by heating on air is metallic silver, as the silver compounds readily decompose. Substance **C** contains silver and probably sulphur and oxygen as it evolves sulphur oxide by heating in vacuum.
   1.10 g of **C** contains 0.90 g of Ag, so 1 mol of Ag is in 132 g of **C**. The mass of the elements other than Ag is (132 – 108) g = 24 g, which corresponds to 1/2S and 1/2O. So, the empirical formula is $AgS_{1/2}O_{1/2}$ or Ag_2SO.
   (b) The light brown color of the precipitate after the addition of barium salt means the formation of barium sulphate which is unsoluble in acids. The sulphate groups on the surface of the precipitate are substituted by perchlorate-ions from solution. So, basing on the formula Ag_2SO and assuming the presence of sulphate, the formula $Ag_8S_3SO_4$ can be suggested.
   (c) **Equation 1:**
   $16\ AgNO_3 + 6\ Na_2S_2O_3 + 6\ H_2O \longrightarrow 2\ [Ag_8S_3]SO_4\downarrow + 4\ Na_2SO_4 + 4\ NaNO_3 + 12\ HNO_3$
   Equations 2 – 4:
   $[Ag_8S_3]SO_4 + 2\ O_2 \longrightarrow 8Ag + 4\ SO_2$
   $[Ag_8S_3]SO_4 \longrightarrow 2\ Ag_2S + 4\ Ag + 2\ SO_2.$
   $SO_2 + Ca(OH)_2 \longrightarrow CaSO_3 + H_2O$ or $2\ SO_2 + Ca(OH)_2 \longrightarrow Ca(HSO_3)_2$

3. We can assume that the sulphate-ions in **C** are substituted by nitrate-ions.
   For a formula unit containing n silver atoms, molar mass is (108*n* / 0.775) g/mol = 139.35n g/mol. For n = 3 we get M = 418 g/mol. That corresponds to 418 – 108·3 = 94 that is NO_3 + S. So, **D** is $[Ag_3S]NO_3$.
   $[Ag_8S_3]SO_4 + AgNO_3 + 2\ NaNO_3 \longrightarrow 3\ [Ag_3S]NO_3 + Na_2SO_4$

Solution to problem 5

1a. The area of a hexagon is S = $5.16 \cdot 10^{-20}$ m^2.
   The number of hexagons per gram of carbon, n, is $n = N_A \cdot \frac{3}{6} \cdot \frac{1}{12} = 2{,}51 \cdot 10^{22}\ g^{-1}$
   The area per gram is $S_{total} = S \cdot n \cdot 2 = 2590\ m^2/g$
   (In case of two-dimensional material both sides of the layer are open for adsorption and have to be taken into consideration. The total area of hexagons should be multiplied by two!)

1b. Graphene is on the solid support and only one side of the plane works. One molecule of nitrogen falls on 6 atoms of carbon (three hexagons) (see fig.2).

Mass of nitrogen adsorbed per gram of graphene:

$\frac{m_{N_2}}{m_C} = \frac{1 \cdot 28}{6 \cdot 12}$ = 0.39; m_{N_2} = 0.39 g

$V_{N_2} = \frac{(\frac{m}{M}) \cdot R \cdot T}{p} = \frac{(\frac{0,39}{28}) \cdot 8.314 \cdot 298}{100000}$ m^3= 0.34 dm^3.

2. The equilibrium constant for the adsorption on graphite surface is

K(graphite) = $\frac{n(CCl_4\ an\ graphite)}{p(CCl_4)} = \frac{2,0 \cdot 10^{-7}\ m,ol/m^2}{6.6 \cdot 10^{-5}\ bar}$ = 3.0·10^{-3} mol·m^{-2}·bar^{-1}

The equilibrium constant needs to be re-calculated for the graphene surface. There is a 10% difference in enthalpies of adsorption on graphene and on graphite, respectively, while the entropies are the same, so

$\frac{K(graphene)}{K(graphite)} = e^{-(\Delta H_{graphene} - \Delta H_{graphite})/RT}$ = e$^{-3510/8.314 \cdot 298)}$ = 0.24

K(graphene) = 0.24 K(graphite) K(graphene) = 7.2·10^{-4} mol·m^{-2}·bar^{-1}

The adsorption of CCl_4 on graphene is calculated based on the equilibrium constant for graphene surface and the area of graphene surface in m^2 /g. One side of the graphene layer works in this case,

S_{total} = 2590/2 m^{2}g^{-1} = 1295 m^{2}g^{-1}

n = K(graphene) · p(CCl_4) · S_{total} = 7.2·10^{-4} mol·m^{-2}·bar^{-1} · 10^{-4} bar · 1295 m^{2}g^{-1}

n = 9.3 mol/g

3. The lower limit of detectable concentration of a substance on the graphene surface is

n = $\left(\frac{10^9}{6,022 \cdot 12^{23}/mol}\right)$ /10^{-4} m^2 = 1,7·10^{-11} mol/m^2

The equilibrium constant and the enthalpy of adsorption of ethane on graphite are given in Fig.3: M(ethane) = 30 g/mol; ln 30 = 3.4 ; ln K = –11.8, ΔH^o = –22.5 kJ·mol^{-1}

K_{ethane} = 7.5 mol·m^{-2}·bar^{-1}

This equilibrium constant needs to be re-calculated to the graphene surface (see question 2):

K_{ethane}(graphene) = K_{ethane}(graphite) · e$^{-2250/8.314 \cdot 293)}$ = 7.5 mol·m^{-2}·bar^{-1} · 04

K_{ethane}(graphene) = 3.0 mol·m^{-2}·bar^{-1}

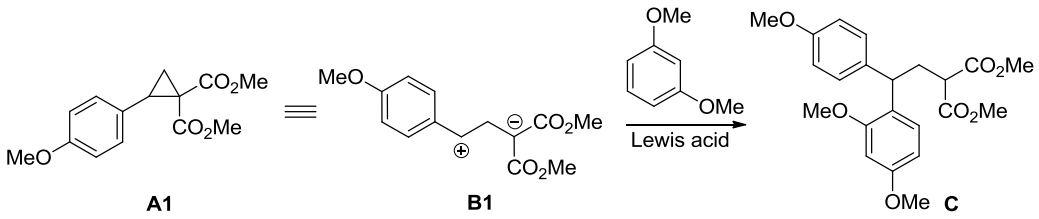
The partial pressure of ethane is

$p_{ethane} = \frac{n(\text{ethane on graphene})}{K_{ethane}(\text{graphene})} = \frac{1.7 \cdot 10^{-11}}{3.0 \cdot 10^{-6}}\ bar$ = 5.7·10^{-6} bar

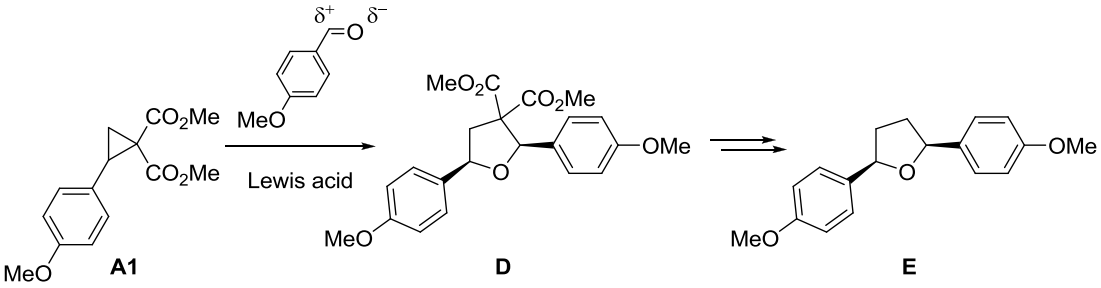
Content of ethane= 5.7·10^{-6} / 1.013 · 100% = 5.6·10^{-4} %

Solution to problem 6

1. Reaction of **A1** with 1,3-dimethoxybenzene as a nucleophile proceeds as Friedel-Crafts alkylation. Electrophiles attacks onto *ortho-/para*-position. Attack onto C4 position of arene proceeds easier than attack onto sterically more hindered C2 atom.



2. **A1** reacts similarly to 1,3-zwitterion **B1**. It is the 3-atom component.
Therefore, 4-methoxybenzaldehyde is a two-atom component.
Benzene ring is not prone to react as two-atom component. So, C=O group participates in the reaction. Accounting for its polarization, carbonyl oxygen reacts with a positive end of 1,3-zwitterion **B1**.
Product has *cis*-geometry (see below)
Therefore, **D** is *cis*-dimethyl 2,5-diaryltetrahydrofuran-3,3-dicarboxylate.
Decarboxylation of **D** produces 2,5-bis(4-methoxyphenyl)tetrahydrofuran **E** (accounting for its molecular formula). It has *cis*-arrangement of aryl groups as **E** has a plane of symmetry.



3.

	Ratio of the number of hydrogen-containing groups					**Composition**
	Non-aromatic				Aromatic	
	CH	CH_2	CH_3	OH		
F	1	1	1+1+1	0	4 in total	C 63.62%, H 6.11%
G	1+1+1	0	2+1	0	4 in total	C 63.62%, H 6.11%
H	1	1	1+1+1	0	4 in total	C 63.62%, H 6.11%
I	1+1+1	1+1	2+1+1+1+1	0	7 in total	C 63.62%, H 6.11%
J	0	0	1+1	1	5 in total	C 67.22%, H 5.22%
K	1+1	1	2+1+1+1	0	1	C 59.24%, H 6.23%
L	1+1+1+1+1	1	2+2+1+1+1+1	0	5 in total	C 61.21%, H 6.18%

F and **G** are isomers of **A1**. **G** has three CH groups instead of the cyclopropane fragment, two equivalent ester groups and unchanged aromatic fragment. So, **G** is $ArCH{=}CHCH(CO_2Me)_2$ which is formed by cyclopropane-to-alkene isomerization as (*E*)-isomer (more stable than *Z*-isomer).

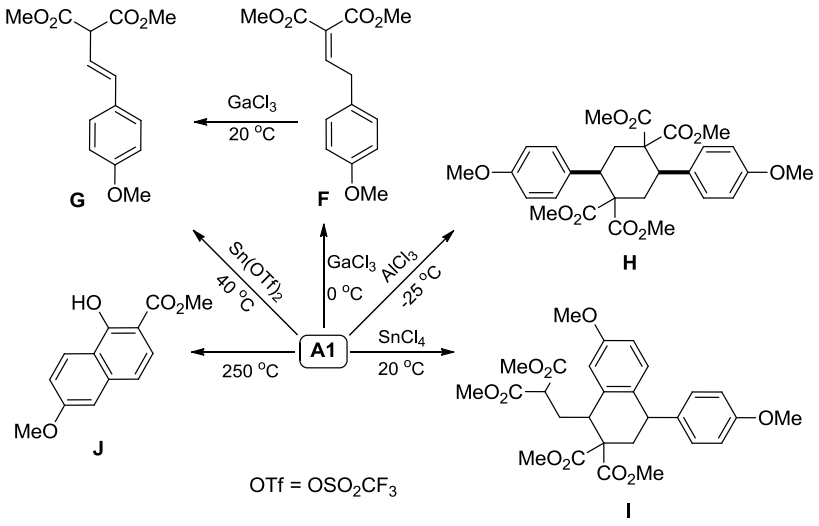
F has CH_2 and CH groups, two different ester groups and unchanged aromatic fragment. **F** is formed from **A1** and undergoes secondary isomerization into **G**. Therefore, **F** is $ArCH_2CH{=}C(CO_2Me)_2$.

I has twice as many protons as **A1**. It means that isomeric **H** and **I** are dimers of **A1**. Indeed, in problem it is directly stated that two molecules of **A1** react when **I** is formed.
H is highly symmetric. The aromatic fragment is not changed during its formation. So, **H** is a result of the symmetric dimerization of **A1** when positive end of **B1** of one molecule reacts with negative end of **B1** of another molecule, and *vice versa.* Such dimerization produces cyclohexane. Its *cis*-isomer has C_2 axis of symmetry; *trans*-isomer has center of symmetry. Therefore, **H** is *cis*-isomer.

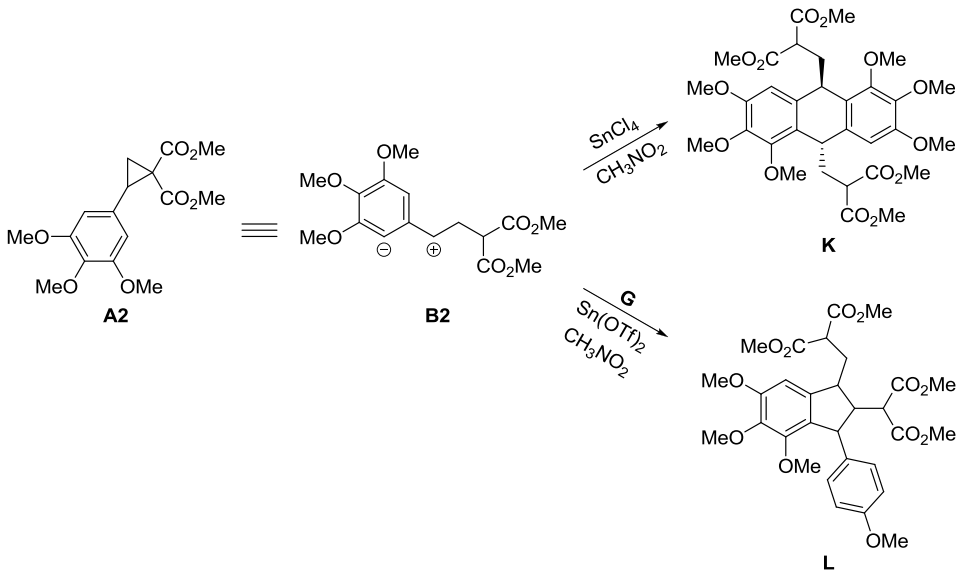
According to symmetry and table data, **K** is symmetric dimer of **A2**. Moreover, aromatic/non-aromatic protons ratio in **K** less than that in **A2**. Accounting for question 1, it is possible to deduce that benzylic carbon atom of one **A2** molecules reacts as electrophiles with *ortho*-position of aromatic fragment (nucleophilic center) of another molecule, and *vice versa*. In this reaction **A2** reacts as an equivalent of 1,3-zwitterion **B2**. Therefore, **K** is 9,10-dihydroanthracene derivative. The major isomer has the center of symmetry, *i.e.*, it has *trans*-arrangement of alkyl substituents.

I has 7 aromatic protons, *i.e.*, it has one aromatic proton less than **H** in which arene fragments are intact. In the process leading to **I**, one molecule of **A1** reacts as an equivalent of **B1**, another **A1** reacts as an equivalent of **B2**. In other words, one new C-C bond in **I** is formed *via* Friedel-Crafts alkylation of aromatic group in the first **A1** molecule by positive end of 1,3-zwitterion producing from the second **A1** molecule. Another C-C bond is formed *via* coupling of electrophilic benzylic carbon of the first **A1** molecule with nucleophilic malonate carbon of the second **A1** molecule. Therefore, **I** is tetraline derivative.

J has 12 protons. From composition data its molecular formula can be determined as $C_{13}H_{12}O_4$, *i.e.* it has one C atom, four H atoms, and one O atom less than **A1**. Moreover, **J** has no aliphatic hydrogens except the protons of methyl and OH groups. It is possible if a new aromatic ring is formed *via* intramolecular Friedel-Crafts reaction. For it, **A1** is isomerized under heating into (*Z*)-isomer of **G** followed by intramolecular acylation of aromatic moiety producing 1-hydroxy-7-methoxynaphthalene-2-carboxylate (**J**).



L has 36 protons. From composition data its molecular formula is $C_{30}H_{36}O_{12}$. It corresponds to combination of **A2** and **G**. Since **A2** reacts as an equivalent of **B2**, it can be supposed that electrophilic center of **B2** attacks C=C bond of **G** in accordance with Markovnikov's rule followed by reaction between the formed cationic center and *ortho*-carbon atom of trimethoxyphenyl substituent producing indane derivative **L**.



Solution to problem 7

1. $2\ MnO_4^- + HCOO^- + 3\ OH^- \longrightarrow 2\ MnO_4^{2-} + CO_3^{2-} + 2\ H_2O$
2. $MnO_4^{2-} + 2\ H_2O + 2\ e^- \longrightarrow MnO_2 + 4\ OH^-$ OR
   $3\ MnO_4^{2-} + 2\ H_2O \longrightarrow MnO_2 + 2\ MnO_4^- + 4\ OH^-$
3a. $C_4H_5O_2^- + 10\ MnO_4^- + 14\ OH^- + 12\ Ba^{2+} \longrightarrow 10\ BaMnO_4 + CH_3COO^- + 2\ BaCO3 + 8\ H_2O$
3b. $[Ag(CN)_2]^-$
3c. $Ag^+ + Ag(CN)_2^- \longrightarrow Ag[Ag(CN)_2]\downarrow$, or $Ag^+ + CN^- \longrightarrow AgCN\downarrow$
   So, AgCN or $Ag[Ag(CN)_2]$ is the answer.
3d. Permanganate left after the reaction with crotonic acid: $c_{Mn}V_{Mn} - 10n_{CA}$mmol.
   Cyanide consumed for the residual permanganate: $½(c_{Mn}V_{Mn} - 10n_{CA})$ mmol.
   Cyanide excess: $c_{CN}V_{CN} - ½(c_{Mn}V_{Mn} - 10n_{CA})$
   $2c_{Ag}V_{Ag} = c_{CN}V_{CN} - ½(c_{Mn}V_{Mn} - 10n_{CA})$.
   $\Rightarrow \quad n_{CA} = (2c_{Ag}V_{Ag} - c_{CN}V_{CN} + ½c_{Mn}V_{Mn})/5$
   $n_{CA} = [(2\cdot0.005\cdot5.40 - 0.0100\cdot8.00 + 0.5\cdot0.0400\cdot10.00)/5]$mmol = 0.0348 mmol
   $\Rightarrow \quad m_{CA} = (0.0348\cdot86.09)$ mg = 3.00 mg (M_{CA} = 86.09 g/mol)
4. $10\ MnO_4^- + 1$ Crotonate $\longrightarrow\ 10MnO_4^{2-}$ + products
   Permanganate left after the reaction with crotonic acid $c_{Mn}V_{Mn} - 10n_{CA}$mmol
   Manganate formed: $10n_{CA}$ mmol
   Reactions occurred after iodide addition:
   $2\ MnO_4^- + 10\ I^- + 16\ H^+ \longrightarrow 2\ Mn^{2+} + 5\ I_2 + 8\ H_2O$ and
   $MnO_4^{2-} + 4\ I^- + 8\ H^+ \longrightarrow Mn^{2+} + 2\ I_2 + 4\ H_2O$

Amount of the iodine evolved (mmol I_2):

$2.5n_{KMnO4\ left} + 2n_{K2MnO4.} = 2.5(c_{Mn}V_{Mn} - 10n_{CA}) + 2{\cdot}10n_{CA}$.

$2Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2NaI$ $\quad n_{Na2S2O3} = 2n_{I2} \longrightarrow 5(c_{Mn}V_{Mn} - 10n_{CA}) + 40n_{CA}$

Thus, $5(c_{Mn}V_{Mn} - 10n_{CA}) + 40n_{CA} = c_SV_{S1}$, and $n_{CA} = ½c_{Mn}V_{Mn} - 0.1c_SV_{S1}$

$n_{CA} = 0.5\times0.0400\times10.00 - 0.1\times0.1000\times4.90 = 0.151$ mmol,

$m_{CA} = n_{CA}M_{CA} = 13.00$ mg.

Remark of the editor: To oxidize 0.151 mmol of CA 1.51 mmol of $KMNO_4^-$ is needed. But there are only 0.4 mmol of $KMNO_4^-$ in flask B!

5a. Tin(II) reduction with permanganate in weak alkaline medium led to an insoluble binary manganese compound. Drying conditions suggest it is either one of manganese oxides or their mixture.

The amount of equivalent is just the same for thiosulfate, iodine and the precipitate.

$n_{eq} = V_{s2}\,c_S = 0.1000\times2.5$ mmol = 0.25 mmol

$M_{eq} = 28.6$ mg / 0.25 mmol = 114.4 g/mol.

This is the so called molar mass of the precipitate.

Let us consider possible cases.

- If MnO_2 was formed (scheme: $2MnO_4^- + 3Sn(II) \longrightarrow 2MnO_2\downarrow + 3Sn(IV)$, $MnO_2 + 4H^+ + 2I^- \longrightarrow I_2 + Mn^{2+} + 2H_2O$ and $I_2 + 2S_2O_3^{2-} \longrightarrow 2I^- + S_4O_6^{2-}$), the molar mass in the reaction with iodide would be: (86.94/2) g/mol = 43.47 g/mol.
- If Mn_2O_3 was formed ($Mn_2O_3 + 2I^- + 6H^+ \longrightarrow I_2 + 2Mn^{2+} + 3H_2O$), the molar mass of its equivalent in the reaction with iodide would be: (157.88/4) g/mol = 78.9 g/mol.
- In the experiment, the molar mass of the equivalent is even higher, thus manganese compounds, not oxidizing iodide, can be present in the precipitate (i.e. manganese (II). The only possible variant is manganese(II, III) oxide ($Mn_3O_4 + 2\ I^- + 8H^+ \longrightarrow I_2 + 3\ Mn^{2+} + 4H_2O$). The molar mass of the latter: (228.9/2) g/mol = 114.4 g/mol.

Reaction: $6\ MnO_4^- + 13\ Sn(OH)_4^{2-} + 16\ H_2O \longrightarrow 2\ Mn_3O_4\downarrow + 13\ Sn(OH)_6^{2-} + 6\ OH^-$

5b. $n_{Sn} = 13/2{\cdot}\ n_{Mn3O4}$

$n_{Sn} = ((28.6 / 228.9) \cdot 13/2)$ mmol = 0.812 mmol

$m_{Sn} = 96.4$ mg.

Solution to problem 8

1. V(**A**) : V(**B**) = n(**A**) : n(**B**) = 1 : 3 $\Rightarrow$ Vol. fraction of **A** = 25 %; Vol. fraction of **B** = 75 %.
2. Molecular mass of the **A** and **B** mixture equals 12.0·2.0 g/mol = 24.0 g/mol.
   The variant of two gases, both with molecular masses of 24.0 g/mol is impossible. Thus, one of the gases is lighter, whereas the other is heavier.

Reaction of ^{13}C-methylamine with water under anaerobic conditions can theoretically lead to two nitrogen-free gases with the molecular mass lower than 24.0 g/mol: H_2, or $^{13}CH_4$. Further considerations are summed up in the table.

Light gas	Volume fraction in %	Molecular mass of the heavy gas, g/mol
H_2	25	31.3
	75	90.0
$^{13}CH_4$	25	26.3
	75	45.0

Thus, the only possible variant is: $^{13}C^{16}O_2$ (**A**) and $^{13}C^{1}H_4$ (**B**).

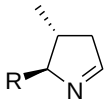
3. $4\ ^{13}CH_3NH_3^+ + 2\ H_2O \longrightarrow 3\ ^{13}CH_4 + {}^{13}CO_2 + 4NH_4^+$

4. The molecular mass of **X**: (238 + 17 (OH-group)) g/mol = 255 g/mol.
The number of oxygens in **X**: $\frac{255 \cdot 0{,}188}{16} = 3$
Two lysines contain 12 carbons and 4 nitrogens, 16 in total.
From comparison of lines 1 and 2 of the table: 15 of 16 carbons and nitrogens are found in **X**.
From comparison of lines 1 and 3 of the table: 1 of 2 ε-amino nitrogens is lost during **X** biosynthesis.
X contains 12 carbons and 3 nitrogens.
The rest of the molecular mass: (255 – 12·12 – 3·14 – 3·16) g/mol = 21 g/mol is due to hydrogen (21 atoms) $\Rightarrow$ **X** = $C_{12}H_{21}N_3O_3$

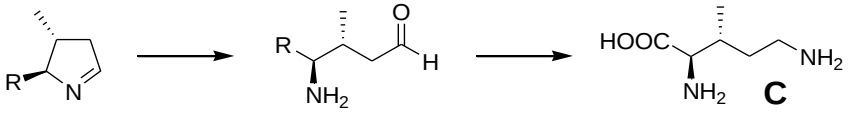
5. **C** is an isomer of lysine, thus $2 \cdot C_6H_{14}N_2O_2 = C_{12}H_{28}N_4O_4$ enter the reaction of **D** synthesis.
One molecule of water is formed at each of the steps [**C** + lysine $\longrightarrow$ **D** ($C_{12}H_{28}N_4O_4 - H_2O = C_{12}H_{26}N_4O_3$)] and [**E** $\longrightarrow$ **X** (**(**$C_{12}H_{21}N_3O_3 + H_2O = C_{12}H_{23}N_3O_4$)].
Thus, loss/gain of atoms at **D**→**E** step: $C_{12}H_{24}N_4O_3 - C_{12}H_{21}N_3O_4$, minus NH_3, plus O. Thus, it is oxidative deamination:
R-CH_2-NH_2 + [O] $\longrightarrow$ R-CH=O + NH_3 (schematically).

C $C_6H_{14}N_2O_2$	D $C_{12}H_{26}N_4O_3$	E $C_{12}H_{23}N_3O_4$
☒ Oxidative deamination;	☐ Decarboxylation;	☐ Intermolecular deamination;
☐ Hydroxylation;	☐ Peptide bond hydrolysis.	

6. H atom bound to the 4th or 5th C atom would mean the loss of chirality, thus it is unambiguously attributed to the 3rd C atom.
It is needed to decide about the amino group forerunning the heterocyclic nitrogen to attribute the positions of the other two substituents.
Nitrogen is included in the cycle due to the reaction of an amino and formyl groups, the latter appearing as a result of the oxidative deamination.
The size of the cycle suggests it was the α–amino group, thus:
the 3rd position – H; the 4th position – Me; the 5th position – R.

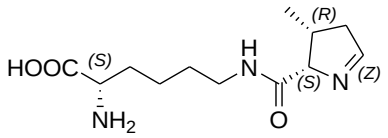


7. Moving backwards (**X**→**D**) one gets that **C** is (*3R*)-3-methyl-*D*-ornithine:



Stereochemistry of **C** is derived from that of the above cyclic fragment with an account that no isomerization occurs on the way from **C** to **X**.

Both amino groups of lysine can form the peptide bond with the carboxylic group of **C**. Still, involvement of only the ε-amino group will provide **X** as α-amino acid. **X** is pyrrolysine, the 22nd amino acid of the genetic code:



8.

Nitrogen base	The number of bases in the codon				
	1	2	3	0 or 1	1 or 2
A	☑				
C				☑	
G				☑	
U	☑				

A has 1 amino group and 0 oxygen atoms
C has 1 amino group and 1 oxygen atom
G has 1 amino group and 1 oxygen atom
U has 0 amino groups and 2 oxygen atoms
2 amino groups per 3 bases suggest one U.
There are 2 amino groups and 1 oxygen atom per two bases left. A is one of these.
Either G or C is the last one.

9a. The fragment contains only four U, which can be used as the starting point to determine the reading frame. There should be only one A in the triplet. UGA and UAG are the options, the latter met twice. Both are STOP codons in the table. But the fragment of mRNA represents coding sequence! Within definite nucleotide motives, the STOP codons can be responsible for amino acid incorporation into proteins. Therefore, 8 amino acids encoded in the fragment (if UGA is STOP codone, then 7 amino acids residues:

…AA|UAG|AAU|UAG|CGG|AAC|AGA|GGG|UGA|C… Number of amino acids = 8

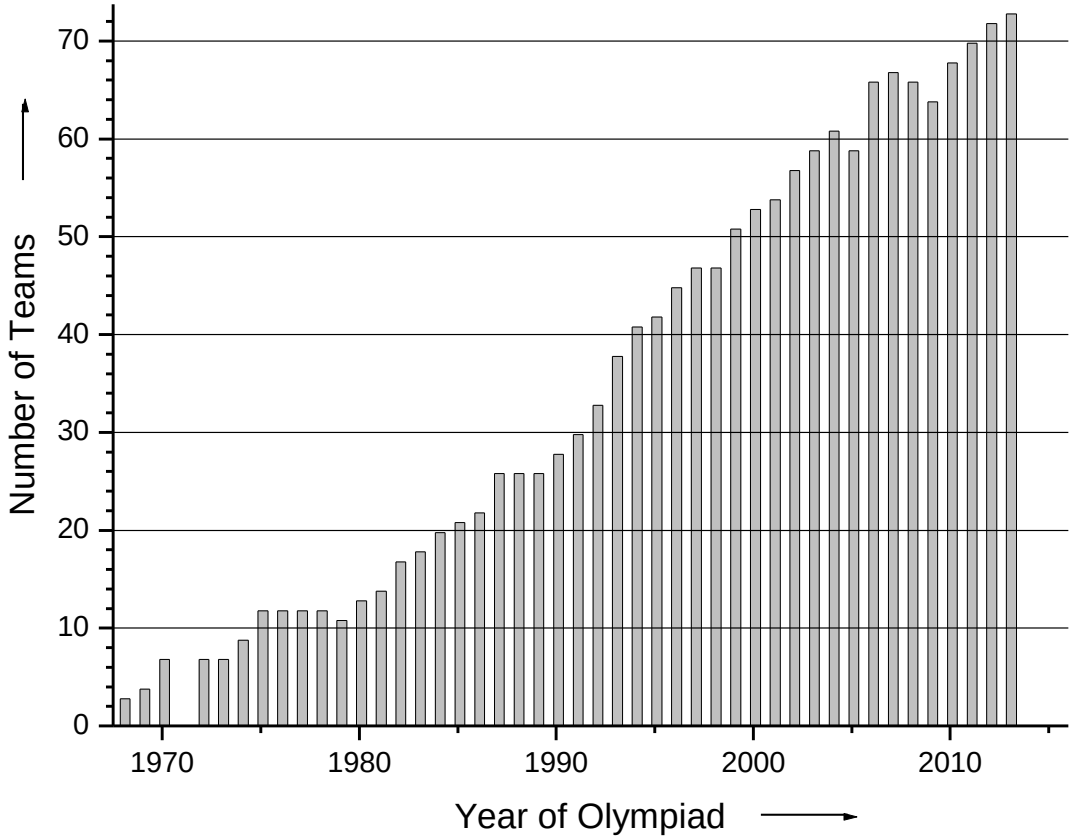
9b. Since only one codon is responsible for the incorporation of **X** residues into proteins in archaea, it is UGA or UAG. There are more than one **X** residue in the polypeptide fragment, thus it is UAG (met twice), while UGA encodes Sec.

X	Asn	X	Arg	Asn	Arg	Gly	Sec		

About the history of the International Chemistry-Olympiads

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

Number of teams attending the IChO



The participating countries are shown in the following table.

Participating Delegations

●= 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
Argentina																											+	+	+	+	+
Armenia																															
Australia																			o	+	+	+	+	+	+	+	+	+	+	●	+
Austria							+	+	+	+	+		+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Azerbaijan																													o	o	
Belarus																												+	+	+	+
Belgium							+	+	+			+				+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Brazil																													o	o	+
Bulgaria			+	+	+		+	+	+	+	+	+	+	●	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Canada																o	o	+	+	+	+	+	+	+	+	+	+	+	●	+	+
China																			+	+	+	+	+	+	+	+	●	+	+	+	+
Chinese Taipei																								+	+	+	+	+	+	+	+
Costa Rica																															
Croatia																														o	o
Cuba																	+	o	+	+	+	+	+		+	+	+	+	+		+
Cyprus																						o	+	+	+	+	+	+	+	+	+
Czech Rep.																									+	+	+	+	+	+	+
Czechoslovakia	●	+	+	+	+	+	+	+	●	+	+	+	+	+	+	+	●	+	+	+	+	+	+	+							
Denmark														+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
DDR		o	+	+	+	+	+	●	+	+	+	+	+	+	+		+	+	+	+	●	+									
Egypt																															
El Salvador																															
Estonia																										+	+	+	+	+	+
Finland									o	+	+	+	+	+	+	+	+	+	+	●	+	+	+	+	+	+	+	+	+	+	+
France												o	+	+	+	+	+	+	+	+	●	+	+	+	+	+	+	+	+	+	+
fYROM (Macedonia)																															
Georgia																															
Germany						o	+	+	+	+	+	+	+	+	+	●	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Greece																+	+	+	+		+	+	+	+	+	+	+	+	+	+	+
Hungary	+	+	●	+	+	+	●	+	+	+	+	+	+	+	+	+	+	+	●	+	+	+	+	+	+	+	+	+	+	+	+
Iceland																															
India																													o	o	+
Indonesia																												o	+	+	+
Iran																									+	+	+	+	+	+	+
Ireland																												o	o	+	+
Israel																															
↑ 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

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Year → / Country ↓	00	01	02	03	04	05	06	07	08	09	10	11	12	13
Argentina	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Armenia					o	o	+	+	+	+	+	+	+	+
Australia	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Austria	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Azerbaijan	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Belarus	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Belgium	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Brazil	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Bulgaria	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Canada	+	+	+	+	+	+	+	+	+	+	+	+	+	+
China	+	+	+	+	+		+	+	+	+	+	+	+	+
Chinese Taipei	+	+	+	+	+	•	+	+	+	+	+	+	+	+
Costa Rica									o	o	+	+	+	+
Croatia	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Cuba		+	+	+	+	+	+	+	+	+	+	+		
Cyprus	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Czech Rep.	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Czechoslovakia														
Denmark	•	+	+	+	+	+	+	+	+	+	+	+	+	+
DDR														
Egypt	o	o	+	+	+	+	+					+	+	
El Salvador												o	o	+
Estonia	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Finland	+	+	+	+	+	+	+	+	+	+	+	+	+	+
France	+	+	+	+	+	+	+	+	+	+	+	+	+	+
fYROM (Macedonia)												o	o	+
Georgia													o	o
Germany	+	+	+	+	•	+	+	+	+	+	+	+	+	+
Greece	+	+	+	•	+	+	+	+	+	+	+	+	+	+
Hungary	+	+	+	+	+	+	+	+	•	+	+	+	+	+
Iceland	o	o	+	+	+	+	+	+	+	+	+	+	+	+
India	+	•	+	+	+	+	+	+	+	+	+	+	+	+
Indonesia	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Iran	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Ireland	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Israel					o	o	+	+	+	+	+	+	+	+
↑ Country / Year →	00	01	02	03	04	05	06	07	08	09	10	11	12	13

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Italy												+	+	+	+	+	o	o	+	+	+	+	+	+	+	+	+	+	+	+	+
Japan																															
Yugoslavia						+	+	+	+					+	+	+	+	+	+												
Kazakhstan																												o	o	+	+
Kenya																													o		
Korea																								+	+	+	+	+	+	+	+
Kuwait															o	o			+	+	+	+	+		+	+	+	+	+		+
Kyrgyzstan																												o	o	+	
Liechtenstein																															
Latvia																							+	+	+	+	+	+	+	+	+
Lithuania																							+	+	+	+	+	+	+	+	+
Malaysia																															
Mexico																								+	+	+	+	+	+	+	+
Moldova																															
Mongolia																															
Montenegro																															
Netherlands												+	+	+	+	+	+	●	+	+	+	+	+	+	+	+	+	+	+	+	+
New Zealand																								+	+	+	+	+	+	+	+
Nigeria																															
Norway												o	+	+	+	+	+	+	+	+	+	+	+	+	●	+	+	+	+	+	
Oman																															
Pakistan																															
Peru																															
Philippines																														o	
Poland	+	●	+	+	+	+	+	+	+	●	+	+	+	+	+	+	+	+	+	+	+	+	●	+	+	+	+	+	+	+	+
Portugal																															
Romania		+	+	+	●	+	+	+	+	+	+	+	+	+	●	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
GUS/Russ.Fed																								+	+	+	+	●	+	+	+
Saudi Arabia																															
Serbia																															
Singapore																			o	+		+	+	+	+	+	+	+	+	+	+
Slovakia																									+	+	+	+	+	+	+
Slovenia																							+	+	+	+	+	+	+	+	+
Spain										o																		+	+	+	+
Sweden						+	+	+	+	+	+	+	+	●	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Switzerland																		o	+	+	+	+	+	+	+	+	+	+	+	+	+
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•= host. + = participant. o = observer

Year → / Country ↓	00	01	02	03	04	05	06	07	08	09	10	11	12	13
Italy	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Japan			o	+	+	+	+	+	+	+	•	+	+	+
Yugoslavia			o											
Kazakhstan	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Kenya		o												
Korea	+	+	+	+	+	+	•	+	+	+	+	+	+	+
Kuwait	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Kyrgyzstan	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Liechtenstein										o	o	o	+	o
Latvia	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Lithuania	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Malaysia					o	+	+	+	+		+	+	+	+
Mexico	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Moldova					o		o	+	+	+	+	+	+	+
Mongolia		o			o	o	+	+	+	+	+	+	+	+
Montenegro													o	o
Netherlands	+	+	•	+	+	+	+	+	+	+	+	+	+	+
New Zealand	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Nigeria								o			o	o	+	+
Norway	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Oman														o
Pakistan					o	o	+	+	+	+	+	+	+	+
Peru			o	o	+	+		+	+	+	+	+	+	+
Philippines														
Poland	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Portugal		o	o	+	+	+	+	+	+	+	+	+	+	+
Romania	+	+	+	+	+	+	+	+	+	+	+	+	+	+
GUS/Russ.Fed	+	+	+	+	+	+	+	•	+	+	+	+	+	•
Saudi Arabia					o	o	+	+		o	o	+	+	+
Serbia											o	o	+	+
Singapore	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Slovakia	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Slovenia	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Spain	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Sweden	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Switzerland	+	+	+	+	+	+	+	+	+	+	+	+	+	+
↑ Country / Year →	00	01	02	03	04	05	06	07	08	09	10	11	12	13

Participating Delegations

•= host. + = participant. o = observer

Year → / Country ↓	68	69	70	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99
Syria																															
Tajikistan																															
Thailand																					o	+	+	+	+	+	+	+	+	+	+
Turkey									o	+															o	+	+	+	+	+	+
Turkmenistan																															o
UdSSR			+	•	+	+	+	+	+	+	•		+	+	+	+	+	+	+	+				+							
Ukraine																										+	+	+	+	+	+
United Kingdom												o		o	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
United States													o		o	+	+	+	+	+	+	+	+	•	+	+	+	+	+	+	+
Uruguay																													o	o	+
Uzbekistan																															
Venezuela														o		o									+	+	+	+	+	+	+
Vietnam																												+	+	+	+
↑ Country / Year →	68	69	70	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99

Participating Delegations

•= host. + = participant. o = observer

Year → / Country ↓	00	01	02	03	04	05	06	07	08	09	10	11	12	13
Syria									o	o	+	+	+	+
Tajikistan			o	o	+	+	+	+	+		+	+	+	+
Thailand	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Turkey	+	+	+	+	+	+	+	+	+	+	+	•	+	+
Turkmenistan	o	o	+	+	+		+	+	+	+	+	+	+	+
UdSSR														
Ukraine	+	+	+	+	+	+	+	+	+	+	+	+	+	+
United Kingdom	+	+	+	+	+	+	+	+	+	•	+	+	+	+
United States	+	+	+	+	+	+	+	+	+	+	+	+	•	+
Uruguay	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Uzbekistan												o	o	+
Venezuela	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Vietnam	+	+	+	+	+	+	+	+	+	+	+	+	+	+
↑ Country / Year →	00	01	02	03	04	05	06	07	08	09	10	11	12	13

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 concourse						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 107)

	1989	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000
IChO held in	**DDR**	**F**	**PL**	**USA**	**I**	**N**	**RC**	**RUS**	**CDN**	**AUS**	**T**	**DK**
1	DDR	RC	RC	RC	RC	RC	RC	IR	H	SGP	USA	RC
.	D	PL	RO	H	TPE	GB	IR	RC	D	USA	ROK	RUS
.	RC	D	H	PL	USA	USA	RO	RUS	TR	ROK	RC	USA
.	BG	USA	PL	USA	I	A	A	A	TPE	RC	IR	H
5	SU	CS	NL	A	GUS	SGP	D	D	IR	H	RO	TPE
.	H	RO	USA	GUS	H	ROK	GB	USA	RUS	RA	H	A
.	PL	F	I	D	D	TPE	SK	UA	ROK	RUS	TPE	SK
.	RO	A	D	RO	CDN	CZ	TPE	CZ	RC	AUS	UA	BY
.	CS	DDR	N	F	SGP	GUS	I	H	SGP	D	PL	VN
10	I	H	GB	I	CZ	IR	CZ	RO	PL	GB	AUS	TR
.	NL	GB	CS	SGP	A	D	RUS	GB	USA	PL	VN	SGP
.	GB	I	SU	CS	RO	H	H	TPE	UA	A	D	D
.	A	AUS	A	AUS	P	RO	AUS	BY	AUS	RO	RA	ROK
.	USA	SGP	AUS	NL	NZ	DK	SGP	SGP	CDN	TPE	BY	IR
15	S	NL	DK	DK	ROK	I	F	RA	RO	SK	T	CZ
.	F	N	SGP	ROK	LV	T	TR	TR	A	NL	F	FIN
.	N	DK	CDN	GB	IR	NZ	PL	F	T	IR	TR	T
.	AUS	T	BG	CH	DK	UA	USA	I	EST	UA	SGP	MEX
.	CDN	FIN	F	T	AUS	AUS	DK	AUS	CZ	VN	IND	GB
20	DK	CDN	S	LV	NL	F	RA	ROK	VN	LT	GB	AUS
.	FIN	BG	T	NZ	LT	PL	ROK	EST	F	TR	RUS	IND
.	B	C	CH	S	SK	NL	UA	CDN	S	BY	MEX	CDN
.	C	S	LV	LT	F	SK	LT	T	BY	F	A	RA
.	GR	CH	LT	N	C	CDN	T	VN	NZ	I	IRL	UA
25	CH	B	FIN	CDN	GB	LT	NL	SK	LV	T	NZ	PL
.	KWT	GR	C	SLO	T	S	CH	CH	RA	FIN	I	NZ
.		KWT	GR	BG	BG	N	BG	NL	SLO	CZ	CDN	BG
.		CY	B	TPE	B	BG	S	NZ	GB	CDN	LT	F
.			CY	B	S	FIN	NZ	DK	SK	S	NL	DK
30			SLO	FIN	FIN	EST	EST	PL	LT	BG	SK	NL
.				GR	SLO	LV	CDN	SLO	I	N	BG	B
.				CY	GR	CH	MEX	MEX	DK	MEX	KZ	RO
.				MEX	MEX	MEX	N	LV	NL	CH	DK	KZ
.					N	SLO	SLO	N	IRL	SLO	CH	LT
35					CH	B	LV	CY	N	EST	CZ	CH
.					YV	CY	CY	BG	MEX	CY	FIN	SLO
.					CY	GR	B	S	CH	LV	B	EST
.					KWT	TR	GR	LT	CY	DK	S	S
.						YV	FIN	E	E	NZ	CY	YV
40						C	YV	B	FIN	GR	EST	CY
.						KWT	KWT	GR	BG	KZ	LV	HR
.							C	FIN	YV	E	SLO	I
.								YV	GR	IRL	YV	RI
.								C	B	B	BR	N
45								KWT	RI	KS	E	AZ
.									KWT	YV	N	IRL
.									C	RI	RI	E
.											GR	LV
.											ROU	GR
50											C	BR

(List of abbreviations see 107)

	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012
IChO held in	**IND**	**NL**	**GR**	**D**	**TPE**	**ROK**	**RUS**	**H**	**GB**	**J**	**TR**	**USA**
1	RC	RC	RC	RC	ROK	RC	RC	RC	TPE	RC	RC	TPE
.	ROK	T	IR	ROK	VN	TPE	RUS	RUS	RC	T	ROK	ROK
.	USA	TPE	ROK	RUS	IR	ROK	TPE	UA	ROK	ROK	RUS	RUS
.	RUS	ROK	T	UA	RUS	RUS	PL	ROK	RUS	J	RI	IND
5	IR	A	BY	D	AZ	VN	ROK	T	SGP	TPE	USA	RC
.	TR	UA	RUS	PL	TPE	T	D	BY	J	H	T	SGP
.	IND	USA	IND	TPE	T	J	T	VN	USA	CZ	SGP	J
.	AUS	PL	SGP	H	RA	Pl	IND	TPE	H	SGP	CDN	D
.	TPE	IND	D	TR	D	IND	H	H	IR	USA	H	H
10	T	D	TPE	VN	IND	D	SK	SGP	GB	IR	IR	UA
.	SGP	IR	UA	IND	A	SK	LT	KZ	RO	RUS	TR	RI
.	PL	H	PL	IR	CZ	DK	USA	A	T	TR	IND	USA
.	RO	RUS	CDN	RO	UA	SGP	VN	PL	D	LT	CZ	BY
.	F	CDN	CZ	LT	PL	BR	GB	IR	IND	D	F	VN
15	SK	TR	RO	CZ	AUS	CDN	BY	IND	PL	PL	J	RO
.	H	AUS	KZ	USA	TR	AZ	EST	RO	AUS	GB	TPE	LIT
.	VN	GB	VN	SGP	H	UA	UA	AUS	A	IND	D	CZ
.	CZ	SGP	EST	CDN	SK	USA	RI	D	BY	RI	SK	KZ
.	RA	E	GB	AZ	USA	H	IR	SK	VN	RO	KZ	RA
20	BY	SK	AUS	AUS	GB	CZ	RO	TR	F	A	AUS	PL
.	C	BY	H	KZ	RO	AUS	AUS	LT	RI	VN	VN	SK
.	D	VN	SK	GB	BY	IRL	A	EST	TR	SK	RO	IR
.	GB	FIN	USA	J	SGP	F	KZ	I	LT	CDN	GB	A
.	UA	F	YV	A	J	IR	SGP	GB	UA	EST	BY	GB
25	A	LT	IND	BY	RI	A	NZ	CDN	EST	AUS	PL	AUS
.	MEX	CZ	F	SK	LV	TR	CZ	NZ	CZ	UA	A	IL
.	DK	KZ	A	T	BG	RI	F	BR	SK	F	LT	HR
.	CDN	LV	I	RA	HR	GB	TR	USA	CDN	RA	EST	BR
.	EST	NL	TR	EST	MEX	RO	J	LV	I	NZ	RA	CDN
30	RI	RO	AZ	F	KZ	NL	ARM	RI	RA	BY	UA	NZ
.	HR	RA	MEX	NZ	LT	HR	SLO	F	NZ	KZ	FIN	TR
.	I	EST	LT	SLO	F	LT	RA	CZ	TM	BR	SLO	EST
.	N	HR	NL	HR	EST	KZ	BR	J	MEX	IL	I	LV
.	BG	BG	FIN	LV	CDN	SLO	CDN	DK	KZ	HR	BR	F
35	CY	NZ	HR	NL	I	EST	I	RA	IL	SLO	HR	ARM
.	KZ	I	J	I	DK	RA	MAL	MEX	BR	FIN	NZ	I
.	B	DK	DK	CH	SLO	BR	IL	SLO	HR	DK	TM	NL
.	LT	SLO	RA	FIN	FIN	TJ	IRL	IL	AZ	NL	LV	TM
.	NZ	N	GR	RI	NL	LV	NL	AZ	DK	E	S	DK
40	CH	YV	LT	S	IRL	MAL	CH	HR	S	I	NL	TJ
.	E	MEX	E	BG	GR	S	S	TM	LV	LV	PE	YVA
.	FIN	BR	TM	KS	NZ	IRL	LV	BG	IRL	BG	PK	BG
.	SLO	S	BR	E	KS	IL	DK	MGL	FIN	CR	TJ	SLO
.	NL	RI	BG	GR	S	FIN	MD	IRL	N	CH	E	CH
45	LV	TM	CH	BR	B	IS	E	MAL	E	IRL	MEX	FIN
.	BR	B	NZ	TM	BR	I	BG	E	NL	MEX	CH	MEX
.	S	IRL	IS	CY	CH	CY	TM	S	MGL	MGL	MGL	MGL
.	YV	CH	IRL	YVA	P	N	HR	NL	PE	MAL	IL	T
.	IRL	C	CY	IRL	IS	TM	PK	CH	PK	N	CY	PK
50	GR	CY	KS	IS	N	CH	N	ROU	SLO	S	BG	AZ

(List of abbreviations see 107)

	2013	2014	2015	2016	2017	2018	2019	2020	2021	2022	2023	2024
IChO held in	**RUS**											
1	RC											
.	ROK											
.	TPE											
.	USA											
5	H											
.	SGP											
.	RUS											
.	PL											
.	UA											
10	IND											
.	VN											
.	T											
.	BY											
.	J											
15	KZ											
.	IR											
.	SK											
.	CZ											
.	RI											
20	D											
.	RO											
.	A											
.	LIT											
.	AUS											
25	GB											
.	TR											
.	NZ											
.	HR											
.	F											
30	DK											
.	MD											
.	CDN											
.	LV											
.	SLO											
35	RA											
.	SRB											
.	BR											
.	EST											
.	UZ											
40	AZ											
.	I											
.	E											
.	IL											
.	CY											
45	N											
.	ARM											
.	PK											
.	CH											
.	BG											
50	TJ											

(List of abbreviations see 107)

List of abbreviations

A	Austria
ARM	Armenia
AUS	Australia
AZ	Azerbaijan
B	Belgium
BG	Bulgaria
BR	Brazil
BY	Belarus
C	Cuba
CDN	Canada
CH	Switzerland
CS	Czechoslovacia
CY	Cyprus Republic
CZ	Czech Republic
D	Germany
DDR	German Democratic Republic
DK	Denmark
E	Spain
EAK	Kenya
EST	Estonia
ET	Egypt
F	France
FIN	Finland
GB	United Kingdom
GR	Greece
GUS	Commonwealth of Independent States
H	Hungary
HR	Croatia
I	Italy
IL	Israel
IND	India
IR	Iran
IRL	Ireland
IS	Iceland
J	Japan
KS	Kyrgyzstan
KWT	Kuwait
KZ	Kazakhstan
LV	Latvia
LT	Lithuania
MAL	Malaysia
MD	Moldova
MEX	Mexico
MGL	Mongolia
N	Norway
NL	Netherlands
NZ	New Zealand
P	Portugal
PE	Peru
PK	Pakistan
PL	Poland
RA	Argentina
RI	Indonesia
RC	China
RO	Romania
ROK	South Korea
ROU	Uruguay
RUS	Russian Federation
S	Sweden
SGP	Singapore
SK	Slovakia
SLO	Slovenia
SRB	Serbia
SU	Soviet Union
T	Thailand
TJ	Tajikistan
TM	Turkmenistan
TPE	Chinese Taipei
TR	Turkey
UA	Ukraine
USA	United States of America
VN	Vietnam
WAN	Nigeria
YU	Yugoslavia
YVA	Venezuela