

36th IChO Theoretical Problems

- use only the pen and calculator provided
- time 5 hours
- problem booklet 17 pages
- answer sheets: 21 pages
- draft paper (will not be marked): 3 sheets (more are available on request)
- total number of points: 169
- your name and student code write it on **every** answer sheet
- relevant calculations write them down in the appropriate boxes, otherwise you will get no points
- atomic masses use only the periodic system 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
- restroom break ask your supervisor
- official English-language version available on request, **for clarification only**, ask your supervisor.
- after the stop signal put your answer sheets in the correct order (if they aren't), put them in the envelope (don't seal), deliver them at the exit
- problem booklet keep it, together with the pen and calculator.

GOOD LUCK

Periodic table of elements

with atomic masses / u

1 H 1.01																	2 He 4.00
3 Li 6.94	4 Be 9.01											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.88	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	32 Ge 72.61	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc 98.91	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.90	54 Xe 131.29
55 Cs 132.91	56 Ba 137.3	57-71	72 Hf 178.49	73 Ta 180.95	74 W 183.84	75 Re 186.21	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.19	83 Bi 208.98	84 Po 208.98	85 At 209.99	86 Rn 222.02
87 Fr 223	88 Ra 226	89-103	104 Rf 261	105 Db 262	106 Sg 263	107 Bh 264	108 Hs 265	109 Mt 268									
			57 La 138.91	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm 144.92	62 Sm 150.36	63 Eu 151.96	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97
			89 Ac 227	90 Th 232	91 Pa 231	92 U 238	93 Np 237	94 Pu 244	95 Am 243	96 Cm 247	97 Bk 247	98 Cf 251	99 Es 252	100 Fm 257	101 Md 258	102 No 259	103 Lr 262

Constants and useful formulas

f	p	n	μ	m	k	M	G	T
femto	pico	nano	micro	milli	kilo	mega	giga	tera
10 ⁻¹⁵	10 ⁻¹²	10 ⁻⁹	10 ⁻⁶	10 ⁻³	10 ³	10 ⁶	10 ⁹	10 ¹²

Gas constant	R = 8.314 J K ⁻¹ mol ⁻¹	Faraday constant	F = 96485 C mol ⁻¹
Use as standard pressure:	p = 1.013 · 10 ⁵ Pa		
Use as standard temperature:	T = 25°C = 298.15 K		
Avogadro's number	N _A = 6.022 · 10 ²³ mol ⁻¹	Planck constant	h = 6.626 · 10 ⁻³⁴ J s
Speed of light	c = 3.00 · 10 ⁸ m s ⁻¹		

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

$$\Delta G = -nEF$$

$$\Delta G^0 = -RT \ln K$$

$$\Delta G = \Delta G^0 + RT \ln Q \quad \text{with } Q = \frac{\text{product of } c(\text{products})}{\text{product of } c(\text{reactands})}$$

$$\Delta H(T_1) = \Delta H^0 + (T_1 - 298.15 \text{ K}) \cdot C_p \quad (C_p = \text{constant})$$

Arrhenius equation	$k = A \cdot e^{-\frac{E_a}{R \cdot T}}$
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Ideal gas law	$pV = nRT$
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Nernst equation	$E = E^0 + \frac{RT}{nF} \cdot \ln \frac{c_{ox}}{c_{red}}$
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Bragg's law	$n\lambda = 2d \cdot \sin \theta$
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Beer- Lambert Law	$A = \log \frac{P_0}{P} = \varepsilon c \cdot d$
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$p = \frac{F}{A}$	$F = ma$
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$V(\text{cylinder}) = \pi r^2 h$	$A(\text{sphere}) = 4\pi r^2$	$V(\text{sphere}) = \frac{4}{3} \pi r^3$
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1 J = 1 N m	1 N = 1 kg m s ⁻²	1 Pa = 1 N m ⁻²	1 W = 1 J s ⁻¹
1 C = 1 A s			

Problem 1: Thermodynamics

(24 points)

For his 18th birthday party in February Peter plans to turn a hut in the garden of his parents into a swimming pool with an artificial beach. In order to estimate the costs for heating the water and the house, Peter obtains the data for the natural gas composition and its price.

1.1 Write down the chemical equations for the complete combustion of the main components of natural gas, methane and ethane, given in Table 1. Assume that nitrogen is inert under the chosen conditions.

Calculate the reaction enthalpy, the reaction entropy, and the Gibbs energy under standard conditions ($1.013 \cdot 10^5$ Pa, 25.0°C) for the combustion of methane and ethane according to the equations above assuming that all products are gaseous.

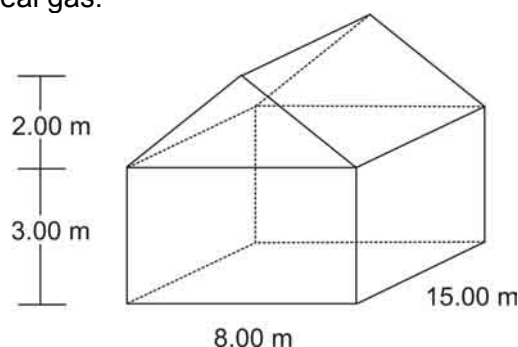
The thermodynamic properties and the composition of natural gas can be found in Table 1.

1.2 The density of natural gas is 0.740 g L^{-1} ($1.013 \cdot 10^5$ Pa, 25.0°C) specified by PUC, the public utility company.

- a) Calculate the amount of methane and ethane (in moles) in 1.00 m^3 of natural gas (natural gas, methane, and ethane are not ideal gases!).
- b) Calculate the combustion energy which is released as thermal energy during the burning of 1.00 m^3 of natural gas under standard conditions assuming that all products are gaseous. (If you do not have the amount from 1.2a) assume that 1.00 m^3 natural gas corresponds to 40.00 mol natural gas.)

According to the PUC the combustion energy will be 9.981 kWh per m^3 of natural gas if all products are gaseous. How large is the deviation (in percent) from the value you obtained in b)?

The swimming pool inside the house is 3.00 m wide, 5.00 m long and 1.50 m deep (below the floor). The tap water temperature is 8.00°C and the air temperature in the house (dimensions given in the figure below) is 10.0°C . Assume a water density of $\rho = 1.00 \text{ kg L}^{-1}$ and air behaving like an ideal gas.



1.3 Calculate the energy (in MJ) which is required to heat the water in the pool to 22.0°C and the energy which is required to heat the initial amount of air (21.0% of O₂, 79.0% of N₂) to 30.0°C at a pressure of 1.013·10⁵ Pa.

In February, the outside temperature is about 5°C in Northern Germany. Since the concrete walls and the roof of the house are relatively thin (20.0 cm) there will be a loss of energy. This energy is released to the surroundings (heat loss released to water and/or ground should be neglected). The heat conductivity of the wall and roof is 1.00 W K⁻¹ m⁻¹.

1.4 Calculate the energy (in MJ) which is needed to maintain the temperature inside the house at 30.0°C during the party (12 hours).

1.00 m³ of natural gas as delivered by PUC costs 0.40 € and 1.00 kWh of electricity costs 0.137 €. The rent for the equipment for gas heating will cost him about 150.00 € while the corresponding electrical heaters will only cost 100.00 €.

1.5 What is the total energy (in MJ) needed for Peter's "winter swimming pool" calculated in 1.3 and 1.4? How much natural gas will he need, if the gas heater has an efficiency of 90.0%?

What are the different costs for the use of either natural gas or electricity? Use the values given by PUC for your calculations and assume 100% efficiency for the electric heater.

Table 1: Composition of natural gas

Chemical Substance	mol fraction x	$\Delta_f H^0$ (kJ mol ⁻¹) ⁻¹	S^0 (J mol ⁻¹ K ⁻¹) ⁻¹	C_p^0 (J mol ⁻¹ K ⁻¹) ⁻¹
CO ₂ (g)	0.0024	-393.5	213.8	37.1
N ₂ (g)	0.0134	0.0	191.6	29.1
CH ₄ (g)	0.9732	-74.6	186.3	35.7
C ₂ H ₆ (g)	0.0110	-84.0	229.2	52.5
H ₂ O (l)	-	-285.8	70.0	75.3
H ₂ O (g)	-	-241.8	188.8	33.6
O ₂ (g)	-	0.0	205.2	29.4

Equation:

$$J = E \cdot (A \cdot \Delta t)^{-1} = \lambda_{\text{wall}} \cdot \Delta T \cdot d^{-1}$$

J energy flow E along a temperature gradient (wall direction z) per area A and time Δt

d wall thickness

λ_{wall} heat conductivity

ΔT difference in temperature between the inside and the outside of the house

Problem 2: Kinetics at catalyst surfaces

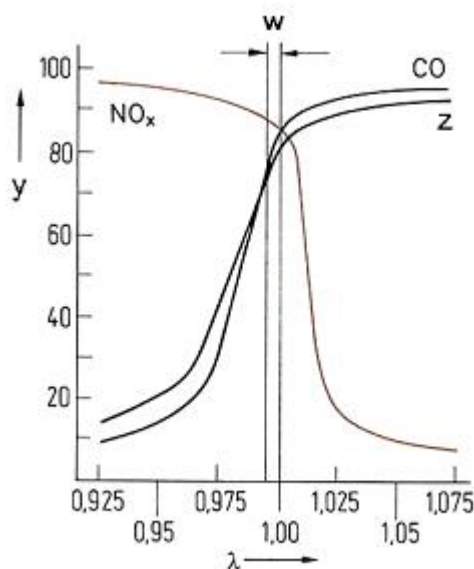
(23 points)

Apart from other compounds the exhaust gases of an Otto engine are the main pollutants carbon monoxide, nitrogen monoxide and uncombusted hydrocarbons, as, for example, octane. To minimize them they are converted to carbon dioxide, nitrogen and water in a regulated three-way catalytic converter.

2.1 Complete the chemical reaction equations for the reactions of the main pollutants in the catalyst.

To remove the main pollutants from the exhaust gas of an Otto engine optimally, the λ -value is determined by an electro-chemical element, the so called lambda probe. It is located in the exhaust gas stream between engine and the three-way catalytic converter.

The lambda value is defined as $\lambda = \frac{\text{amount of air at the inlet}}{\text{amount of air necessary for complete combustion}}$.



w: λ -window
y: conversion efficiency (%)
z: Hydrocarbons

2.2 Decide the questions on the answer sheet concerning the λ probe.

The adsorption of gas molecules on a solid surface can be described in a simple model by using the Langmuir isotherm:

$$\theta = \frac{K \cdot p}{1 + K \cdot p}$$

where θ is the fraction of surface sites that are occupied by the gas molecules, p is the gas pressure and K is a constant.

The adsorption of a gas at 25 °C may be described by using the Langmuir isotherm with $K = 0.85 \text{ kPa}^{-1}$.

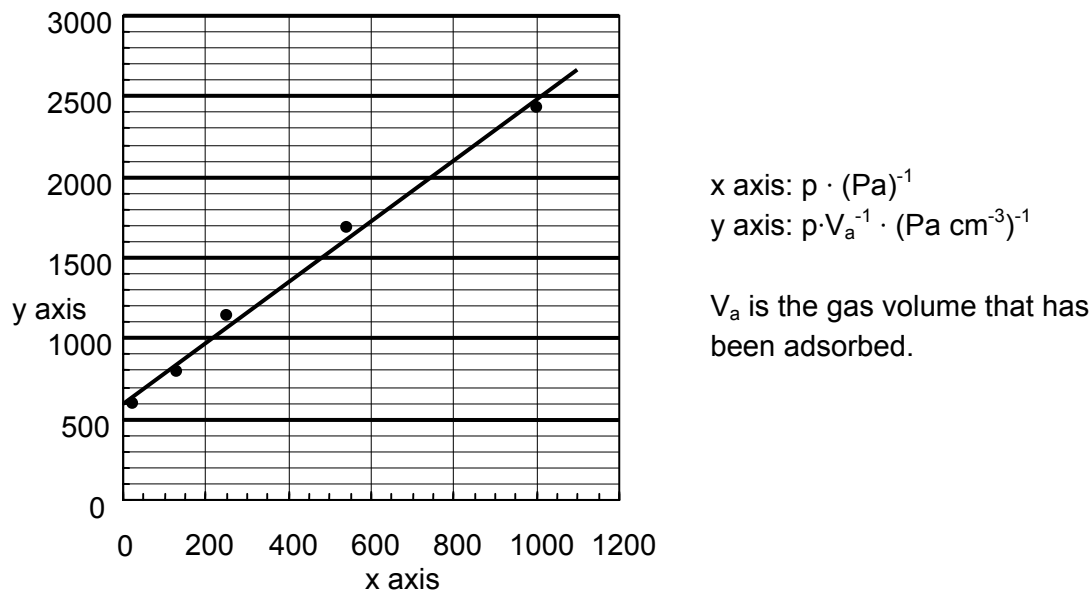
2.3 a) Determine the surface coverage θ at a pressure of 0.65 kPa.

2.3 b) Determine the pressure p at which 15 % of the surface is covered.

2.3 c) The rate r of the decomposition of gas molecules at a solid surface depends on the surface coverage θ (reverse reaction neglected): $r = k \cdot \theta$

Give the order of the decomposition reaction at low and at high gas pressures assuming the validity of the Langmuir isotherm given above (products to be neglected).

2.3 d) Data for the adsorption of another gas on a metal surface (at 25°C)

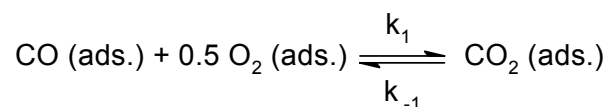


If the Langmuir isotherm can be applied, determine the gas volume $V_{a,\max}$ needed for a complete coverage of the metal surface and the product $K \cdot V_{a,\max}$.

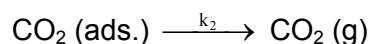
Hint: Set $\theta = V_a / V_{a,\max}$.

Assume that the catalytic oxidation of CO on a Pd surface with equal surface sites proceeds in the following way:

In a first step adsorbed CO and adsorbed O_2 form adsorbed CO_2 in a fast equilibrium,



In a slow second step, CO_2 is then desorbed from the surface:



2.4 Derive the formula for the reaction rate of the $\text{CO}_2(\text{g})$ - formation as a function of the partial pressures of the reaction components.

Hint: Use the Langmuir isotherm with the proper number of gas components

$$\theta(i) = \frac{K_i \cdot p_i}{1 + \sum_j K_j \cdot p_j} \quad j: \text{relevant gas components}$$

Problem 3: Monovalent alkaline earth compounds?

(21 points)

In the past there have been several reports on compounds of monovalent calcium. Until recently the nature of these “compounds” was not known but they are still of great interest to solid state chemists.

Attempts to reduce CaCl_2 to CaCl have been made with

(a) Calcium

(b) Hydrogen

(c) Carbon

3.1 Give the corresponding reaction equations that could potentially lead to the formation of CaCl .

After an attempt to reduce CaCl_2 with the stoichiometric 1:1 molar amount of Ca one obtains an inhomogeneous grey substance. A closer look under the microscope reveals silvery metallic particles and colorless crystals.

3.2 What substance are the metallic particles and the colorless crystals?

When CaCl_2 is attempted to be reduced with elemental hydrogen a white product forms. Elemental analysis shows that the sample contains 52.36 m/m% of calcium and 46.32 m/m% of chlorine.

3.3 Determine the empirical formula of the compound formed!

When CaCl_2 is attempted to be reduced with elemental carbon a red crystalline product forms. The molar ratio of Ca and Cl determined by elemental analysis is $n(\text{Ca}):n(\text{Cl}) = 1.5 : 1$. During the hydrolysis of the red crystalline substance the same gas is evolved as during the hydrolysis of Mg_2C_3 .

3.4 a) Show the two acyclic constitutional isomers of the gas that is formed by hydrolysis.

**b) What compound is formed by the reaction of CaCl_2 with carbon?
(Provided that monovalent calcium does not exist.)**

As none of these attempts lead to the formation of CaCl more consideration has to be given as to the hypothetical structure of CaCl . One can assume that CaCl is likely to crystallize in a simple crystal structure.

It is the radius ratio of cation $r(\text{M}^{m+})$ and anion $r(\text{X}^{n-})$ of salts that often determines the crystal structure of a particular compound as shown for MX compounds in the table below.

Coordination number of M	Surrounding of X	Radius ratio r_M/r_X	Structure type	estimated $\Delta_L H^0$ for CaCl
3	Triangular	0.155-0.225	BN	- 663.8 kJ mol ⁻¹
4	Tetrahedral	0.225-0.414	ZnS	- 704.8 kJ mol ⁻¹
6	Octahedral	0.414-0.732	NaCl	- 751.9 kJ mol ⁻¹
8	Cubic	0.732-1.000	CsCl	- 758.4 kJ mol ⁻¹

$\Delta_L H^0(\text{CaCl})$ is defined for the reaction $\text{Ca}^+(\text{g}) + \text{Cl}^-(\text{g}) \longrightarrow \text{CaCl}(\text{s})$

3.5a) What type of structure is CaCl likely to have?

$[r(\text{Ca}^+) \approx 120 \text{ pm (estimated)}, r(\text{Cl}^-) \approx 167 \text{ pm}]$

Not only the lattice energy $\Delta_L H^0$ for CaCl is important for the decision whether CaCl is thermodynamically stable or not. In order to decide whether it is stable to decomposition into its elements, the standard enthalpy of formation $\Delta_f H^0$ of CaCl has to be known.

3.5b) Calculate the value of $\Delta_f H^0(\text{CaCl})$ with the aid of a Born-Haber-cycle.

heat of fusion	$\Delta_{\text{fusion}} H^0(\text{Ca})$		9.3 kJ mol ⁻¹
ionization enthalpy	$\Delta_{1. \text{IE}} H(\text{Ca})$	$\text{Ca} \longrightarrow \text{Ca}^+$	589.7 kJ mol ⁻¹
ionization enthalpy	$\Delta_{2. \text{IE}} H(\text{Ca})$	$\text{Ca}^+ \longrightarrow \text{Ca}^{2+}$	1145.0 kJ mol ⁻¹
heat of vaporization	$\Delta_{\text{vap}} H^0(\text{Ca})$		150.0 kJ mol ⁻¹
dissociation energy	$\Delta_{\text{diss}} H(\text{Cl}_2)$	$\text{Cl}_2 \longrightarrow 2 \text{ Cl}$	240.0 kJ mol ⁻¹
enthalpy of formation	$\Delta_f H^0(\text{CaCl}_2)$		-796.0 kJ mol ⁻¹
electron affinity	$\Delta_{\text{EA}} H(\text{Cl})$	$\text{Cl} + \text{e}^- \longrightarrow \text{Cl}^-$	- 349.0 kJ mol ⁻¹

To decide whether CaCl is thermodynamically stable to disproportionation into Ca and CaCl₂ the standard enthalpy of this process has to be calculated. (The change of the entropy ΔS is very small in this case, so its influence is negligible.)

3.6 Does the disproportionation of CaCl take place from a thermodynamic point of view? Base your decision on a calculation!

Problem 4: Determining atomic masses

(20 points)

The reaction of the element X with hydrogen leads to a class of compounds that is analogous to hydrocarbons. 5.000 g of X form 5.628 g of a molar 2:1 mixture of the stoichiometric X-analogues of methane and ethane, respectively.

4.1 Determine the molar mass of X from this information. Give the chemical symbol of X, and the 3D-structure of the two products.

The following more complex case is of great historical interest.

The mineral Argyrodite is a stoichiometric compound that contains silver (oxidation state +1), sulphur (oxidation state -2) and an unknown element Y (oxidation state +4). The ratio between the masses of silver and Y in Argyrodite is $m(\text{Ag}) : m(\text{Y}) = 11.88 : 1$. Y forms a reddish brown lower sulfide (oxidation state of Y is +2) and a higher white sulfide (oxidation state of Y is +4). The coloured lower sulfide is the sublimate obtained by heating Argyrodite in a flow of hydrogen. The residues are Ag_2S and H_2S . To convert 10.0 g of Argyrodite completely, 0.295 L of hydrogen are needed at 400 K and 100 kPa.

4.2 Determine the molar mass of Y from this information. Give the chemical symbol of Y, and the empirical formula of Argyrodite.

The atomic masses are correlated with spectroscopic properties.

To determine the vibrational frequency $\tilde{\nu}$ expressed in wave numbers of chemical bonds in IR spectra chemists use Hooke's law which focuses on the frequency of the vibration (attention to units!):

$$\tilde{\nu} = \frac{1}{2\pi c} \cdot \sqrt{\frac{k}{\mu}}$$

$\tilde{\nu}$	vibrational frequency of the bond, in wavenumbers (cm^{-1})
c	speed of light
k	force constant, indicating the strength of the bond ($\text{N m}^{-1} = \text{kg s}^{-2}$)
μ	reduced mass in AB_4 , which is given by $\mu = \frac{3m(\text{A})m(\text{B})}{3m(\text{A}) + 4m(\text{B})}$
$m(\text{A}), m(\text{B})$	the masses of the two bond atoms

The vibrational frequency of the C-H bond of methane is known to be 3030.00 cm^{-1} . The vibrational frequency of the Z-analogue of methane is known to be 2938.45 cm^{-1} . The bond enthalpy of a C-H bond in methane is $438.4 \text{ kJ mol}^{-1}$. The bond enthalpy of a Z-H bond in the Z-analogue of methane is known to be $450.2 \text{ kJ mol}^{-1}$.

4.3 Determine the force constant k of a C-H bond using Hooke's law.

Estimate the force constant k of a Z-H bond, assuming that there is a linear proportionality between force constant and bond enthalpy.

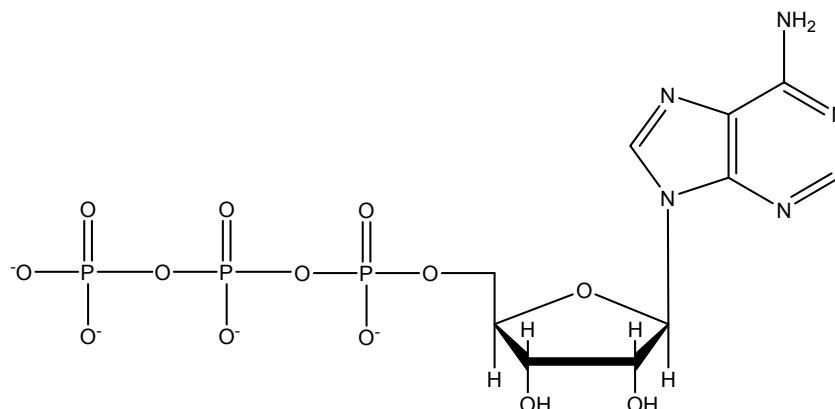
Determine the atomic mass of Z from this information.

Give the chemical symbol of Z

Problem 5: Biochemistry with Thermodynamics

(18 points)

Structure of ATP⁴⁻



Shifting chemical equilibria with ATP:

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:

$$\begin{aligned}c(\text{ATP}^{4-}) &= 2.25 \text{ mmol L}^{-1} \\c(\text{ADP}^{3-}) &= 0.25 \text{ mmol L}^{-1} \\c(\text{HPO}_4^{2-}) &= 1.65 \text{ mmol L}^{-1}\end{aligned}$$

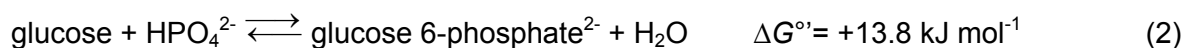
Free energy stored in ATP can be released according to the following reaction:



As the pH is close to 7 in most living cells, biochemists use $\Delta G^{\circ'}$ instead of ΔG° . The standard state of $\Delta G^{\circ'}$ is defined as having a constant pH of 7. In equations with $\Delta G^{\circ'}$ and K' for reactions at pH=7 the concentration of H^+ is therefore omitted. Standard concentration is 1 mol L^{-1} .

5.1 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 unfavourable because of a positive ΔG . The phosphorylation of glucose is an example:



5.2 Calculate first the equilibrium constant K' of reaction (2) and then the ratio $c(\text{glucose 6-phosphate}) / c(\text{glucose})$ 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 hydrolysis of ATP:



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

ATP synthesis:

An adult person ingests about 8000 kJ of energy ($\Delta G'$) per day with the food.

- 5.4 a) What will be the mass of ATP that is produced per day if half of this energy is used for ATP synthesis? Assume a $\Delta G'$ of -52 kJ mol^{-1} for reaction (1), and a molecular weight of 503 g mol^{-1} for ATP.**
- b) What mass of ATP does the human body contain on average if the mean lifetime of an ATP molecule until its hydrolysis is 1 min?**
- c) What happens to the rest of the free energy, which is not used for ATP synthesis? Mark on the answer sheet.**

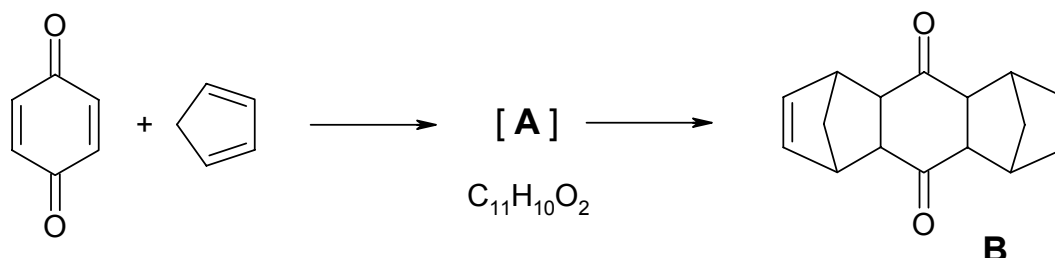
In animals the energy obtained by the oxidation of food is used to pump protons out of specialized membrane vesicles, the mitochondria. ATP-synthase, an enzyme, will allow protons to re-enter the mitochondria if ATP is simultaneously synthesized from ADP and phosphate.

- 5.5 a) How many protons (H^+) are in a spherical mitochondrion with a diameter of $1 \mu\text{m}$ at pH = 7?**
- b) How many protons have to enter into each of the 1000 mitochondria of a liver cell via the ATP-synthase to allow the production of a mass of 0.2 fg of ATP per cell? Assume that 3 protons have to enter for the synthesis of 1 molecule of ATP.**

Problem 6: Diels-Alder Reactions

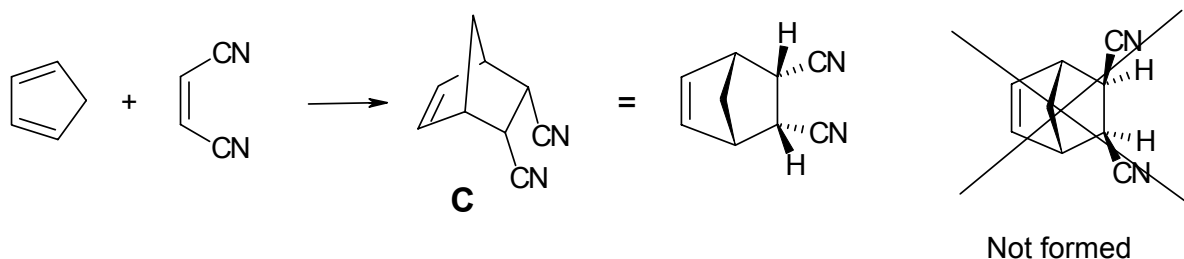
(20 points)

The Diels-Alder reaction, a concerted [4+2]-cycloaddition between a diene and an olefin to yield a cyclohexene, was discovered in 1928 here in Kiel. Prof. Otto Diels and his coworker Kurt Alder mixed *p*-benzoquinone with an excess of cyclopentadiene and obtained the following result:



6.1 Draw the structure of A (without stereochemical information).

The Diels-Alder reaction is a concerted, one-step reaction that proceeds with high stereospecificity. For example, only a single stereoisomer **C** is formed in the following reaction



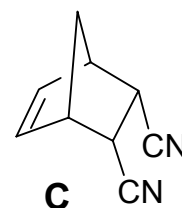
If you use the *E*-isomer of the alkene instead, you will obtain two other stereoisomers **D1** and **D2**.

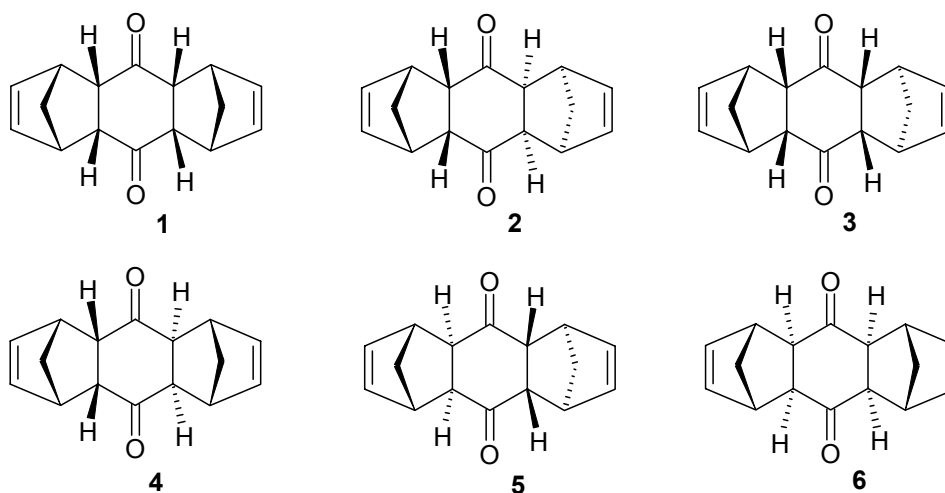
6.2 Give the structures of D1 and D2.

Accordingly, in the original reaction (formation of **B** from cyclopentadiene and benzoquinone) Diels and Alder found only one of the following six conceivable stereoisomers of **B** (see next page).

Hints:

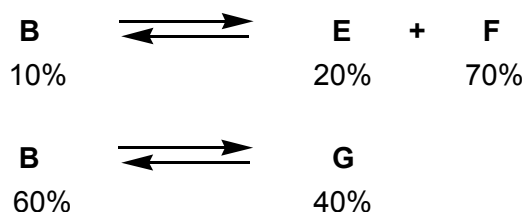
- keep the stereospecific formation of **C** in mind
- and
- the sterically less hindered isomer forms.





6.3 Which single isomer of the six stereoisomers 1-6 of B shown above did they isolate?

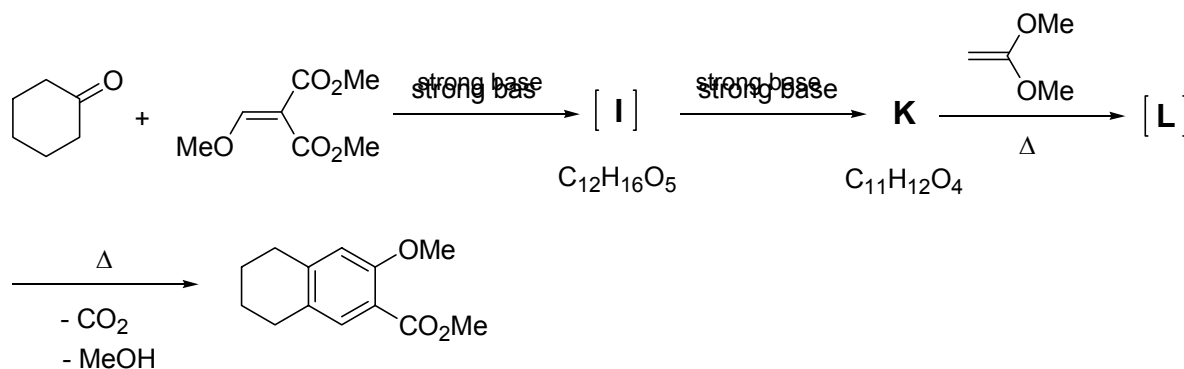
After prolonged heating (15h, 120°C) of the originally isolated stereoisomer **B** (melting point mp: 157°C), Diels and Alder obtained two new stereoisomers **E** (mp: 153°C) and **F** (mp: 163°C). Equilibration of **B** with a catalytic amount of a strong base at 25°C gave a further stereoisomer **G** (mp: 184°C).



6.4 Decide the questions on the answer sheet concerning the Diels-Alder reaction.

Hint: You do not need to know, which of the six stereoisomers 1 - 6 (shown above) corresponds to either E, F or G in order to answer this question.

The Diels-Alder reaction plays also an important role in the following reaction sequence.



6.5 Draw the structures for I, K and L.

Hints: - **K** has only one methyl group.
- **L** is the Diels-Alder adduct of **K** and the alkene shown.

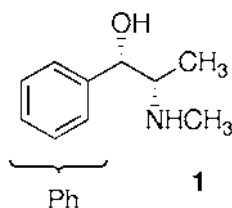
Problem 7: Stereochemistry in Drugs

(21 points)

The Cahn-Ingold-Prelog rules are used to specify the stereochemistry of molecules.

7.1 Order the groups on the answer sheet according to their priority in the Cahn-Ingold-Prelog (CIP)-system.

Pseudoephedrine **1** is a constituent in many common drugs against colds, e.g. in nasal sprays.



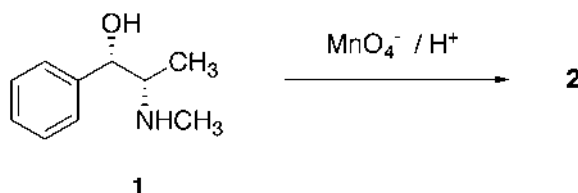
7.2 Mark the stereocenters in 1 with an * on the answer sheet.

Order the substituents on each stereocenter in 1 according to their priority and determine their absolute configuration (R or S).

7.3 Draw a Newman or a sawhorse representation of 1.

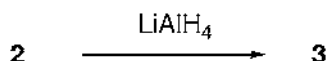
Draw a Fischer representation of 1.

Treatment of **1** with acidic permanganate solutions under mild conditions yields the stimulant Methcathinone **2**:



7.4 Draw the stereochemically correct structure of 2 and a balanced redox equation of the reaction. Indicate in your equation the particular oxidation number on all atoms which undergo a change in their formal oxidation numbers.

The treatment of **2** with LiAlH_4 results exclusively in compound **3**, which differs from **1** in its melting point.



7.5 a) Draw the stereochemically correct structure of 3.

7.5 b) Decide the statements on the answer sheet concerning isomers.

7.5 c) Draw a structural model to rationalize the exclusive formation of 3 from 2.

Problem 8: Colloids

(22 points)

The combination of an inorganic and an organic component on a nanometer scale yields materials with excellent properties. Thus the synthesis of hybrid nanoparticles is of interest.

($T = 298.15\text{ K}$ throughout whole problem)

Solution A is an aqueous solution of CaCl_2 with a concentration of 1.780 g L^{-1} .

Solution B is an aqueous solution of Na_2CO_3 with a concentration of 1.700 g L^{-1} .

$$\text{p}K_{\text{a}1}(\text{H}_2\text{CO}_3) = 6.37$$

$$\text{p}K_{\text{a}2}(\text{HCO}_3^-) = 10.33$$

8.1 Calculate the pH of solution B using reasonable assumptions.

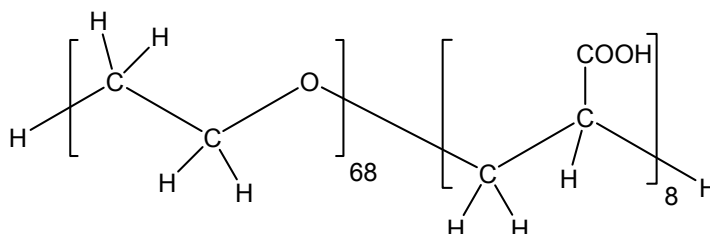
100 mL of solution **A** and 100 mL of solution **B** are mixed to form solution **C**. Solution **C** is adjusted to pH 10. A precipitate forms.

$$K_{\text{sp}}(\text{Ca}(\text{OH})_2) = 6.46 \cdot 10^{-6}\text{ mol}^3\text{ L}^{-3}$$

$$K_{\text{sp}}(\text{CaCO}_3) = 3.31 \cdot 10^{-9}\text{ mol}^2\text{ L}^{-2}$$

8.2 Show by calculation for each of the compounds $\text{Ca}(\text{OH})_2$ and CaCO_3 whether it can be found in the precipitate or not.

In a similar experiment 100 mL of solution **A** additionally contain 2 g of a copolymer consisting of two water soluble blocks: a poly(ethylene oxide) block and a poly(acrylic acid) block:



The polymer does not undergo any chemical reaction (except protolysis of the acid) and yet has a strong effect: after mixing of the two solutions (A+B) no precipitate can be observed. Small calcium carbonate particles with the polymer chains attached to their surface form. The attached polymers prevent further crystal growth and the hybrid particles remain in solution.

8.3. Circle the block of the polymer (on the answer sheet) that attaches to the surface of the growing calcium carbonate crystal.

To characterize the hybrid particles they are separated from the preparation solution and transferred into 50 mL of an aqueous NaOH solution ($c(\text{NaOH}) = 0.19 \text{ mol L}^{-1}$). The solution is diluted by the addition of 200 mL of water. Assume that the new solution contains only the hybrid particles and no additional calcium or carbonate ions. All acidic groups participate in the acid-base equilibrium.

- For the new solution, a pH of 12.30 is measured.
- In electron microscopy you only can see the inorganic particles (not the polymer): Spherical particles of 100 nm diameter are observed.
- The molar mass of the hybrid particles (inorganic and organic part together) is determined to be $M = 8.01 \cdot 10^8 \text{ g mol}^{-1}$
- The charge of the particles is found to be $Z = - 800$ (number of unit charges).

$$(\text{pK}_a(\text{COOH, copolymer}) = 4.88)$$

8.4 *How much of the initial amount of polymer (2 g) can still be found in the hybrid particles?*

8.5. *Calculate which modification of calcium carbonate has been formed.*

Modification	density
Calcite	2.71 g cm^{-3}
Vaterite	2.54 g cm^{-3}
Aragonite	2.95 g cm^{-3}

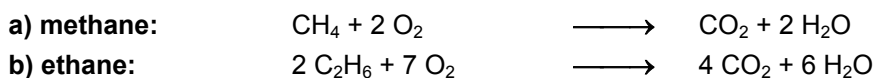
1₁

Name: _____

Student code: _____

1₁**1.1 Chemical equations:**

(2 points)

**Thermodynamic data for the equations:**

(4 points)

$$\begin{aligned}\Delta H^\circ &= [2 \cdot (-241.8) - 393.5 - (-74.6)] \text{ kJ mol}^{-1} = -802.5 \text{ kJ mol}^{-1} \\ \Delta S^\circ &= [2 \cdot (188.8) + 213.8 - 186.3 - 2 \cdot 205.2] \text{ J mol}^{-1} \text{ K}^{-1} = -5.3 \text{ J mol}^{-1} \text{ K}^{-1} \\ \Delta G^\circ &= -802.5 \text{ kJ mol}^{-1} - 298.15 \text{ K} \cdot (-5.3 \text{ J mol}^{-1} \text{ K}^{-1}) = -800.9 \text{ kJ mol}^{-1}\end{aligned}$$

Methane: $\Delta H^\circ = -802.5 \text{ kJ mol}^{-1}$ $\Delta S^\circ = -5.3 \text{ J mol}^{-1} \text{ K}^{-1}$ $\Delta G^\circ = -800.9 \text{ kJ mol}^{-1}$

$$\begin{aligned}\Delta H^\circ &= [6 \cdot (-241.8) - 4 \cdot 393.5 - 2 \cdot (-84.0)] \text{ kJ mol}^{-1} = -2856.8 \text{ kJ mol}^{-1} \\ \Delta S^\circ &= [6 \cdot 188.8 + 4 \cdot 213.8 - 2 \cdot 229.2 - 7 \cdot 205.2] \text{ J mol}^{-1} \text{ K}^{-1} = +93.2 \text{ J mol}^{-1} \text{ K}^{-1} \\ \Delta G^\circ &= -2856.8 \text{ kJ mol}^{-1} - 298.15 \text{ K} \cdot (93.2 \text{ J mol}^{-1} \text{ K}^{-1}) = -2884.6 \text{ kJ mol}^{-1}\end{aligned}$$

Ethane: $\Delta H^\circ = -2856.8 \text{ kJ mol}^{-1}$ $\Delta S^\circ = +93.2 \text{ J mol}^{-1} \text{ K}^{-1}$ $\Delta G^\circ = -2884.6 \text{ kJ mol}^{-1}$

1.2 a) Amount of methane and ethane in 1 m³ natural gas:

(7 points)

(idea 2 points)

$$m = \rho \cdot V = 0.740 \text{ g L}^{-1} \cdot 1000 \text{ L} = 740 \text{ g}$$

(1 point)

$$\begin{aligned}M_{\text{av}} &= \sum_i x(i)M(i) = 0.0024 \cdot 44.01 \text{ g mol}^{-1} + 0.0134 \cdot 28.02 \text{ g mol}^{-1} \\ &\quad + 0.9732 \cdot 16.05 \text{ g mol}^{-1} + 0.011 \cdot 30.08 \text{ g mol}^{-1} \\ &= 16.43 \text{ g mol}^{-1}\end{aligned}$$

(2 points)

$$n_{\text{tot}} = m (M_{\text{av}})^{-1} = 740 \text{ g} \cdot (16.43 \text{ g/mol})^{-1} = 45.04 \text{ mol}$$

(1 point)

$$n(i) = x(i) \cdot n_{\text{tot}} \quad n(\text{CH}_4) = x(\text{CH}_4) \cdot n_{\text{tot}} = 0.9732 \cdot 45.04 \text{ mol} = 43.83 \text{ mol}$$

$$n(\text{C}_2\text{H}_6) = x(\text{C}_2\text{H}_6) \cdot n_{\text{tot}} = 0.0110 \cdot 45.04 \text{ mol} = 0.495 \text{ mol}$$

(1 point)

1.2 b) Energy of combustion, deviation:

(2 points)

$$\begin{aligned}E_{\text{comb.}}(\text{H}_2\text{O}(\text{g})) &= \sum_i n(i) \Delta_c H^\circ(i) = 43.83 \text{ mol} \cdot (-802.5 \text{ kJ mol}^{-1}) + 0.495 \text{ mol} \cdot 0.5 \cdot (-2856.8 \text{ kJ mol}^{-1}) \\ &= -35881 \text{ kJ}\end{aligned}$$

$$E_{\text{comb.}}(\text{H}_2\text{O}(\text{g})) = -35881 \text{ kJ}$$

(1 point)

Deviation from PUC

$$E_{\text{PUC}}(\text{H}_2\text{O}(\text{g})) = 9.981 \text{ kWh m}^{-3} \cdot 1 \text{ m}^3 \cdot 3600 \text{ kJ (kWh)}^{-1} = 35932 \text{ kJ}$$

$$\begin{aligned}\text{deviation } \Delta E &= (E_{\text{comb.}}(\text{H}_2\text{O}(\text{g})) - E_{\text{PUC}}(\text{H}_2\text{O}(\text{g})) \cdot 100\% \cdot [E_{\text{comb.}}(\text{H}_2\text{O}(\text{g}))]^{-1} \\ &= (35881 \text{ kJ} - 35932 \text{ kJ}) \cdot 100\% \cdot (35881 \text{ kJ})^{-1} = -0.14\%\end{aligned}$$

$$\text{deviation} = -0.14 \%$$

(1 point)

1₂

Name: _____

Student code: _____

1₂**1.3 Energy for heating the water:****(4 points)**Volume of water: $V_{\text{water}} = 22.5 \text{ m}^3$ (0.5 points) $n_{\text{water}} = V_{\text{water}} \rho_{\text{water}} (M_{\text{water}})^{-1} = 22.5 \text{ m}^3 \cdot 10^6 \text{ g m}^{-3} \cdot (18.02 \text{ g mol}^{-1})^{-1} = 1.249 \cdot 10^6 \text{ mol}$ (0.5 points) $E_{\text{water}} = n_{\text{water}} \cdot C_p \cdot \Delta T = 1.249 \cdot 10^6 \text{ mol} \cdot 75.30 \text{ J K}^{-1} \text{ mol}^{-1} \cdot 14 \text{ K} = 1316 \text{ MJ}$ (0.5 points) **$E_{\text{water}} = 1316 \text{ MJ}$** (1.5 points)**Energy for heating the air**Volume of the house is: $V_{\text{air}} = 15 \text{ m} \cdot 8 \text{ m} \cdot 3 \text{ m} + 0.5 \cdot 15 \text{ m} \cdot 8 \text{ m} \cdot 2 \text{ m} = 480 \text{ m}^3$ (1 point) $n_{\text{air}} = pV \cdot (RT)^{-1} = 1.013 \cdot 10^5 \text{ Pa} \cdot 480 \text{ m}^3 \cdot (8.314 \text{ J (K mol)}^{-1} \cdot 283.15 \text{ K})^{-1} = 2.065 \cdot 10^4 \text{ mol}$ (0.5) $C_p(\text{air}) = 0.21 \cdot 29.4 \text{ J (K mol)}^{-1} + 0.79 \cdot 29.1 \text{ J (K mol)}^{-1} = 29.16 \text{ J (K mol)}^{-1}$ (0.5 points) $E_{\text{air}} = n_{\text{air}} \cdot C_p(\text{air}) \cdot \Delta T = 2.065 \cdot 10^4 \text{ mol} \cdot 29.17 \text{ J (K mol)}^{-1} \cdot 20 \text{ K} = 12.05 \text{ MJ}$ (0.5 points) **$E_{\text{air}} = 12.05 \text{ MJ}$** (2.5)**1.4 Energy for maintaining the temperature:****(2 points)**

surface area of the house:

 $A_{\text{house}} = 3 \text{ m} \cdot 46 \text{ m} + 8 \text{ m} \cdot 2 \text{ m} + ((2 \text{ m})^2 + (4 \text{ m})^2)^{1/2} \cdot 2 \cdot 15 \text{ m} = 288.16 \text{ m}^2$ (1 point)Heat conductivity: $\lambda_{\text{wall}} = 1 \text{ J (s K m)}^{-1}$ Energy flux along a temperature gradient (wall thickness $d = 0.2 \text{ m}$) $J = E_{\text{loss}} (A \cdot \Delta t)^{-1} = \lambda_{\text{wall}} \cdot \Delta T \cdot d^{-1}$ $E_{\text{loss}} = 288.16 \text{ m}^2 \cdot (12 \cdot 60 \cdot 60 \text{ s}) \cdot 1 \text{ J (s K m)}^{-1} \cdot 25 \text{ K} \cdot (0.2 \text{ m})^{-1} = 1556 \text{ MJ}$ (1 point) **$E_{\text{loss}} = 1556 \text{ MJ}$**

1₃

Name: _____

Student code: _____

1₃**1.5 Total energy and costs:****(3 points)**total energy: $E_{\text{tot}} = E_{\text{water}} + E_{\text{air}} + E_{\text{loss}} = 1316 \text{ MJ} + 12 \text{ MJ} + 1556 \text{ MJ} = 2884 \text{ MJ}$ **total energy** **$E_{\text{tot}} = 2884 \text{ MJ}$** **(0.5)**2884 MJ corresponds to $2.884 \cdot 10^6 \text{ kJ} \cdot (3600 \text{ s h}^{-1} \cdot 9.981 \text{ kJ s}^{-1} \text{ m}^{-3} \cdot 0.9)^{-1} = 89.18 \text{ m}^3$ **volume of gas** **$V = 89.18 \text{ m}^3$** **(1)**

2884 MJ correspond to a cost of:

 $0.40 \text{ €m}^{-3} \cdot 89.18 \text{ m}^3$ = 35.67 €

rent for equipment: 150.00 €

total cost of gas heating = 185.67 € **(0.5)**

2884 MJ correspond to a cost of

 $2.884 \cdot 10^6 \text{ kJ} \cdot 0.137 \text{ €} \cdot (3600 \text{ s h}^{-1} \cdot 1 \text{ kJ s}^{-1} \text{ h})^{-1} = 109.75 \text{ €}$

rent for equipment: 100.00 €

total cost of electric heating = 209.75 € **(1)**

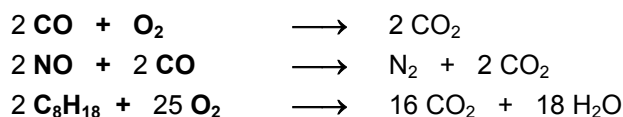
2₁

Name: _____

Student code: _____

2₁**2.1 Reaction equations:**

(3 points)

**2.2 Questions concerning the λ probe:**

(3 points)

	true	false	no decision possible
If the λ -value is in the range of the λ -window, carbon monoxide and hydrocarbons can be oxidised at the three-way catalytic converter.	x	<input type="checkbox"/>	<input type="checkbox"/>
With $\lambda > 1$, carbon monoxide and hydrocarbons can be oxidised at the three-way catalytic converter.	x	<input type="checkbox"/>	<input type="checkbox"/>
With $\lambda < 0.975$, nitrogen oxides can be reduced poorly.	<input type="checkbox"/>	x	<input type="checkbox"/>

2.3 a) Surface coverage:

(1 point)

$$\theta = \frac{0.85 \text{ kPa}^{-1} \cdot 0.65 \text{ kPa}}{1 + 0.85 \cdot 0.65}$$

$$\theta = 0.356 \text{ or } 35.6 \%$$

2.3 b) Pressure at which 15% of the surface is covered:

(2 points)

$$\theta = \frac{K \cdot p}{1 + K \cdot p} \Leftrightarrow K \cdot p = \theta + \theta \cdot K \cdot p \Leftrightarrow p \cdot (K - \theta \cdot K) = \theta \Leftrightarrow p = \frac{\theta}{K - \theta \cdot K} \quad (1 \text{ point})$$

$$\theta = 0.15$$

$$p = 0.21 \text{ kPa}$$

(1 point)

2.3 c) Orders of decomposition:

(3 points)

order of the decomposition reaction at low gas pressures	1	(1.5 points)
order of the decomposition reaction at high gas pressures	0	(1.5 points)

notes:

$$\begin{aligned}
 r &= k \cdot \theta = k \cdot \frac{K \cdot p}{1 + K \cdot p}, \quad p \text{ low} \Rightarrow p \ll \frac{1}{K} \Rightarrow r = k \cdot K \cdot p \quad \text{reaction order 1.} \\
 p \text{ high} &\Rightarrow p \gg \frac{1}{K} \Rightarrow r = k \quad \text{reaction order 0.}
 \end{aligned}$$

2.3 d) Gas volume $V_{a,max}$ and product $K \cdot V_{a,max}$: (4 points)

$$\frac{1}{\theta} = \frac{1}{K \cdot p} + 1 = \frac{V_{a,max}}{V_a} \quad \Rightarrow \quad \frac{1}{K \cdot V_{a,max}} + \frac{p}{V_{a,max}} = \frac{p}{V_a} \quad (2)$$

$$\text{slope: } \frac{1}{V_{a,max}} = 1.9 \text{ cm}^{-3} \quad \Rightarrow \quad V_{a,max} = 0.53 \text{ cm}^3 \quad (1)$$

$$\text{intercept: } \frac{1}{K \cdot V_{a,max}} = 6 \cdot 10^2 \text{ Pa cm}^{-3} \quad \Rightarrow \quad K \cdot V_{a,max} = 1.7 \cdot 10^{-3} \text{ Pa}^{-1} \text{ cm}^3 \quad (1)$$

2.4 Equation for reaction rate: (7 points)

The information given in the text leads directly to $r = k_2 \cdot \theta_{CO_2}$ (2)

The law of mass action for the first step of the mechanism is given by

$$\theta_{CO_2} = \frac{k_1}{k_{-1}} \cdot \theta_{CO} \cdot \theta_{O_2}^{\frac{1}{2}}, \quad (2) \quad \Rightarrow \quad r = k_2 \cdot \frac{k_1}{k_{-1}} \cdot \theta_{CO} \cdot \theta_{O_2}^{\frac{1}{2}}. \quad (1)$$

The Langmuir isotherm gives:

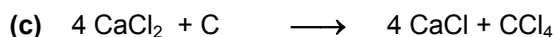
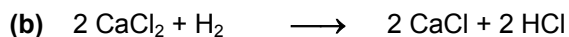
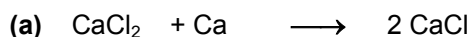
$$\theta_{CO} = \frac{K_{CO} \cdot p_{CO}}{1 + K_{CO_2} \cdot p_{CO_2} + K_{CO} \cdot p_{CO} + K_{O_2} \cdot p_{O_2}} \quad \text{and} \quad \theta_{O_2} = \frac{K_{O_2} \cdot p_{O_2}}{1 + K_{CO_2} \cdot p_{CO_2} + K_{CO} \cdot p_{CO} + K_{O_2} \cdot p_{O_2}} \quad (1.5)$$

$$r = k_2 \frac{k_1}{k_{-1}} \frac{K_{CO} \cdot p_{CO} \cdot (K_{O_2} \cdot p_{O_2})^{\frac{1}{2}}}{(1 + K_{CO_2} \cdot p_{CO_2} + K_{CO} \cdot p_{CO} + K_{O_2} \cdot p_{O_2})^{\frac{3}{2}}}. \quad (0.5)$$

3₁

Name: _____

Student code: _____

3₁**3.1 Chemical equations:****(3 points)****3.2****(2 points)****silvery metallic particles:** Ca**colorless crystals:** CaCl_2 *Note: CaCl cannot be obtained by a conventional solid state reaction of Ca and CaCl_2* **3.3 Empirical formula:****(4 points)**

$$100 \% - (m/m\% \text{ Ca} + m/m\% \text{ Cl}) = m/m\% \text{ X}$$

$$100 \% - (52.36\% + 46.32\%) = 1.32\% \text{ X} \quad (1)$$

$$\begin{aligned} \text{mol\% of Ca} &= 52.36 \text{ m/m\%} / M(\text{Ca}) \\ &= 52.36 \text{ m/m\%} / 40.08 \text{ g mol}^{-1} \\ &= 1.31 \text{ mol\%} \end{aligned} \quad (0.5)$$

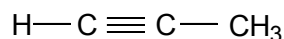
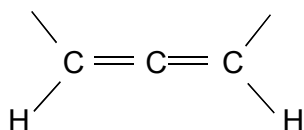
$$\begin{aligned} \text{mol\% of Cl} &= 46.32 \text{ m/m\%} / M(\text{Cl}) \\ &= 46.32 \text{ m/m\%} / 35.45 \text{ g mol}^{-1} \\ &= 1.31 \text{ mol\%} \end{aligned} \quad (0.5)$$

$$\begin{aligned} \text{mol\% of X} &= 1.32 \% \text{ X} / M(\text{H}) \\ &= 1.32 \% \text{ X} / 1.01 \text{ g mol}^{-1} \\ &= 1.31 \text{ mol\%} \end{aligned} \quad (1)$$

$$n(\text{Ca}) : n(\text{Cl}) : n(\text{H}) = 1 : 1 : 1$$

empirical formula CaClH (1)

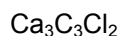
Notes: The reaction of CaCl_2 with hydrogen does not lead to CaCl. The hydride CaClH is formed instead. The structure of this compound was determined by X-ray structure analysis which is not a suitable method to determine the position of light elements like hydrogen. Thus, the presence of hydrogen was missed and CaClH was thought to be CaCl for quite a long time.

3.4 a) Structures only:**(2 points)**

3₂

Name: _____

Student code: _____

3₂**3.4 b) Empirical formula of the compound formed:****(2 points)**

Notes: If the ratio of $n(\text{Ca}):n(\text{Cl}) = 1.5 : 1$ [or better = $3 : 2$ which can be rewritten as $\text{CaCl}_2 \cdot 2\text{Ca}^{2+} = \text{Ca}_3\text{Cl}_2^{4+}$] is given and the reduction product must contain a C_3^{4-} anion which needs two Ca^{2+} cations for electroneutrality, the composition $\text{Ca}_3\text{C}_3\text{Cl}_2$ will follow.

3.5 a) Structure type CaCl likely to have:**(1 point)**

$$r(\text{Ca}^+)/r(\text{Cl}^-) = 120 \text{ pm}/167 \text{ pm} = 0.719$$

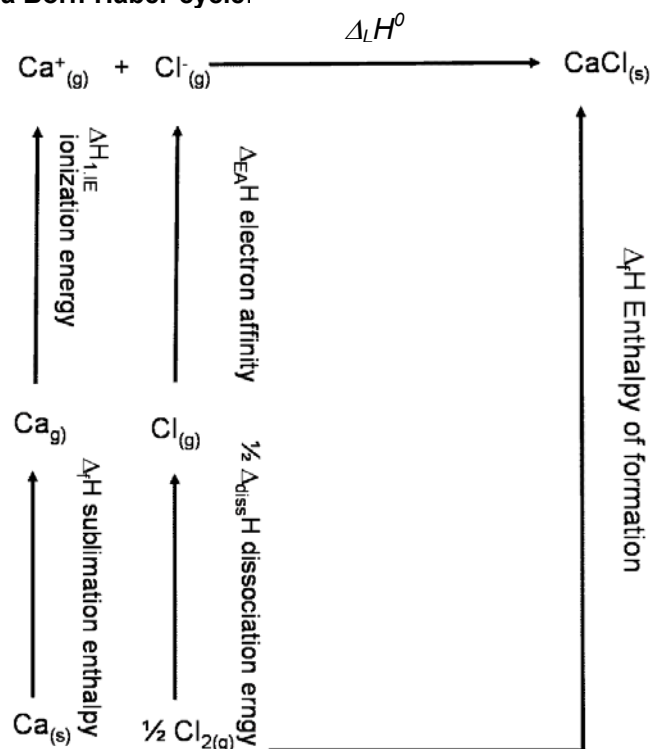
NaCl
☒

CsCl
☐

ZnS
☐

BN
☐

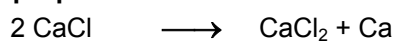
no decision possible
☐

3.5 b) $\Delta_f H^\circ(\text{CaCl})$ with a Born-Haber-cycle:**(5 points)**

Summing up of all the single steps of the Born-Haber-cycle:

$$\begin{aligned} \Delta_f H^\circ(\text{CaCl}) &= \Delta_{\text{subl}} H^\circ(\text{Ca}) + \Delta_{1, \text{IE}} H(\text{Ca}) + \frac{1}{2} \Delta_{\text{diss}} H(\text{Cl}_2) + \Delta_{\text{EA}} H(\text{Cl}) + \Delta_L H(\text{CaCl}) \\ &= (159.3 \quad + 589.7 \quad + 120 \quad - 349.0 \quad - 751.9) \text{ kJ mol}^{-1} \\ &\quad (1) \quad (0.5) \quad (1) \quad (0.5) \quad (1) \end{aligned}$$

$$\Delta_f H^\circ(\text{CaCl}) = -231.9 \text{ kJ mol}^{-1} \quad (1)$$

3.6 Stability to disproportionation:**(2 points)**

$$\Delta H = \Delta_f H^\circ(\text{CaCl}_2) - 2 \Delta_f H^\circ(\text{CaCl}) = -796.0 \text{ kJ mol}^{-1} + 463.8 \text{ kJ mol}^{-1} = -332.2 \text{ kJ mol}^{-1} \quad (1)$$

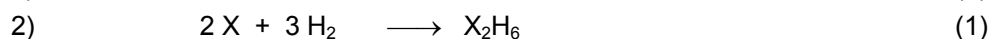
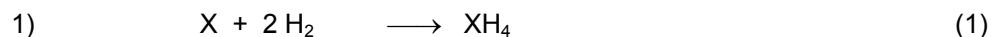
disproportionation yes no no decision possible, more information needed

☐ x ☐ (1)

4₁

Name: _____

Student code: _____

4₁**4.1 Atomic mass of X, symbol of X, structures:****(7 points)**

$$I) \quad 5.0 \text{ g} = [n_1(X) + n_2(X)] \cdot M(X)$$

$$II) \quad 5.628 \text{ g} = n_1(XH_4) \cdot [M(X) + 4 \cdot 1.01 \text{ g mol}^{-1}] + n_2(X_2H_6) \cdot [2M(X) + 6 \cdot 1.01 \text{ g mol}^{-1}]$$

$$III) \quad n_1(XH_4) = 2n_2(X_2H_6) \quad (2)$$

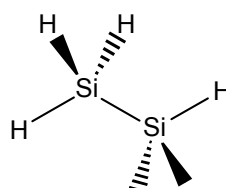
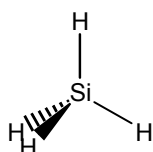
$$III, I) \rightarrow I') \quad 2n_1(X) \cdot M(X) = 5.0 \text{ g}$$

$$III, II) \rightarrow II') \quad n_1(X) \cdot [2M(X) + 7.07 \text{ g mol}^{-1}] = 5.628 \text{ g}$$

$$I', II') \rightarrow VI) \quad (5.0 \text{ g}) \cdot [2M(X)]^{-1} = (5.628 \text{ g}) \cdot [2M(X) + 7.07 \text{ g mol}^{-1}]^{-1} \quad (1)$$

$$M(X) = 3.535 \text{ g mol}^{-1} \cdot (5.628 \text{ g})^{-1} \cdot [(5.0 \text{ g})^{-1} - (5.628 \text{ g})^{-1}]^{-1}$$

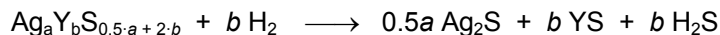
$$M(X) = 28.14 \text{ g mol}^{-1}$$

atomic mass of X $M(X) = 28.14 \text{ g mol}^{-1}$ chemical symbol of X: Si (1)**3D structures of the two products:**(1)

4₂

Name: _____

Student code: _____

4₂**4.2 Atomic mass of Y and empirical formula of Argyrodite:****(9 points)**

$$\text{I)} \quad 10\text{ g} = n(\text{Ag}_a\text{Y}_b\text{S}_{0.5a+2b}) \cdot [a \cdot 107.87\text{ g mol}^{-1} + b \cdot M(\text{Y}) + (0.5 \cdot a + 2 \cdot b) \cdot 32.07\text{ g mol}^{-1}] \quad (3)$$

$$\text{II)} \quad n(\text{H}_2) = \frac{p \cdot V(\text{H}_2)}{RT} \qquad n(\text{H}_2) = \frac{100\text{kPa} \cdot 0.295 \cdot 10^{-3}\text{ m}^3}{8.314\text{ JK}^{-1}\text{ mol}^{-1} \cdot 400\text{K}}$$

$$n(\text{H}_2) = 8.871 \cdot 10^{-3}\text{ mol} \qquad n(\text{Ag}_a\text{Y}_b\text{S}_{0.5a+2b}) = b^{-1} \cdot 8.871 \cdot 10^{-3}\text{ mol} \quad (1)$$

$$\text{III)} \quad 11.88 = \frac{a \cdot 107.87\text{ g mol}^{-1}}{b \cdot M(\text{Y})} \qquad a \cdot 107.87\text{ g mol}^{-1} = 11.88 \cdot b \cdot M(\text{Y}) \quad (1)$$

$$\text{II, I)} \rightarrow \text{II')} \quad b \cdot 10\text{ g} \cdot (8.871 \cdot 10^{-3}\text{ mol})^{-1} = a \cdot 107.87\text{ g mol}^{-1} + b \cdot M(\text{Y}) + (0.5 \cdot a + 2b) \cdot 32.07\text{ g mol}^{-1}$$

$$b \cdot 1127\text{ g mol}^{-1} = a \cdot 107.87\text{ g mol}^{-1} + b \cdot M(\text{Y}) + (0.5 \cdot a + 2b) \cdot 32.07\text{ g mol}^{-1}$$

$$\text{III, II')} \rightarrow \text{IV)} \quad b \cdot 1127\text{ g mol}^{-1} = 11.88 \cdot b \cdot M(\text{Y}) + b \cdot M(\text{Y}) + (0.5 \cdot a + 2b) \cdot 32.07\text{ g mol}^{-1}$$

$$b \cdot 1127\text{ g mol}^{-1} = 11.88 \cdot b \cdot M(\text{Y}) + b \cdot M(\text{Y}) + (0.5 \cdot \frac{11.88 \cdot b \cdot M(\text{Y})}{107.87\text{ g mol}^{-1}} + 2b) \cdot 32.07\text{ g mol}^{-1}$$

$$M(\text{Y}) = 72.57\text{ g mol}^{-1} \quad (2)$$

$$\text{atomic mass } M(\text{Y}) = 72.57\text{ g mol}^{-1} \quad (1)$$

$$M(\text{Y}) = 72.57\text{ g mol}^{-1} \rightarrow \text{III} \qquad a:b = 8:1 \quad (1)$$

chemical symbol of Y: Ge**empirical formula of Argyrodite:**Ag₈GeS₆

4₃

Name: _____

Student code: _____

4₃**4.3 The force constants of a C-H bond:****(1 point)**

$$k(\text{C-H}) = [2\pi \cdot c \cdot \tilde{\nu}(\text{C-H})]^2 \cdot \frac{1}{N_A} \cdot \frac{3M(\text{C}) \cdot M(\text{H})}{3M(\text{C}) + 4M(\text{H})}$$

$$= [2\pi \cdot 3 \cdot 10^{10} \text{ cm} \cdot \text{s}^{-1} \cdot 3030 \text{ cm}^{-1}]^2 \cdot \frac{1}{6.022 \cdot 10^{23} \text{ mol}^{-1}} \cdot \frac{3 \cdot 12.01 \cdot 1.01}{3 \cdot 12.01 + 4 \cdot 1.01} \text{ g mol}^{-1}$$

$$k(\text{C-H}) = 491.94 \text{ N m}^{-1}$$

The force constants of a Z-H bond:**(1 point)**

$$k(\text{Z-H}) = k(\text{C-H}) \cdot \frac{\Delta_b H(\text{Z-H})}{\Delta_b H(\text{C-H})}$$

$$= 491.94 \text{ N m}^{-1} \cdot 450.2 \text{ kJ mol}^{-1} \cdot [438.4 \text{ kJ mol}^{-1}]^{-1}$$

$$k(\text{Z-H}) = 505.18 \text{ N m}^{-1}$$

The atomic mass and symbol of Z:**(2 points)**

$$\frac{3M(\text{Z}) \cdot M(\text{H})}{3M(\text{Z}) + 4M(\text{H})} = \frac{k(\text{Z-H}) \cdot N_A}{[2\pi \cdot c \cdot \tilde{\nu}(\text{Z-H})]^2}$$

$$M(\text{Z}) = \frac{4}{3} \cdot \left(\frac{[2\pi \cdot c \cdot \tilde{\nu}(\text{Z-H})]^2}{k(\text{Z-H}) \cdot N_A} - \frac{1}{M(\text{H})} \right)^{-1}$$

$$M(\text{Z}) = \frac{4}{3} \cdot \left(\frac{[2\pi \cdot 3 \cdot 10^{10} \cdot 2938.45]^2}{505180 \cdot 6.022 \cdot 10^{23}} - \frac{1}{1.01} \right)^{-1} \text{ g mol}^{-1}$$

atomic mass of Z **$M(\text{Z}) = 72.68 \text{ g mol}^{-1}$**

chemical symbol of Z **Ge**

Note: Even if the students find different values (± 2) due to different ways of rounding, they will be able to find Ge as Z has to be an analogue of carbon.

5₁

Name: _____

Student code: _____

5₁**5.1 Actual $\Delta G'$ of reaction (1):****(2 points)**

$$\Delta G' = \Delta G^{\circ'} + RT \ln \frac{c(\text{ADP}^{3-})/(1 \text{ mol L}^{-1}) \cdot c(\text{HPO}_4^{2-})/(1 \text{ mol L}^{-1})}{c(\text{ATP}^{4-})/(1 \text{ mol L}^{-1})} \quad (0.5)$$

$$= -30500 \text{ J mol}^{-1} + 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \cdot 298.15 \text{ K} \cdot \ln (0.00025 \cdot 0.00165 / 0.00225) \quad (1)$$

$$= -30.5 \text{ kJ mol}^{-1} - 21.3 \text{ kJ mol}^{-1}$$

$$= -51.8 \text{ kJ mol}^{-1} \quad (0.5)$$

$$\Delta G' = -51.8 \text{ kJ mol}^{-1}$$

5.2 Equilibrium constant K' of reaction (2), ratio $c(\text{glucose 6-phosphate}) / c(\text{glucose})$: (3 points)

$$\Delta G^{\circ'} = -RT \cdot \ln K' \quad (0.5)$$

$$K' = e^{-\Delta G^{\circ'}/RT} \quad (0.5)$$

$$= e^{-13800 \text{ J/mol} / (8.314 \text{ J/(mol K)} \cdot 298.15 \text{ K})}$$

$$= 0.0038 \quad (0.5)$$

$$K' = \frac{c(\text{glucose 6-phosphate})/(1 \text{ mol L}^{-1})}{c(\text{glucose})/(1 \text{ mol L}^{-1}) \cdot c(\text{HPO}_4^{2-})/(1 \text{ mol L}^{-1})} \quad (0.5)$$

$$\frac{(\text{glucose 6-phosphate})}{(\text{glucose})} = K' \cdot c(\text{HPO}_4^{2-}) \cdot (1 \text{ mol L}^{-1})^{-1} \quad (0.5)$$

$$= 0.0038 \cdot 0.00165$$

$$= 6.3 \cdot 10^{-6} \quad (0.5)$$

$$K' = 0.0038$$

 $(\Sigma 1.5)$

$$\frac{c(\text{glucose 6-phosphate})}{c(\text{glucose})} = 6.3 \cdot 10^{-6}$$

 $(\Sigma 1.5)$

5₂

Name: _____

Student code: _____

5₂**5.3 ΔG° and K' of reaction (3), ratio $c(\text{glucose 6-phosphate}) / c(\text{glucose})$:** (4 points)

$$\Delta G^\circ(3) = \Delta G^\circ(1) + \Delta G^\circ(2) \quad (0.5)$$

$$= -30.5 \text{ kJ mol}^{-1} + 13.8 \text{ kJ mol}^{-1}$$

$$= -16.7 \text{ kJ mol}^{-1} \quad (0.5)$$

$$\Delta G^\circ = -RT \cdot \ln K' \quad (0.5)$$

$$K' = e^{-\Delta G^\circ / RT}$$

$$= e^{16700 \text{ J/mol} / (8.314 \text{ J/(mol K)} \cdot 298.15 \text{ K})} \quad (0.5)$$

$$= 843 \quad (0.5)$$

$$K' = \frac{c(\text{glucose 6-phosphate}) \cdot c(\text{ADP}^{3-})}{c(\text{glucose}) \cdot c(\text{ATP}^{4-})} \quad (0.5)$$

$$\frac{c(\text{glucose 6-phosphate})}{c(\text{glucose})} = K' \cdot \frac{c(\text{ATP}^{4-})}{c(\text{ADP}^{3-})} \quad (0.5)$$

$$= 843 \cdot 2.25 \text{ mmol L}^{-1} / 0.25 \text{ mmol L}^{-1} \quad (0.5)$$

$$= 7587$$

$$\Delta G^\circ = -16.7 \text{ kJ mol}^{-1} \quad (\Sigma 1) \quad K' = 843 \quad (\Sigma 1.5) \quad \frac{c(\text{glucose 6-phosphate})}{c(\text{glucose})} = 7587 \quad (\Sigma 1.5)$$

5.4 a) Mass of ATP produced per day: (2 points)

$$\text{Energy available for ATP synthesis: } 8000 \text{ kJ day}^{-1} \cdot 0.5 = 4000 \text{ kJ day}^{-1} \quad (0.5)$$

$$\text{Energy required for synthesis of ATP: } 52 \text{ kJ mol}^{-1}$$

$$\text{Amount of ATP produced: } 4000 \text{ kJ day}^{-1} / 52 \text{ kJ mol}^{-1} = 76.9 \text{ mol day}^{-1} \quad (0.5)$$

$$\text{Mass of ATP produced: } 76.9 \text{ mol day}^{-1} \cdot 503 \text{ g mol}^{-1} = 38700 \text{ g day}^{-1} = 38.7 \text{ kg day}^{-1} \quad (1)$$

$$m_{\text{day-1}} = 38.7 \text{ kg day}^{-1}$$

5.4 b) Mass of ATP in the human body: (1 points)

$$\text{Average lifetime: } 1 \text{ day} = 1440 \text{ min} \quad 1 \text{ min} = 1440^{-1} \text{ day} \quad (0.5)$$

$$\text{Mass of ATP in the body: } 38.7 \text{ kg day}^{-1} / (1440 \text{ min day}^{-1}) \cdot 1 \text{ min} = 26.9 \text{ g} \quad (0.5)$$

$$m_{\text{body}} = 26.9 \text{ g}$$

5.4 c) What happens to the rest of the free energy? Mark one correct answer: (2 points)

It is used to reduce the entropy of the body. ☐

It is released from the body in the O-H bonds of the water molecule and the C=O bonds of the carbon dioxide molecule. ☐

It is used to regenerate the state of the enzymes which act as catalysts in the production of ATP. ☐

It heats the body of the person. ☒

5₃

Name: _____

Student code: _____

5₃**5.5 a) How many protons are in a spherical mitochondrion with a diameter of 1 μm at pH=7?****(2 points)**

$$\begin{aligned}
 V &= 4/3 \pi r^3 \\
 &= 4/3 \pi (0.5 \cdot 10^{-6} \text{ m})^3 \\
 &= 5.2 \cdot 10^{-19} \text{ m}^3 &= 5.2 \cdot 10^{-16} \text{ L} & (0.5) \\
 c &= 10^{-7} \text{ mol L}^{-1} & (0.5) \\
 n &= V \cdot c \cdot N_A & (0.5) \\
 &= 5.2 \cdot 10^{-16} \text{ L} \cdot 10^{-7} \text{ mol L}^{-1} \cdot 6.022 \cdot 10^{23} \text{ mol}^{-1} = 31 & (0.5)
 \end{aligned}$$

$$n = 31$$

5.5 b) How many protons have to enter a mitochondrion?**(2 points)**

Number of ATP molecules:

$$n(\text{ATP}) = \frac{m(\text{ATP}) \cdot N_A}{M(\text{ATP})} = \frac{0.2 \cdot 10^{-15} \text{ g} \cdot 6.022 \cdot 10^{23} \text{ mol}^{-1}}{503 \text{ g mol}^{-1}} = 239400 \quad (1)$$

$$\text{Number of } H^+ \text{ per cell} \quad n(H^+_{\text{per cell}}) = n(\text{ATP}) \cdot 3 = 718300 \quad (0.5)$$

$$\text{Number of } H^+ \text{ per mitochondrion: } n(H^+_{\text{mit}}) = n(H^+_{\text{per cell}}) / 1000 = 718 \quad (0.5)$$

$$n(H^+_{\text{mit}}) = 718$$

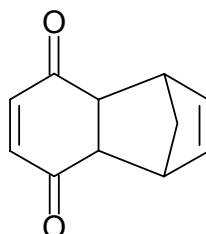
6₁

Name: _____

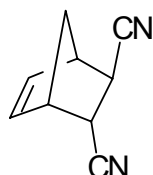
Student code: _____

6₁**6.1 Structure of A only:****(2 points)**

[A]:

**6.2 Structures of D1, D2 only:****(2 points)**

D1:

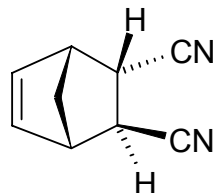
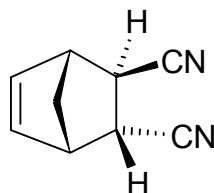


(1)

D2:

(1)

alternatively, the following structures are also correct:

*Note: The two compounds are enantiomers***6.3 Correct structure of B (circle only one):****(4 points)**

1

☒

3

4

5

6

Notes: The Diels-Alder reaction gives products with an endo-stereochemistry. The preference of this configuration was outlined in problem 6.2, structure C. As shown in structure C this endo-configuration is characterized by the two H atoms and the CH₂-bridge of the bicyclic system being on the same side of the ring. Only structures 1 and 2 of the six stereoisomers have an endo,endo stereochemistry. All other isomers have at least one exo configuration. In structure 1 the three rings form a U-shaped molecule which is sterically more hindered than structure 2 which has a zig-zag structure.

2 points are given for answer 1.

6₂

Name: _____

Student code: _____

6₂

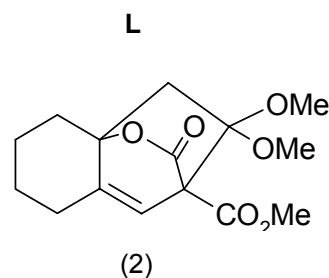
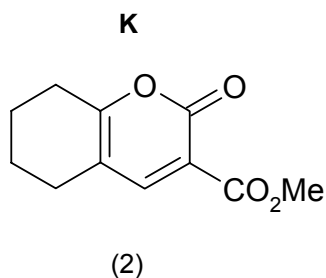
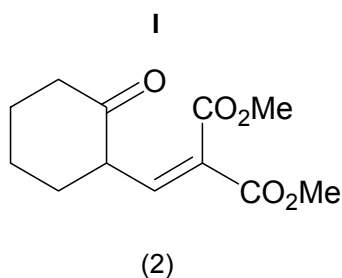
6.4 Decide the questions concerning the Diels-Alder reaction.

(6 points)

	true	false	no decision possible
The Diels-Alder reaction is reversible	x	<input type="checkbox"/>	<input type="checkbox"/>
The formation of B in the original reaction is thermodynamically controlled	<input type="checkbox"/>	x	<input type="checkbox"/>
B is thermodynamically more stable than E	<input type="checkbox"/>	x	<input type="checkbox"/>
E is thermodynamically less stable than F	x	<input type="checkbox"/>	<input type="checkbox"/>
G is an enantiomer of B	<input type="checkbox"/>	x	<input type="checkbox"/>
G is thermodynamically more stable than F	<input type="checkbox"/>	<input type="checkbox"/>	x

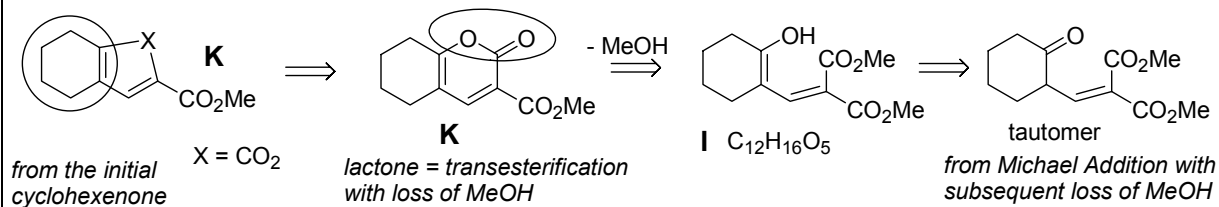
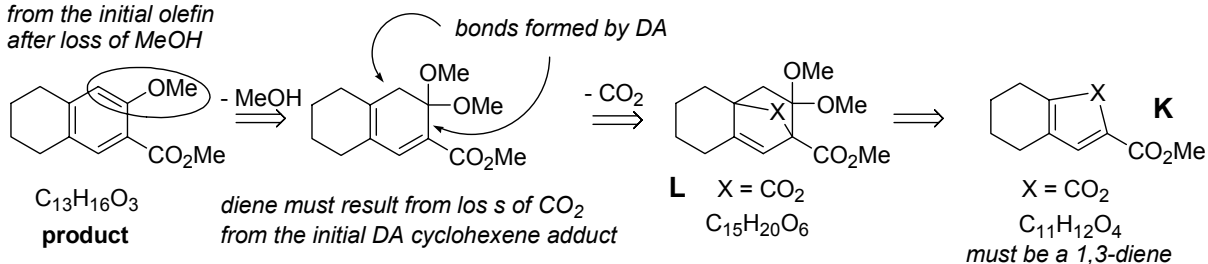
6.5 Structures of I, K, L only:

(6 points)



Notes:

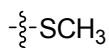
from the initial olefin
after loss of MeOH



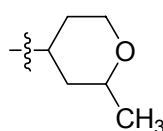
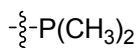
7₁

Name: _____

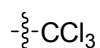
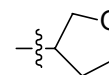
Student code: _____

7₁**7.1 Fill in < or > (A < B means A has a priority lower than B) :****(3 points)**

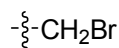
>



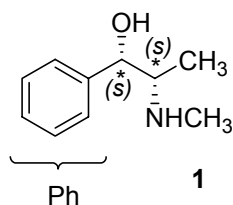
<



<



1 point each

7.2**(4 points)**

* : 0.25 points each
 S: 0.75 points each
 Σ: 2 points

highest priority

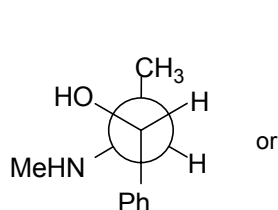
lowest priority

OH	CH(NHCH ₃)CH ₃	Ph	H
NHCH ₃	CH(OH)Ph	CH ₃	H

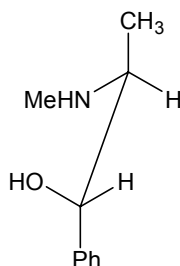
(1)

(1)

(Penalty: each wrongly indicated stereocenter, minus 0.5 point)

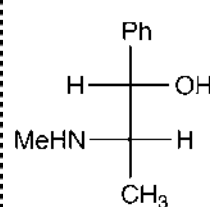
7.3 Newman projection or sawhorse projection of 1:**Fischer projection of 1:**

or

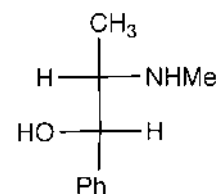
(Me = CH₃)

0.5 points for each correct stereocenter.

(1 point)



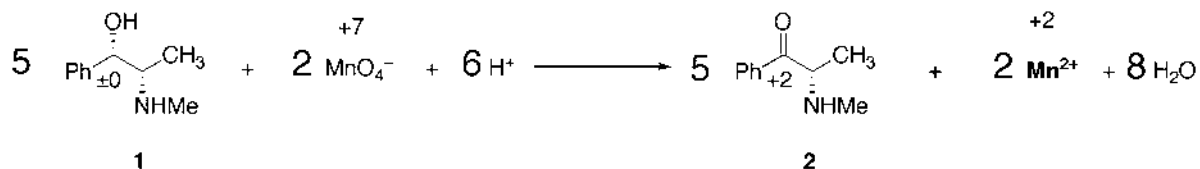
or

(Me = CH₃)

1 point for each correct stereocenter. Any projection which shows the correct stereocenter is accepted.

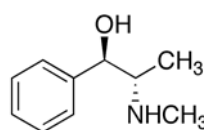
(2 points)

7.4 Equation with oxidation numbers and stereochemically correct structure of 2: (4 points)



1 point for structure 2, 1 point for stoichiometry, 2 points for oxidation numbers (0.5 points for each)

7.5a) Structure of 3 (correct stereochemistry): (2 points)



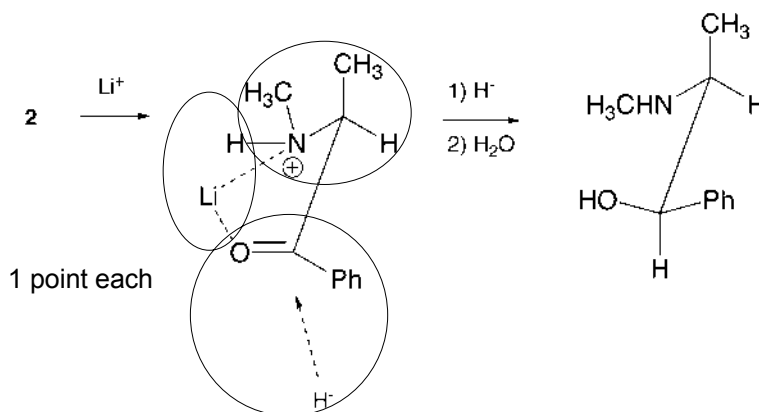
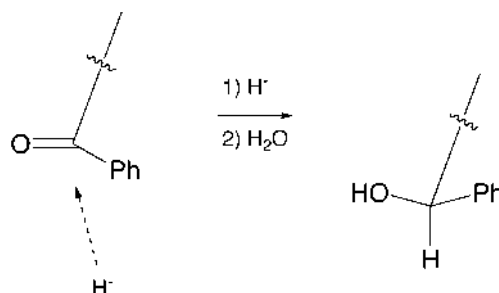
1 point for correct formula, 1 point for correct stereochemistry

7.5b) Statements concerning isomers: (2 points)

	true	false
1 and 3 are stereo-isomers	x	<input type="checkbox"/>
1 and 3 are enantiomers	<input type="checkbox"/>	x
1 and 3 are diastereomers	x	<input type="checkbox"/>
1 and 3 are conformational isomers	<input type="checkbox"/>	x

0.5 points each

7.5c) Draw a structural model to rationalize the exclusive formation of 3 from 2 (3 points)

*Notes: Attack of hydride occurs from the sterically least hindered side.**Full points will also be given for an explanation using the formation of a hydrogen bond.**1 point will be given for any representation indicating the attack of hydride on the correct face of the carbonyl group, i.e.*

8.1 pH of solution B:**(3 points)**

$$K_{b2} = \frac{c(\text{HCO}_3^-)/(1 \text{ mol L}^{-1}) \cdot c(\text{OH}^-)/(1 \text{ mol L}^{-1})}{c(\text{CO}_3^{2-})/(1 \text{ mol L}^{-1})} \quad (1) \quad K_{b2} = \frac{10^{-14}}{10^{-10.33}}$$

$$K_{b2} = 2.14 \cdot 10^{-4}$$

$$K_{b1} = 2.34 \cdot 10^{-8}$$

Since $K_{b2} \gg K_{b1}$, only one protonation step of the CO_3^{2-} has to be considered.

$$\begin{aligned} c(\text{HCO}_3^-) = c(\text{OH}^-) = x & \quad \text{and} \quad c(\text{CO}_3^{2-}) = c_0(\text{CO}_3^{2-}) - x \\ c_0(\text{Na}_2\text{CO}_3) = \frac{1.700 \text{ g L}^{-1}}{105.99 \text{ g mol}^{-1}} & \quad c_0(\text{Na}_2\text{CO}_3) = c_0(\text{CO}_3^{2-}) = 0.016 \text{ mol L}^{-1} \quad (0.5) \end{aligned}$$

$$K_{b2} = \frac{x^2/(1 \text{ mol L}^{-1})}{(c_0(\text{CO}_3^{2-}) - x)} \quad (1) \quad x = c(\text{OH}^-) = 1.75 \cdot 10^{-3} \text{ mol L}^{-1}$$

Solving equation: 0.5 points

pH = 11.2

8.2 Ca(OH)₂, CaCO₃ in the precipitate?**(6 points)**

$$M(\text{CaCl}_2) = 110.98 \text{ g mol}^{-1} \quad \text{pH} = 10, c(\text{OH}^-) = 10^{-4} \text{ mol L}^{-1} \quad (0.5)$$

$$c_0(\text{Na}_2\text{CO}_3) = \frac{1.700 \text{ g L}^{-1}}{105.99 \text{ g mol}^{-1} \cdot 2} \quad c(\text{CaCl}_2) = \frac{1.780 \text{ g L}^{-1}}{110.98 \text{ g mol}^{-1} \cdot 2}$$

$$c_0(\text{Na}_2\text{CO}_3) = 8.0 \cdot 10^{-3} \text{ mol L}^{-1} \quad (0.5) \quad c(\text{CaCl}_2) = c_0(\text{Ca}^{2+}) = 8.0 \cdot 10^{-3} \text{ mol L}^{-1} \quad (0.5)$$

Calculations for Ca(OH)₂:

$$c(\text{OH}^-)^2 \cdot c_0(\text{Ca}^{2+}) = 8 \cdot 10^{-11} \text{ mol}^3 \text{ L}^{-3} < 6.46 \cdot 10^{-6} \text{ mol}^3 \text{ L}^{-3} = K_{sp}(\text{Ca(OH)}_2) \quad \text{no precipitate}$$

(1) (0.5)

Calculations for CaCO₃:
(regarding proteolysis: 1 point)

$$K_{b2} = \frac{c(\text{HCO}_3^-) \cdot c(\text{OH}^-)}{c(\text{CO}_3^{2-})}, \quad c(\text{HCO}_3^-) = \frac{K_{b2}}{c(\text{OH}^-)} \cdot c(\text{CO}_3^{2-})$$

$$c(\text{HCO}_3^-) = 2.14 \cdot c(\text{CO}_3^{2-}) \quad \text{and} \quad c(\text{HCO}_3^-) + c(\text{CO}_3^{2-}) = c_0(\text{Na}_2\text{CO}_3)$$

$$2.14 \cdot c(\text{CO}_3^{2-}) + c(\text{CO}_3^{2-}) = 8.0 \cdot 10^{-3} \text{ mol L}^{-1} \quad (1)$$

$$\text{Initial concentration of } \text{CO}_3^{2-} \text{ in solution C: } c(\text{CO}_3^{2-}) = 2.55 \cdot 10^{-3} \text{ mol L}^{-1} \quad (0.5)$$

$$\text{Initial concentration of } \text{Ca}^{2+} \text{ in solution C: } c(\text{Ca}^{2+}) = 8.0 \cdot 10^{-3} \text{ mol L}^{-1}$$

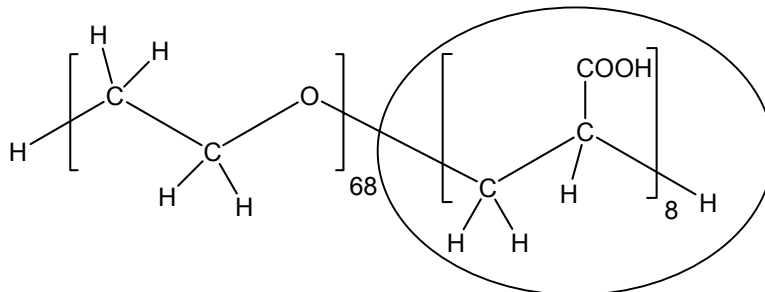
$$\text{hence } c(\text{CO}_3^{2-}) \cdot c(\text{Ca}^{2+}) = 2.04 \cdot 10^{-5} \text{ mol}^2 \text{ L}^{-2} > 3.31 \cdot 10^{-9} \text{ mol}^2 \text{ L}^{-2} = K_{sp}(\text{CaCO}_3) \quad \text{precipitate}$$

(0.5)

Ca(OH)₂ will be found in the precipitate **yes** ☐ **no** ☒
CaCO₃ will be found in the precipitate **yes** ☒ **no** ☐

8.3 Circle the block that attaches to the CaCO₃ crystal:

(1 point)



Notes: Both polymer blocks are hydrophilic. The acrylic acid block will preferably bind to the crystal since it is more polarized and additionally charged. The polymer binds to the surface at positions where there is an excess of calcium ions on the surface of the ionic crystal.

8.4 How much of the initial amount of polymer (2 g) can still be found in the hybrid particles?

(7 points)

pH and pK_a lead to the total concentration of COOH groups in the solution: (1)

$$c(\text{COO}^-) = x \quad c(\text{COOH}) = c_0(\text{COOH}) - x \quad x = c_0(\text{OH}^-) - c(\text{OH}^-) \quad (1)$$

$$c_0(\text{OH}^-) = \frac{50 \text{ mL}}{250 \text{ mL}} \cdot 0.19 \text{ mol L}^{-1} \quad c_0(\text{OH}^-) = 0.038 \text{ mol L}^{-1}$$

$$c(\text{OH}^-) = 10^{-1.7} \text{ mol L}^{-1} = 0.02 \text{ mol L}^{-1} \quad (0.5) \quad x = 0.018 \text{ mol L}^{-1} \quad (0.5)$$

$$K_b = \frac{(c_0(\text{COOH}) - x) / (1 \text{ mol L}^{-1}) \cdot c(\text{OH}^-) / (1 \text{ mol L}^{-1})}{x / (1 \text{ mol L}^{-1})}$$

$$c_0(\text{COOH}) = \frac{K_b x \cdot (1 \text{ mol L}^{-1})}{c(\text{OH}^-)} + x \quad (1) \quad c_0(\text{COOH}) = \left(\frac{0.018 \cdot 10^{-9.12}}{0.02} + 0.018 \right) \text{ mol L}^{-1}$$

$$c_0(\text{COOH}) = 0.018 \text{ mol L}^{-1}$$

$$(\text{Or as } \text{pH} \gg \text{p}K_a: \quad c_0(\text{COOH}) = c(\text{COOH}) + x \approx x)$$

(calculate polymer mass from c₀(COOH): 0.5 point)

$$\text{Total concentration of polymer chains} \quad c(\text{polymer}) = \frac{c_0(\text{COOH})}{8} \quad (0.5)$$

$$M(\text{polymer}) = M(\text{C}_{160}\text{O}_{84}\text{H}_{306}) = 3574.66 \text{ g mol}^{-1} \quad (0.5) \quad (0.5)$$

$$m(\text{polymer}) = c(\text{polymer}) \cdot V \cdot M(\text{polymer}) \quad (0.5)$$

$$m(\text{polymer}) = \frac{c_0(\text{COOH}) \cdot V \cdot M(\text{polymer})}{8} = \frac{0.018 \cdot 0.250 \cdot 3574.66}{8} \text{ g} = 2.0 \text{ g} \quad (0.5)$$

8₃

Name: _____

Student code: _____

8₃**8.5 Modification of CaCO₃:****(5 points)**

The charge of the particles is caused by the number of protolized COOH groups per particle.

$$c(\text{COO}^-) \approx c_0(\text{COOH}), \alpha \approx 1$$

Number of COOH groups per particle: $N_{\text{COOH}} = \frac{|Z|}{\alpha} \quad N_{\text{COOH}} = 800 \quad (1)$

Number of polymer chains per particle: $N_{\text{polymer}} = \frac{N_{\text{COOH}}}{8} = 100 \quad (1)$

The number of polymers per particle indicates the mass of polymer per particle. Thus, the mass of the calcium carbonate particle can be calculated:

$$M(\text{CaCO}_3 \text{ particle}) = M(\text{total particle}) - N_{\text{polymer}} \cdot M(\text{polymer}) \quad (1)$$

$$M(\text{CaCO}_3 \text{ particle}) = 8.01 \cdot 10^8 \text{ g mol}^{-1} - 100 \cdot 3574.66 \text{ g mol}^{-1}$$

$$M(\text{CaCO}_3 \text{ particle}) = 8.01 \cdot 10^8 \text{ g mol}^{-1}$$

Mass of one CaCO₃ particle: $m(\text{CaCO}_3 \text{ particle}) = M(\text{CaCO}_3 \text{ particle}) \cdot N_A^{-1} \quad (0.5)$

and with the volume of the spherical particle ($V = \frac{4}{3} \cdot \pi \cdot r^3$) the density can be calculated:

$$\rho(\text{CaCO}_3) = \frac{m(\text{CaCO}_3 \text{ particle})}{V(\text{CaCO}_3 \text{ particle})} = \frac{3 \cdot m(\text{CaCO}_3 \text{ particle})}{4\pi \cdot r^3} \quad (1)$$

$$= \frac{3(M(\text{total particle}) - N_{\text{polymer}} \cdot M(\text{polymer}))}{N_A \cdot 4\pi \cdot r^3}$$

$$= \frac{3 \cdot 8.01 \cdot 10^8 \text{ g mol}^{-1}}{N_A \cdot 4\pi (5 \cdot 10^{-6} \text{ cm})^3} = 2.54 \text{ g cm}^{-3} \quad (0.5)$$

The modification of calcium carbonate is Calcite ☐ Vaterite ☒ Aragonite ☐

36th IChO Practical Problems

- **safety rules** follow them as in the preparatory problems described, in particular you have to wear safety goggles all the time, no eating or drinking is allowed in the lab.
- **violating safety rules** you get one warning, offend again: you are out.
- **problem booklet** 12 pages with 2 problems. Start with problem 1 and continue until a hint is given to start problem 2.
- **time** 5 hours, 30 minutes warning before the end.
- **answer sheets:** 3 pages
- **your name and student code** write it on **every** answer sheet.
- **answers** only in the appropriate boxes of the answer sheets, nothing else will be marked. Relevant calculations have to be shown.
- **use only the pen and calculator provided**
- **results** the number of significant figures in numerical answers must conform to the rules of evaluation of experimental error. Mistakes will result in penalty points even if your experimental technique is flawless.
- **burette** read it as accurately as possible.
- **more chemicals** of Na₂EDTA, Na₂S₂O₃, superconductor solution, superconductor solid, polycarbonate or bisphenol A needed? Ask the instructor. You get a penalty of -5 points only for each of these extra chemicals.
- **questions** concerning safety, apparatus, chemicals, organisation, toilet break: **ask your instructor.**
- **chemical waste** only in the designated containers.
- **official English-language version** **available** on request **for clarification only.** Ask the instructor.
- **after the stop signal** put your answer sheets in the envelope (don't seal), deliver them at the appropriate instructor room. Keep the problem booklet together with the pen and calculator.

You must stop your work immediately after the stop signal has been given. A delay of 5 minutes will result in zero points for the current task.

Periodic table of elements

with atomic masses / u

1 H 1.01																	2 He 4.00
3 Li 6.94	4 Be 9.01											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.88	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	32 Ge 72.61	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc 98.91	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.90	54 Xe 131.29
55 Cs 132.91	56 Ba 137.3	57-71 103	72 Hf 178.49	73 Ta 180.95	74 W 183.84	75 Re 186.21	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.19	83 Bi 208.98	84 Po 208.98	85 At 209.99	86 Rn 222.02
87 Fr 223	88 Ra 226	89-103	104 Rf 261	105 Db 262	106 Sg 263	107 Bh 264	108 Hs 265	109 Mt 268									
			57 La 138.91	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm 144.92	62 Sm 150.36	63 Eu 151.96	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97
			89 Ac 227	90 Th 232	91 Pa 231	92 U 238	93 Np 237	94 Pu 244	95 Am 243	96 Cm 247	97 Bk 247	98 Cf 251	99 Es 252	100 Fm 257	101 Md 258	102 No 259	103 Lr 262

Apparatus

During the practical examination some of your glassware will have to be used more than once. Clean it carefully.

The hoods and the equipment within will also be used by several students. The numbers of your hood and of your instructor room is written on your bench.

apparatus

2 beakers (100 mL)
1 beaker (weighed, labelled "beaker A")
1 beaker (weighed, labelled "beaker B")
1 beaker (400 mL)
1 pair of "rubber fingers" for handling hot beakers
1 bottle with dem. water (500 mL)
2 brackets for condenser and flask
1 bracket for the burette with sleeve
1 burette (25 mL)
1 suction filter (90 mm)
1 condenser (NS 29)
1 Erlenmeyer flask (100 mL, NS 29)
4 Erlenmeyer flask (300 mL)
1 g fibreglass
6 filter papers for problem 1
6 filter papers for problem 2
1 filter rack
2 folded filter papers for problem 1
1 funnel for analysis $\varnothing = 80$ mm
1 funnel for liquids $\varnothing = 100$ mm
1 funnel for powder $\varnothing = 80$ mm
1 funnel for the burette
2 glass rods 15 cm
1 glass rod 21 cm
1 graduated cylinder (10 mL)
1 graduated cylinder (100 mL)

apparatus

1 heating plate with magnetic stirrer
1 magnetic stirring bar
3 melting-point tubes in a test tube (labelled "tube B")
1 measure for melting point tubes
1 Pasteur pipette (2 mL, grad.) with ball
1 Peleus ball
1 pipette (25 mL)
1 plastic plug (NS 29)
1 glass-ceramics (Ceran™) plate
1 pair of protective glasses
1 role of pH paper
2 shards (2.5 cm x 2.5 cm)
2 sleeves for the brackets
1 spatula
1 micro spatula
2 stands
1 suction bottle (500 mL) with ring
1 Teflon coupling (NS 29)
4 test tubes
1 test-tube rack
1 volumetric flask (100 mL)
1 volumetric flask (250 mL)
75 cm glass tube
1 pair of tweezers
1 wiper
1 test-tube brush

Chemicals for each student

No	chemicals	formula	conc.	amount	R phrases	S phrases
1	polycarbonate (Makrolon)	-	solid	2.54 g	-	-
2	ethanol	C ₂ H ₅ OH	96 %	150 mL	11	7-16
3	hydrochloric acid	HCl	25 %	60 mL	36/37/38	26
4	sodium chloro acetate	ClCH ₂ COONa	solid	5 g	25-38-50	22-37-45-61
5	sodium hydroxide	NaOH	solid	4 g	35	26-37/39-45
6	sodium-hydroxide solution	NaOH	10%	100 mL	35	26-36/37/39-45
7	disodium-EDTA solution	Na ₂ -EDTA	0.1000 mol L ⁻¹	100 mL	22-36/37/38	26-36
8	sodium acetate	CH ₃ COONa	solid	10 g	-	-
9	sodium-iodide solution	NaI	10 %	80 mL	-	22-24/25 *
10	sodium-thiosulfate solution	Na ₂ S ₂ O ₃	0.01000 mol L ⁻¹	100 mL	-	-

11	starch solution	-	-	20 mL	-	-
12	sulfuric acid	H ₂ SO ₄	2 mol L ⁻¹	50 mL	35	26-30-45
13	superconductor solution	La _x M _(2-x) CuO ₄	-	-	22 ¹⁾	22-24/25 ¹⁾
14	superconductor solid	La _x M _(2-x) CuO ₄	solid	250 mg	22	22-24/25
15	xylene orange indicator	-	solid	500 mg	8	16-41
27	bisphenol A ²⁾	C ₁₅ H ₁₆ O ₂	solid		36/37/38-43	24-26-37
28	bisphenol A ³⁾	C ₁₅ H ₁₆ O ₂	solid		36/37/38-43	24-26-37

¹⁾ for the solid compound

²⁾ will be handed out by the instructor on request during problem 1

³⁾ will be handed out after the first step of problem 1 in the appropriate instructor room

Chemicals that have to be used in common (to be found in the hoods)

No	chemicals	formula	conc.		R phrases	S phrases
16	acetic acid	CH ₃ COOH	2 mol L ⁻¹		10-35	23.2-26-45
17	ammonia solution	NH ₃ (aq)	25 %		34-50	26-36/37/39-45-61
18	ammonium-carbonate solution	(NH ₄) ₂ CO ₃	2 mol L ⁻¹		36/37/38 *	26-37/39 *
19	ammonium-oxalate solution	(NH ₄) ₂ C ₂ O ₄	0.25 mol L ⁻¹		21/22 *	24/25 *
20	ammonium-sulfate solution	(NH ₄) ₂ SO ₄	1 mol L ⁻¹		-	-
21	calcium-sulfate solution	CaSO ₄	satur.		-	-
22	perchloric acid	HClO ₄	10 %		34	23-26-36-45
23	potassium-dichromate solution	K ₂ Cr ₂ O ₇	0.05 mol L ⁻¹		43	24-37-45-60

* for the solid compound

Chemicals to perform a blank test which can be obtained from the instructor:

No	chemicals	formula	conc.		R phrases	S phrases
24	barium-chloride dihydrate	BaCl ₂ · 2 H ₂ O	solid		20-25	45
25	calcium-chloride hexahydrate	CaCl ₂ · 6 H ₂ O	solid		36	22-24
26	strontium-chloride hexahydrate	SrCl ₂ · 6 H ₂ O	solid		-	22-24/25

Risk phrases (R)

R 8	Contact with combustible material may cause fire.
R 10	Flammable.
R 11	Highly flammable.
R 20	Harmful by inhalation.
R 22	Harmful if swallowed.
R 25	Toxic if swallowed.
R 34	Causes burns.
R 35	Causes severe burns.
R 36	Irritating to eyes.
R 37	Irritating to respiratory system.
R 38	Irritating to skin.
R 43	May cause sensitization by skin contact.
R 50	Very toxic to aquatic organisms.

Combination of risk phrases

R 21/22	Harmful in contact with skin and if swallowed.
R 36/37/38	Irritating to eyes, respiratory system and skin.

Safety phrases (S)

S 7	Keep container tightly closed.
S 16	Keep away from sources of ignition - No smoking.
S 22	Do not breathe dust.
S 23	Do not breathe gas/fumes/vapour/spray (appropriate wording to be specified by the manufacturer).
S 23.2	Do not breathe vapour.
S 24	Avoid contact with skin.
S 26	In case of contact with eyes, rinse immediately with plenty of water and seek medical advice.
S 30	Never add water to this product.
S 36	Wear suitable protective clothing.
S 37	Wear suitable gloves.
S 41	In case of fire and/or explosion do not breathe fumes.
S 45	In case of accident or if you feel unwell, seek medical advice immediately (show the label where possible).
S 60	This material and its container must be disposed of as hazardous waste.
S 61	Avoid release to the environment. Refer to special instructions / Safety data sheets.

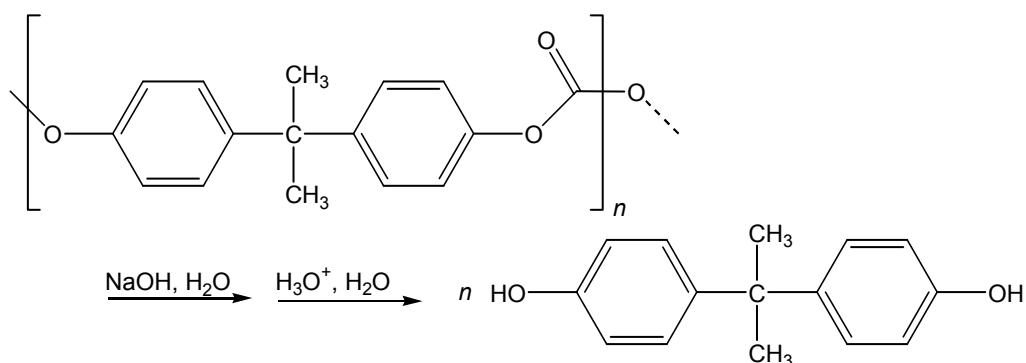
Combination of safety phrases (S)

S 24/25	Avoid contact with skin and eyes.
S 36/37/39	Wear suitable protective clothing, gloves and eye/face protection.
S 37/39	Wear suitable gloves and eye/face protection.

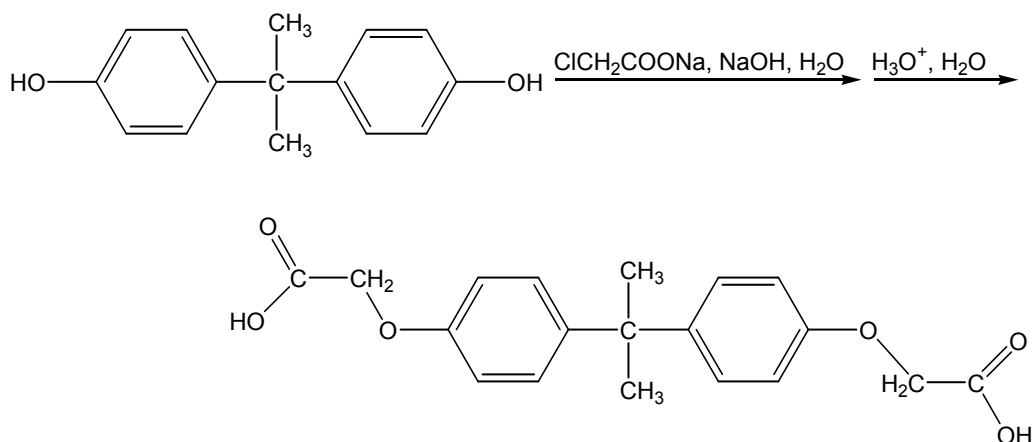
1. Two-Step Organic Synthesis of 2,2-Bis(*p*-phenyleneoxyacetic acid)propane (Bisphenol A bis(carboxymethyl)ether) (100 points)

Introduction

In the first step the sodium salt of bisphenol A results as an intermediate from the alkaline hydrolysis of a polycarbonate. By adding an acid this salt is converted into the free 2,2-bis(4-hydroxyphenyl)propane (bisphenol A).



In the second step bisphenol A reacts with sodium chloroacetate to form the phenolic ether, bisphenol A bis(carboxymethyl)ether.



- In each step the product has to be isolated.
(Drying and weighing will be done by the organizer.)
- For the product of step 2 three melting point tubes have to be filled.
(Filling of the melting point tubes in step 1 will be done by the organizer.)
(The melting points will be determined by the organizer.)
- When the organizer receives your labelled beaker A of step 1 you will get 2.00 g of bisphenol A as starting material for the second step.
- Answer the additional questions on the answer sheet **P1**.
- Do not remove the Ceran plate from the magnetic stirrer.

Procedures

Step 1 Preparation of bisphenol A by alkaline hydrolysis of a polycarbonate

Preparation:

- Put the pre-weighed 2.54 g of polycarbonate (No. 1), 4.0 g of sodium hydroxide (No. 5) and 3 mL of demineralized water into a 100 mL Erlenmeyer flask with ground-glass joint.
- Close the flask with a plastic plug and swirl it gently so that the solution does not contact the ground-glass joint. For aeration open the plastic plug occasionally. Strong heating can be observed, as the sodium hydroxide partially dissolves.
- Remove the plastic plug after swirling for about 4 minutes, add a magnetic stirring bar and put the flask onto a heating plate. Put a reflux condenser above the neck of the flask. Use a Teflon coupling as a connection between flask and condenser. Fix the apparatus tightly to a stand.
- Finally, add 20 mL of ethanol (No. 2) through the condenser while stirring the reaction mixture.
- Heat the reaction mixture under reflux for 60 minutes. In the beginning adjust the thermostat of the heating plate to maximum. When the mixture starts boiling reduce the heat carefully, so that the mixture is kept under gentle reflux.
- A white precipitate is formed on heating.

During this waiting period you are highly advised to start working on the analytical chemistry experiment.

Isolation:

- Stop heating after one hour, allow the reaction mixture to cool down to ambient temperature, remove the condenser, add 25 mL of demineralized water and transfer the reaction mixture into a 400 mL beaker. Rinse the Erlenmeyer flask with 25 mL of demineralized water and add this to the contents of the beaker.
- Finally, fill up to 150 mL with demineralized water.
- If the reaction mixture is not clear, the mixture has to be filtered over fibre glass into an Erlenmeyer flask.
- Add slowly 15 mL of hydrochloric acid (No. 3) stirring the mixture simultaneously with a glass rod. A rather oily or sometimes crystalline precipitate is formed.
- Ask your instructor for some seed crystals of bisphenol A (No. 27) in order to accelerate the crystallization.
- Stir the reaction mixture thoroughly with the glass rod. For a quantitative crystallisation continue stirring from time to time till the supernatant aqueous solution is nearly clear.
- Collect the crude product by vacuum filtration, wash it twice with 10 mL portions of demineralized water and transfer it quantitatively into the tared and labelled beaker A.
- **For drying and weighing deliver your labelled beaker A into the instructor room.**
- Afterwards you will get a small jar filled with 2.00 g of bisphenol A (No. 28), your starting material of the second step.

- On delivery of your product and on receipt of the starting material you have to sign. Even if you do not have any bisphenol A, please bring the empty beaker A to the instructors' room in order to get the starting material for step 2.

Step 2 Reaction of Bisphenol A with Chloroacetic Acid forming 2,2-Bis(*p*-phenyleneoxyacetic acid)propane (Bisphenol A bis(carboxymethyl)ether)

Preparation:

- Pour all the bisphenol A (No. **28**) you have received from the organizer when you had finished step 1 into a 100 mL Erlenmeyer flask with ground-glass joint.
- Add 10 mL of an aqueous sodium-hydroxide solution (No. **6**), 1 mL of demineralized water and a magnetic stirring bar.
- Put the flask onto a heating plate. Put a reflux condenser above the neck of the flask. Use a Teflon coupling as a connection between flask and condenser. Fix the apparatus tightly to a stand.
- Heat the reaction mixture with gentle stirring until a clear solution is formed.
- Remove the heating plate and the condenser and add 5.0 g of the sodium salt of chloroacetic acid (No. **4**) to the reaction mixture.
- After reconnecting the flask with the reflux condenser, heat the mixture to reflux with vigorous stirring for 30 min.
- Initially a clear solution is formed on heating. In some cases a colorless solid precipitates. If the complete mixture becomes solid in the course of the reaction, heating **must** be stopped.
- After that, 50 mL of ethanol (No. **2**) are added carefully through the condenser (beware of sudden boiling!). The mixture is stirred and heated under reflux for 5 minutes. A colourless solid precipitates, or the crystallisation which has already started is completed.

Isolation:

- After leaving it to cool down for 5 minutes, transfer the reaction mixture with another 50 mL of ethanol (No. **2**) quantitatively to a beaker. The reaction mixture should be stirred vigorously.
- The magnetic stirring bar is removed and the reaction mixture is filtered through a suction filter. Solids which separate in the filtrate are rejected. Rinse the beaker with 10 mL of ethanol (No. **2**). The precipitate is washed twice with 10 mL portions of ethanol (No. **2**). (The filtrate must be disposed of in the organic solvent waste!)
- Transfer the precipitate quantitatively into a beaker, add a stirring bar and dissolve it in 150 mL of demineralized water. The mixture must be stirred vigorously. Larger lumps of the solid must be crushed with the spatula.
- If the solution is not clear, it has to be filtered over a folded filter paper into an Erlenmeyer flask.

- The slow addition of 5 mL of hydrochloric acid (No. 3) to the stirred reaction mixture results in the formation of a white precipitate.
- Collect the crude product by vacuum filtration, wash it twice with 10 mL portions of demineralized water and transfer it quantitatively into the tared and labelled beaker B.
- Take a small sample of the product with a micro spatula, crush it and dry it on a shard. Fill three melting point tubes with the homogenized, dried sample. For a close-packed and 5 mm high filling use the 75 cm glass tube and the measure.
- **Put all three melting point tubes into the test tube B, which is labelled with your student code, and give it together with your labelled beaker B with the product to the instructor. On delivery you have to sign.**

2. Qualitative and Quantitative Analysis of a Superconductor (113 points)

Introduction

Superconductors based on lanthanum cuprate (La_2CuO_4) have the general composition of $\text{La}_x\text{M}_{(2-x)}\text{CuO}_4$ ($\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$).

This problem consists of two parts:

- the qualitative determination of the alkaline earth metal(s)
- the quantitative determination of lanthanum and copper.

Read the burette as accurately as possible. Report your results on the answer sheets.
Answer the additional questions and write the results with adequate accuracy.
The qualitative and quantitative parts of this experiment may be done in any order.

Procedures

2.1 Qualitative determination of the alkaline earth metal(s) (If the hood is occupied start with the titration 2.2)

In this experiment you have to use the superconductor as a solid ($\text{La}_x\text{M}_{(2-x)}\text{CuO}_4$; No. **14**).
At the beginning, lanthanum has to be separated as an insoluble residue.

All steps must be carried out in the hood!

Dissolve the complete sample in a beaker in about 5 mL of perchloric acid (No. **22**) by heating the mixture. Add 5 mL of demineralized water afterwards.
Cool down the solution until it is lukewarm.

Add about 5 mL of demineralized water and then ammonia solution (No. **17**), until the reaction mixture shows a basic reaction. Lanthanum precipitates as hydroxide and copper forms an intense blue-coloured tetraammine complex. The precipitate is filtered off and washed with a small amount of demineralized water.

An excess of ammonium-carbonate solution (No. **18**) is added to the filtrate and the mixture is being boiled for some minutes. The alkaline earth metal(s) will precipitate as carbonate(s). The precipitate is filtered off and washed a few times with a small amount of demineralized water.

Then, the precipitate is dissolved in acetic acid (No. **16**). Add sodium acetate (No. **9**) and an excess of potassium-dichromate solution (No. **23**). In the presence of barium, yellow BaCrO_4 precipitates. After boiling the mixture for one minute barium chromate is filtered off and washed with demineralized water.
(If there is no barium chromate precipitation, proceed in a way as if there were precipitation.)

Ammonia solution (No. **17**) is added to the clear filtrate until it is basic. Add an excess of ammonium-carbonate solution (No. **18**) and boil the mixture for some minutes. In the presence of strontium and/or calcium, white carbonate(s) precipitate(s).

The precipitate is filtered off and washed a few times with demineralized water.

Then it is dissolved in a mixture of about 2 mL of demineralized water and a few drops of hydrochloric acid (No. 3). This solution is divided between two test tubes:

- Saturated calcium-sulfate solution (No. 21) is added to one of the test tubes. In the presence of strontium a small amount of white strontium sulfate precipitates. To accelerate the precipitation, you can grind the inner surface of the test tube with a glass rod for a few minutes.
- Ammonium-sulfate solution (No. 20) is added to the second test tube. In the presence of strontium and/or calcium, white sulfate(s) precipitate(s). The precipitate is filtered off and washed with a very small amount of demineralized water.
1 mL of ammonium-oxalate solution (No. 19) is added to the filtrate. In the presence of calcium, white calcium oxalate precipitates after a few minutes.

Preparation of the superconductor parent solution

There is a superconductor solution ($\text{La}_x\text{M}_{(2-x)}\text{CuO}_4$ in perchloric acid; No. 13) in a volumetric flask.

Fill it up with demineralized water to a volume of 250.0 mL. From now on this solution is called "parent solution".

2.2 Quantitative determination of the total content of lanthanum and copper

Transfer 25.00 mL of the parent solution into an Erlenmeyer flask.

Add about 5-6 piled spatula of sodium acetate (CH_3COONa ; No. 8) and 2 micro spatula of xylenol orange indicator (No. 15) to this solution and make up with demineralized water to a volume of about 75 mL.

The pH-value has to be about **pH 6** before the determination, otherwise add more sodium acetate.

Titrate the solution with $\text{Na}_2\text{-EDTA}$ solution (No. 7). The color of the solution changes from light violet to intensely light-green. (In between, the color changes a few times.)

Repeat this procedure as many times as necessary.

2.3 Quantitative determination of the copper content

Transfer 25.00 mL of your parent solution (No. 13) into the 100 mL volumetric flask and fill up with demineralized water to a volume of 100.0 mL.

For each titration, transfer 25.00 mL of this solution into an Erlenmeyer flask and add sodium hydroxide solution (No. 6), until the solution shows an alkaline reaction. During this procedure, a blue precipitate forms. Add sulfuric acid (No. 12) until the blue precipitate dissolves. The solution has to be acidic (**pH 1-2**) and will contain a small amount of a white precipitate.

Add 10 mL of sodium-iodide solution (No. 9), and swirl the Erlenmeyer flask for about 1 minute. Titrate the solution with sodium-thiosulfate solution (No. 10). Add some starch

solution (No. **11**) as an indicator just before the end of the titration. At the end, the solution has to be colourless for at least 60 seconds.

Repeat this procedure as many times as necessary.

P1₁

Name: _____

Student code: _____

P1₁

1.1 You started with 2.54 g of polycarbonate. Determine the theoretical yield of bisphenol A in g. (2 points)

$$M_1 (\text{polycarbonate}) = M_1 (\text{C}_{16}\text{H}_{14}\text{O}_3)_n \text{H}_2 \approx M_1 (\text{C}_{16}\text{H}_{14}\text{O}_3) = 254.30 \text{ g/mol}$$

$$m_1 = 2.54 \text{ g}$$

$$M_2 (\text{C}_{15}\text{H}_{16}\text{O}_2) = 228.31 \text{ g/mol}$$

$$m_2 = m_1 \cdot M_1^{-1} \cdot M_2$$

2.28 g**Theoretical yield of bisphenol A:**

exact answer: 2 *points*; incorrect mathematical rounding, more or less than two figures after the decimal point (e.g. 2.3 g, 2.281 g): 1 *point*; wrong or missing answer: 0 *points*.

1.2 Determine your theoretical yield of bisphenol A bis(carboxymethyl)ether in g based on 2.00 g bisphenol A. (2 points)

$$M_2 (\text{C}_{15}\text{H}_{16}\text{O}_2) = 228.31 \text{ g/mol}$$

$$m_2 = 2.00 \text{ g}$$

$$M_3 (\text{C}_{19}\text{H}_{20}\text{O}_6) = 344.39 \text{ g/mol}$$

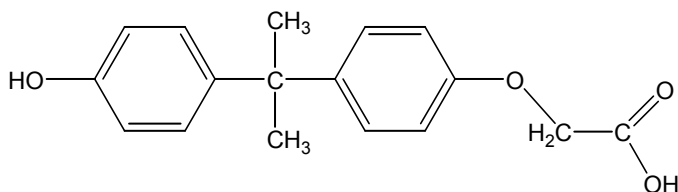
$$m_3 = m_2 \cdot M_2^{-1} \cdot M_3$$

3.02 g**Theoretical yield of bisphenol A bis(carboxymethyl)ether:**

exact answer: 2 *points*; incorrect mathematical rounding, more or less than two figures after the decimal point (e.g. 3.0 g, 3.017 g): 1 *point*; wrong or missing answer: 0 *points*.

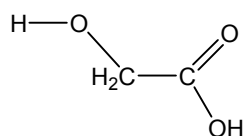
1.3 Unwanted by-products are possible in the second step. Write down the structural formulas of two most probable unwanted by-products. (6 points)

1. Bisphenol A reacts only once with sodium chloroacetate (monosubstitution):



(3)

2. Alkaline hydrolysis of sodium chloroacetate:

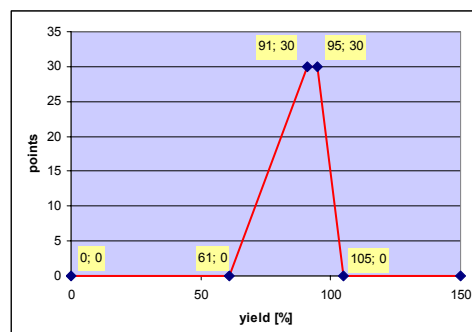


(3)

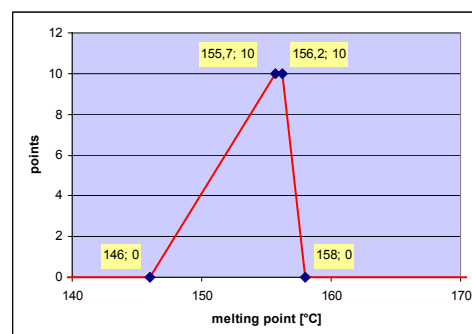
For each of the two answers - exact structural formula: 3 *points*, one careless mistake: 1 *point less*, two careless mistakes: 2 *points less*, wrong or missing answers: 0 *points*.

P1₂**Grading scheme for mentors only****P1₂****1.4 Step 1, yield [%] of the product measured by the organizer: (30.0 points)**

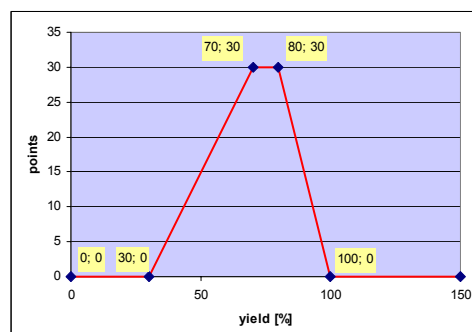
$$\begin{aligned}
 f(x) &= 0 & x < 61 \\
 f(x) &= x - 61 & 61 \leq x \leq 91 \\
 \mathbf{f(x) = 30} & & \mathbf{91 < x \leq 95} & \quad \mathbf{\text{master value}} \\
 f(x) &= -3x + 315 & 95 < x \leq 105 \\
 f(x) &= 0 & x > 105 \\
 m_2 \cdot M_1 \cdot m_1^{-1} \cdot M_2^{-1} \cdot 100 &= x \quad [\%]
 \end{aligned}$$

**1.5 Step 1, melting point [°C] of the product measured by the organizer: (10.0 points)**

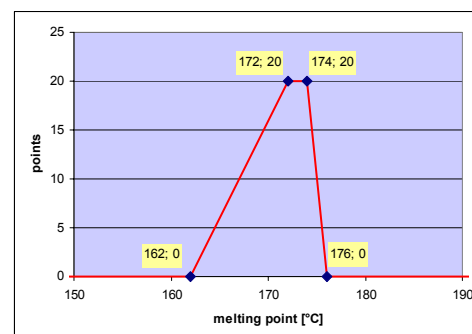
$$\begin{aligned}
 f(x) &= 0 & x < 146.0 \\
 f(x) &= +1.03093x + 150.51546 & 146.0 \leq x < 155.7 \\
 \mathbf{f(x) = 10} & & \mathbf{155.7 \leq x \leq 156.2} & \quad \mathbf{\text{master value}} \\
 f(x) &= -5.55556x + 877.77778 & 156.2 < x \leq 158.0 \\
 f(x) &= 0 & x > 158.0
 \end{aligned}$$

**1.6 Step 2, yield [%] of the product measured by the organizer: (30.0 points)**

$$\begin{aligned}
 f(x) &= 0 & x < 30 \\
 f(x) &= 0.75x - 22.5 & 30 \leq x \leq 70 \\
 \mathbf{f(x) = 30} & & \mathbf{70 < x \leq 80} & \quad \mathbf{\text{master value}} \\
 f(x) &= -1.5x + 150 & 80 < x \leq 100 \\
 f(x) &= 0 & x > 100 \\
 m_3 \cdot M_2 \cdot m_2^{-1} \cdot M_3^{-1} \cdot 100 &= x \quad [\%]
 \end{aligned}$$

**1.7 Step 2, melting point [°C] of the product measured by the organizer: (20.0 points)**

$$\begin{aligned}
 f(x) &= 0 & x < 162 \\
 f(x) &= 2x - 324 & 162 \leq x \leq 172 \\
 \mathbf{f(x) = 20} & & \mathbf{172 < x \leq 174} & \quad \mathbf{\text{master value}} \\
 f(x) &= -10x + 1760 & 174 < x \leq 176 \\
 f(x) &= 0 & x > 176
 \end{aligned}$$



A penalty of 10 points will be given if melting point tubes are not filled by the student.

Accuracy of points for 1.4 – 1.7: rounding value is one digit after the decimal point.

P2₁

Name: _____

Student code: _____

P2₁**2.1 Which alkaline earth metal(s) can be found in the superconductor? Mark only one box! (30)**Ca ☐ (0)Sr ☐ (0)Ba ☒ (30)Ca and Sr ☐ (0)Ca and Ba ☐ (5)Sr and Ba ☐ (15)Ca and Sr and Ba ☐ (10)**Complete the following reaction equations: (2)****2.2 Quantitative determination of the total content of lanthanum and copper. (35)**

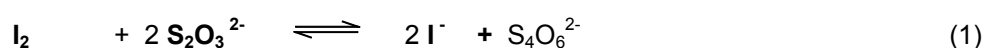
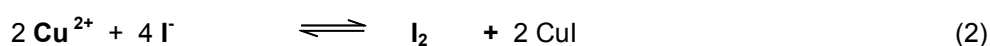
Titration No.	V _{initial} (mL)	V _{final} (mL)	V (mL)
1			
2			
3			
...			
...			
...			

appropriate consumption of 0.1000 mol L⁻¹ EDTA solution V = 11.60*mL
(according to 100 mL of superconductor solution)

2.3 Quantitative determination of the copper content. (35)

Titration No.	V _{initial} (mL)	V _{final} (mL)	V (mL)
1			
2			
3			
...			
...			
...			

appropriate consumption of 0.01000 mol L⁻¹ Na₂S₂O₃ solution V = 10.50* mL
(according to 100 mL of superconductor solution)

Complete the following reaction equations: (3)

* The correct master values will be given to you later,
values with two digits after the decimal point otherwise -1 point

**2.4 Mass (in mg) of copper in your parent solution,
mass (in mg) of lanthanum in your parent solution. (3)**

$$[M(\text{Cu}) = 63.55 \text{ g mol}^{-1}; M(\text{La}) = 138.91 \text{ g mol}^{-1}]$$

Amount of copper:

$$10,50 \text{ mL} \cdot 0.01 \text{ mol L}^{-1} \cdot 4 \cdot 10 \cdot 63.55 \text{ g mol}^{-1} = 266.9 \text{ mg} \quad (1)$$

Amount of lanthanum:

$$[11.60 - (10.50/10 \cdot 4)] \text{ mL} \cdot 0.1 \text{ mol L}^{-1} \cdot 10 \cdot 138.91 \text{ g mol}^{-1} = 1028 \text{ mg} \quad (2)$$

$$\text{mass Cu} \quad m(\text{Cu}) = 266.9 \text{ mg}$$

$$\text{mass La} \quad m(\text{La}) = 1028 \text{ mg}$$

2.5 Assume a fictive consumption of 39.90 mL of 0.1000 mol L⁻¹ EDTA solution and 35.00 mL of 0.01000 mol L⁻¹ Na₂S₂O₃ solution. Calculate the coefficient x in the formula La_xM_(2-x)CuO₄ (M = Ca and/or Sr and/or Ba) and give the exact formula of the superconductor (5)

$$\text{consumption for lanthanum} = [39.90 - (35.00/10 \cdot 4)] \text{ mL} = 25.90 \text{ mL} \quad (2)$$

$$\text{consumption for copper} = (39.90 - 25.90) \text{ mL} = 14.00 \text{ mL} \quad (2)$$

$$n(\text{La}) : n(\text{Cu}) = 25.90 : 14.00 = 1.85 : 1$$

$$\text{coefficient x: } 1.85 \quad \text{formula: La}_{1.85}\text{Ba}_{0.15}\text{CuO}_4 \quad (1)$$

2.2 Complexometric Titration

(35.0 points)

$$P = 35 \cdot \left[1 - \frac{|(C1 - (MV1 \cdot PS / 100)) - ((MV1 \cdot PS / 100) \cdot 0.005)|}{((MV1 \cdot PS / 100) \cdot 0.03) - ((MV1 \cdot PS / 100) \cdot 0.005)} \right]$$

P = points

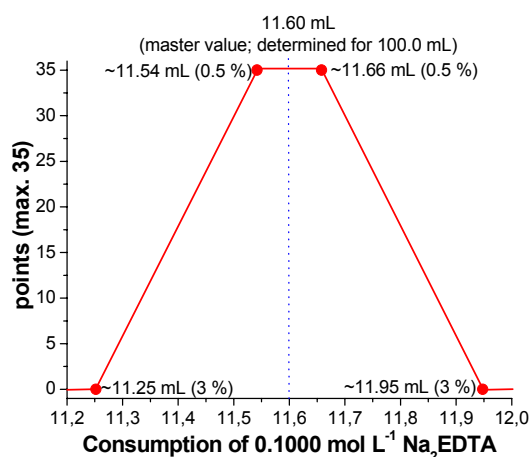
C1 = experimental consumption (mL)

MV1 = actual master value

PS = mL of superconductor solution handed out (100.0, 99.00, 98.00, 97.00 mL)

if P ≥ 35 use the maximum points of 35

if P ≤ 0 use zero points



2.3 Iodometric Titration

(35.0 points)

$$P = 35 \cdot \left[1 - \frac{|(C2 - (MV2 \cdot PS / 100)) - ((MV2 \cdot PS / 100) \cdot 0.0075)|}{((MV2 \cdot PS / 100) \cdot 0.04) - ((MV2 \cdot PS / 100) \cdot 0.0075)} \right]$$

P = points

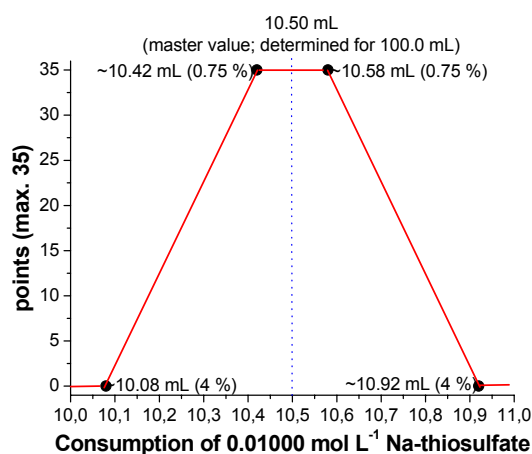
C2 = experimental consumption (mL)

MV2 = actual master value

PS = mL of superconductor solution handed out (100.0, 99.00, 98.00, 97.00 mL)

if P ≥ 35 use the maximum points of 35

if P ≤ 0 use zero points



Accuracy of points for 2.2 and 2.3: rounding value is one digit after the decimal point.