

36th



International Chemistry Olympiad

**8 theoretical problems
2 practical problems**

THE THIRTY-SIXTH INTERNATIONAL CHEMISTRY OLYMPIAD 18–27 JULY 2004, KIEL, GERMANY

<h2>THEORETICAL PROBLEMS</h2>

PROBLEM 1

Thermodynamics

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.

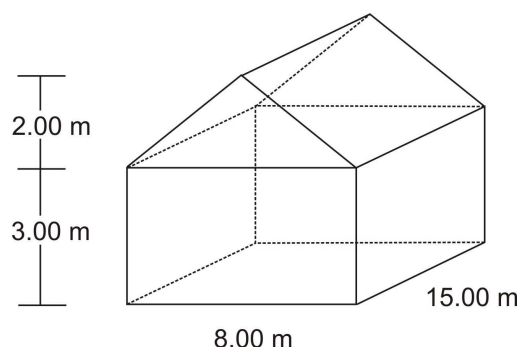
The thermodynamic properties and the composition of natural gas can be found in Table 1.

1.2 The density of natural gas is 0.740 g dm^{-3} (1.013×10^5 Pa, 25.0 °C) specified by PUC, the public utility company.

- 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!).
- 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 m³ 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 $\rho = 1.00 \text{ kg dm}^{-3}$ 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 $1.013 \times 10^5 \text{ Pa}$.

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 $1.00 \text{ W K}^{-1} \text{ m}^{-1}$.

- 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:

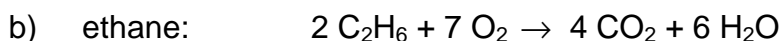
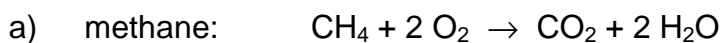
$$J = E \times (A \times \Delta t)^{-1} = \lambda_{\text{wall}} \times \Delta T \times d^{-1}$$

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

SOLUTION**1.1** Chemical equations:

Thermodynamic data for the equations:

$$\Delta H^0 = [2 \times (-241.8) - 393.5 - (-74.6)] \text{ kJ mol}^{-1} = -802.5 \text{ kJ mol}^{-1}$$

$$\Delta S^0 = [2 \times (188.8) + 213.8 - 186.3 - 2 \times 205.2] \text{ J mol}^{-1} \text{ K}^{-1} = -5.3 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\Delta G^0 = -802.5 \text{ kJ mol}^{-1} - 298.15 \text{ K} \times (-5.3 \text{ J mol}^{-1} \text{ K}^{-1}) = -800.9 \text{ kJ mol}^{-1}$$

$$\text{Methane: } \Delta H^0 = -802.5 \text{ kJ mol}^{-1}; \Delta S^0 = -5.3 \text{ J mol}^{-1} \text{ K}^{-1}; \Delta G^0 = -800.9 \text{ kJ mol}^{-1}$$

$$\Delta H^0 = [6 \times (-241.8) - 4 \times 393.5 - 2 \times (-84.0)] \text{ kJ mol}^{-1} = -2856.8 \text{ kJ mol}^{-1}$$

$$\Delta S^0 = [6 \times 188.8 + 4 \times 213.8 - 2 \times 229.2 - 7 \times 205.2] \text{ J mol}^{-1} \text{ K}^{-1} = +93.2 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\Delta G^0 = -2856.8 \text{ kJ mol}^{-1} - 298.15 \text{ K} \times (93.2 \text{ J mol}^{-1} \text{ K}^{-1}) = -2884.6 \text{ kJ mol}^{-1}$$

$$\text{Ethane: } \Delta H^0 = -2856.8 \text{ kJ mol}^{-1}; \Delta S^0 = +93.2 \text{ J mol}^{-1} \text{ K}^{-1}; \Delta G^0 = -2884.6 \text{ kJ mol}^{-1}$$

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

$$m = \rho \times V = 0.740 \text{ g dm}^{-3} \times 1000 \text{ dm}^3 = 740 \text{ g}$$

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

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

$$n(i) = x(i) \cdot n_{\text{tot}}$$

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

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

b) Energy of combustion, deviation:

$$E_{\text{comb.}}(\text{H}_2\text{O}(\text{g})) = \sum_i n(i)\Delta_c H^0(i) = \\ = 43.83 \text{ mol} \times (-802.5 \text{ kJ mol}^{-1}) + 0.495 \text{ mol} \times 0.5 \times (-2856.8 \text{ kJ mol}^{-1}) \\ = -35881 \text{ kJ}$$

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

Deviation from PUC

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

$$\text{Deviation: } \Delta^E = (E_{\text{comb.}}(\text{H}_2\text{O}(\text{g})) - E_{\text{PUC}}(\text{H}_2\text{O}(\text{g})) \times 100\% \times [E_{\text{comb.}}(\text{H}_2\text{O}(\text{g}))]^{-1} \\ = (35881 \text{ kJ} - 35932 \text{ kJ}) \times 100\% \times (35881 \text{ kJ})^{-1} = -0.14\%$$

1.3 Energy for heating the water:

$$\text{Volume of water: } V_{\text{water}} = 22.5 \text{ m}^3$$

$$n_{\text{water}} = V_{\text{water}} \rho_{\text{water}} (M_{\text{water}})^{-1} = 22.5 \text{ m}^3 \times 10^6 \text{ g m}^{-3} \times (18.02 \text{ g mol}^{-1})^{-1} = 1.249 \times 10^6 \text{ mol}$$

$$E_{\text{water}} = n_{\text{water}} \times C_p \times \Delta T = 1.249 \times 10^6 \text{ mol} \times 75.30 \text{ J K}^{-1} \text{ mol}^{-1} \times 14 \text{ K} = 1316 \text{ MJ}$$

Energy for heating the air:

Volume of the house is:

$$V_{\text{air}} = (15 \text{ m} \times 8 \text{ m} \times 3 \text{ m}) + 0.5 \times (15 \text{ m} \times 8 \text{ m} \times 2 \text{ m}) = 480 \text{ m}^3$$

$$n_{\text{air}} = pV(RT)^{-1} = 1.013 \times 10^5 \text{ Pa} \times 480 \text{ m}^3 \times (8.314 \text{ J (K mol)}^{-1} \times 283.15 \text{ K})^{-1} = \\ = 2.065 \times 10^4 \text{ mol}$$

$$C_p(\text{air}) = 0.21 \times 29.4 \text{ J (K mol)}^{-1} + 0.79 \times 29.1 \text{ J (K mol)}^{-1} = 29.16 \text{ J (K mol)}^{-1}$$

$$E_{\text{air}} = n_{\text{air}} \times C_p(\text{air}) \times \Delta T = 2.065 \times 10^4 \text{ mol} \times 29.17 \text{ J (K mol)}^{-1} \times 20 \text{ K} = 12.05 \text{ MJ}$$

1.4 Energy for maintaining the temperature:

Surface area of the house:

$$A_{\text{house}} = 3 \text{ m} \times 46 \text{ m} + 8 \text{ m} \times 2 \text{ m} + ((2 \text{ m})^2 + (4 \text{ m})^2)^{1/2} \times 2 \times 15 \text{ m} = 288.16 \text{ m}^2$$

Heat conductivity: $\lambda_{\text{wall}} = 1 \text{ J (s K m)}^{-1}$

Energy flux along a temperature gradient (wall thickness $d = 0.2 \text{ m}$)

$$J = E_{\text{loss}} (A \times \Delta t)^{-1} = \lambda_{\text{wall}} \Delta T d^{-1}$$

$$E_{\text{loss}} = 288.16 \text{ m}^2 \times (12 \cdot 60 \cdot 60 \text{ s}) \times 1 \text{ J (s K m)}^{-1} \times 25 \text{ K} \times (0.2 \text{ m})^{-1} = 1556 \text{ MJ}$$

$$E_{\text{loss}} = 1556 \text{ MJ}$$

1.5 Total energy and costs:

$$\text{Total energy: } E_{\text{tot}} = E_{\text{water}} + E_{\text{air}} + E_{\text{loss}} = 1316 \text{ MJ} + 12 \text{ MJ} + 1556 \text{ MJ} = 2884 \text{ MJ}$$

$$2884 \text{ MJ corresponds to } 2.884 \times 10^6 \text{ kJ} \times (3600 \text{ s h}^{-1} \times 9.981 \text{ kJ s}^{-1} \text{ m}^{-3} \times 0.9)^{-1} = \\ = 89.18 \text{ m}^3$$

Volume of gas: $V = 89.18 \text{ m}^3$

2884 MJ correspond to a cost of:

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

Rent for equipment: 150.00 €

Total cost of gas heating = 185.67 €

2884 MJ correspond to a cost of

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

Rent for equipment: 100.00 €

Total cost of electric heating: 209.75 €

PROBLEM 2

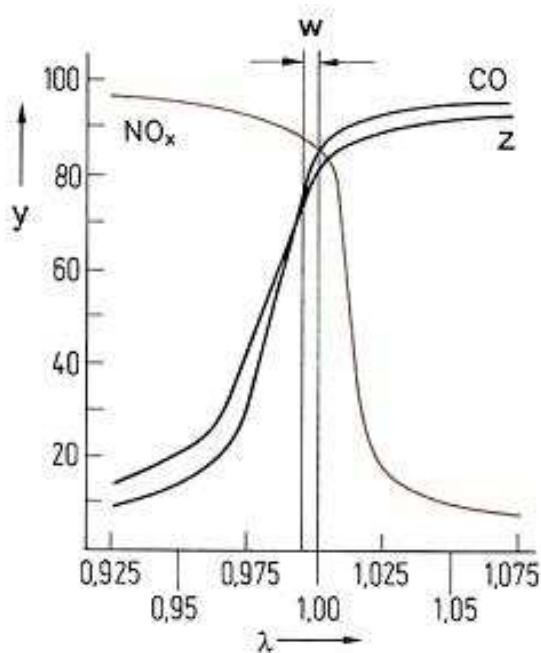
Kinetics at catalyst surfaces

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.

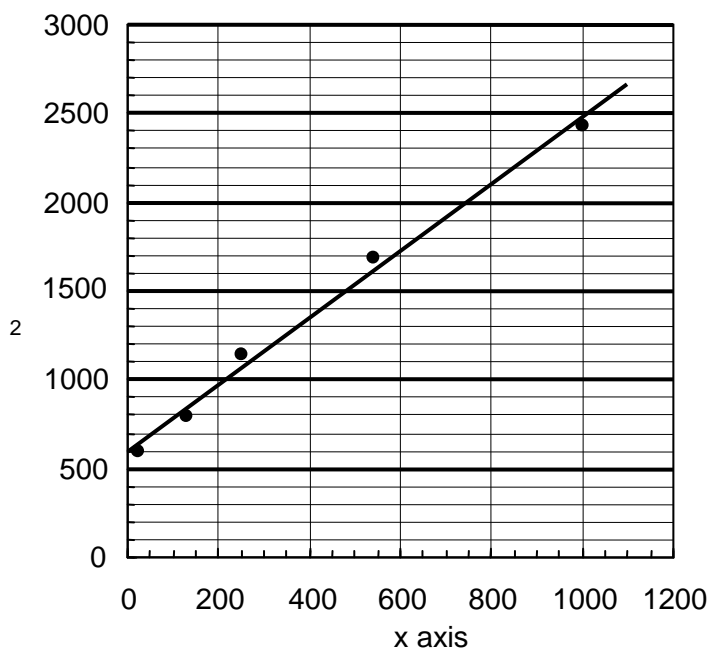
The adsorption of gas molecules on a solid surface can be described in a simple model by using the Langmuir isotherm:

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

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.
 b) Determine the pressure p at which 15 % of the surface is covered.
 c) The rate r of the decomposition of gas molecules at a solid surface depends on the surface coverage θ (reverse reaction neglected): $r = k \theta$
 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).
 d) Data for the adsorption of another gas on a metal surface (at 25 °C)



x axis: $p \cdot (\text{Pa})^{-1}$

y axis: $p \cdot V_a^{-1} \cdot (\text{Pa cm}^{-3})^{-1}$

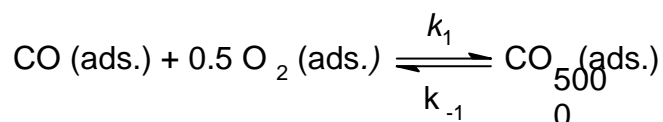
V_a is the gas volume that has been adsorbed.

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

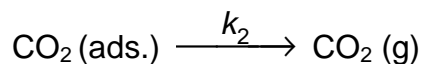
Hint: Set $\theta = V_a / V_{a,\text{max}}$.

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, CO₂ is then desorbed from the surface:



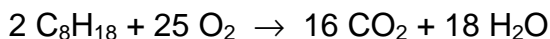
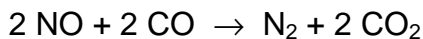
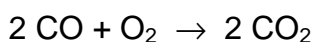
2.4 Derive the formula for the reaction rate of the CO₂(g) - formation as a function of the partial pressures of the reaction components.

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

$$\theta_i = \frac{K_i \times p_i}{1 + \sum_j K_j \times p_j} \quad \text{j: relevant gas components}$$

SOLUTION

2.1 Reaction equations:



2.2 Questions concerning the λ probe:

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.

With $\lambda > 1$, carbon monoxide and hydrocarbons can be oxidised at the three-way catalytic converter.

With $\lambda < 0.975$, nitrogen oxides can be reduced poorly.

2.3 a) Surface coverage:

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

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

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

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

$$p = \frac{\theta}{K - \theta \times K}$$

$$\theta = 0.15$$

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

- c) Orders of decomposition:

Order of the decomposition reaction at low gas pressures 1

Order of the decomposition reaction at high gas pressures 0

Notes:

$$r = k \times \theta = k \frac{K \times p}{1 + K \times p},$$

$$p \text{ low} \Rightarrow p \ll \frac{1}{K} \Rightarrow r = k K p \quad \text{reaction order } 1.$$

$$p \text{ high} \Rightarrow p \gg \frac{1}{K} \Rightarrow r = k \quad \text{reaction order } 0.$$

- d) Gas volume $V_{a,\max}$ and product $K \cdot V_{a,\max}$:

$$\frac{1}{\theta} = \frac{1}{K p} + 1 = \frac{V_{a,\max}}{V_a} \Rightarrow \frac{1}{K V_{a,\max}} + \frac{p}{V_{a,\max}} = \frac{p}{V_a}$$

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

$$\text{Intercept: } \frac{1}{K V_{a,\max}} = 6 \times 10^2 \text{ Pa cm}^{-3} \Rightarrow K V_{a,\max} = 1.7 \times 10^{-3} \text{ Pa}^{-1} \text{ cm}^3$$

2.4 Equation for reaction rate:

The information given in the text leads directly to $r = k_2 \theta_{\text{CO}_2}$

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

$$\theta_{\text{CO}_2} = \frac{k_1}{k_{-1}} \cdot \theta_{\text{CO}} \theta_{\text{O}_2}^{\frac{1}{2}}, \Rightarrow r = k_2 \frac{k_1}{k_{-1}} \theta_{\text{CO}} \theta_{\text{O}_2}^{\frac{1}{2}}.$$

The Langmuir isotherm gives:

$$\theta_{\text{CO}} = \frac{K_{\text{CO}} p_{\text{CO}}}{1 + K_{\text{CO}_2} p_{\text{CO}_2} + K_{\text{CO}} p_{\text{CO}} + K_{\text{O}_2} p_{\text{O}_2}} \quad \text{and} \quad \theta_{\text{O}_2} = \frac{K_{\text{O}_2} p_{\text{O}_2}}{1 + K_{\text{CO}_2} p_{\text{CO}_2} + K_{\text{CO}} p_{\text{CO}} + K_{\text{O}_2} p_{\text{O}_2}}$$

$$r = k_2 \frac{k_1}{k_{-1}} \frac{K_{\text{CO}} p_{\text{CO}} (K_{\text{O}_2} p_{\text{O}_2})^{\frac{1}{2}}}{(1 + K_{\text{CO}_2} p_{\text{CO}_2} + K_{\text{CO}} p_{\text{CO}} + K_{\text{O}_2} p_{\text{O}_2})^{\frac{3}{2}}}$$

PROBLEM 3

Monovalent alkaline earth compounds?

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 colourless crystals.

3.2 What substance are the metallic particles and the colourless 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 % (by mass) of calcium and 46.32 mass % 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 are 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 $r(M^{m+})$ and anion $r(X^{x-})$ 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 $\Delta_L H^\circ$ for CaCl
3	Triangular	0.155 – 0.225	BN	$-663.8 \text{ kJ mol}^{-1}$
4	Tetrahedral	0.225 – 0.414	ZnS	$-704.8 \text{ kJ mol}^{-1}$
6	Octahedral	0.414 – 0.732	NaCl	$-751.9 \text{ kJ mol}^{-1}$
8	Cubic	0.732 – 1.000	CsCl	$-758.4 \text{ kJ mol}^{-1}$

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

3.5 a) 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 $\Delta_L H^\circ$ for CaCl is important for the decision whether CaCl is thermodynamically stable or not. In order to decide whether it is stable against decomposition into its elements, the standard enthalpy of formation $\Delta_f H^\circ$ of CaCl has to be known.

b) Calculate the value of $\Delta_f H^\circ$ (CaCl) with the aid of a Born-Haber-cycle.

heat of fusion	$\Delta_{\text{fusion}} H^\circ(\text{Ca})$		9.3 kJ mol^{-1}
ionization enthalpy	$\Delta_{1. \text{IE}} H(\text{Ca})$	$\text{Ca} \rightarrow \text{Ca}^+$	$589.7 \text{ kJ mol}^{-1}$
ionization enthalpy	$\Delta_{2. \text{IE}} H(\text{Ca})$	$\text{Ca}^+ \rightarrow \text{Ca}^{2+}$	$1145.0 \text{ kJ mol}^{-1}$
heat of vaporization	$\Delta_{\text{vap}} H^\circ(\text{Ca})$		$150.0 \text{ kJ mol}^{-1}$
dissociation energy	$\Delta_{\text{diss}} H(\text{Cl}_2)$	$\text{Cl}_2 \rightarrow 2 \text{ Cl}$	$240.0 \text{ kJ mol}^{-1}$

enthalpy of formation	$\Delta_f H^\ominus(\text{CaCl}_2)$		$-796.0 \text{ kJ mol}^{-1}$
electron affinity	$\Delta_{\text{EA}} H(\text{Cl})$	$\text{Cl} + \text{e}^- \rightarrow \text{Cl}^-$	$-349.0 \text{ kJ mol}^{-1}$

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!

SOLUTION

3.1 Chemical equations:

- (a) $\text{CaCl}_2 + \text{Ca} \rightarrow 2 \text{CaCl}$
 (b) $2 \text{CaCl}_2 + \text{H}_2 \rightarrow 2 \text{CaCl} + 2 \text{HCl}$
 (c) $4 \text{CaCl}_2 + \text{C} \rightarrow 4 \text{CaCl} + \text{CCl}_4$

3.2

Silvery metallic particles: Ca

Colourless crystals: CaCl₂

Note: CaCl cannot be obtained by a conventional solid state reaction of Ca and CaCl₂

3.3 Empirical formula:

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

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

$$\text{mol \% of Ca} = 52.36 \text{ mass \%} / M(\text{Ca})$$

$$= 52.36 \text{ mass \%} / 40.08 \text{ g mol}^{-1} = 1.31 \text{ mol \%}$$

$$\text{mol \% of Cl} = 46.32 \text{ mass \%} / M(\text{Cl})$$

$$= 46.32 \text{ mass \%} / 35.45 \text{ g mol}^{-1} = 1.31 \text{ mol \%}$$

$$\text{mol \% of X} = 1.32 \% \text{ X} / M(\text{H})$$

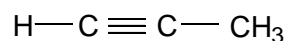
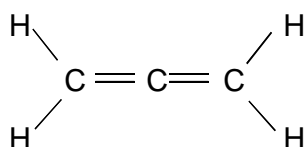
$$= 1.32 \% \text{ X} / 1.01 \text{ g mol}^{-1} = 1.31 \text{ mol \%}$$

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

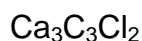
Empirical formula: CaClH

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:



b) Empirical formula of the compound formed:



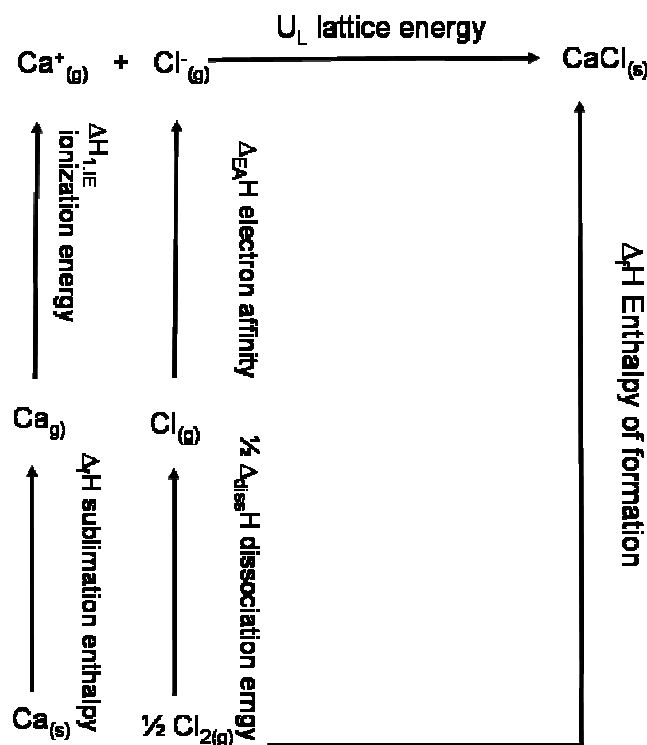
Notes: If the ratio of $n(\text{Ca}) : n(\text{Cl}) = 1.5 : 1$ [or better = $3 : 2$ which can be rewritten as $\text{CaCl}_2 \cdot 2 \text{Ca}^{2+} = \text{Ca}_3\text{Cl}_2^{4+}$] is given and the reduction product must contain a C_3^{4-} anion which needs two Ca^{2+} cations for electroneutrality, the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

3.5 a) Structure type CaCl likely to have:

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

NaCl	CsCl	ZnS	BN	no decision possible
<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>

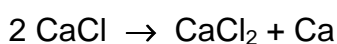
b) $\Delta_f H^\circ(\text{CaCl})$ with a Born-Haber-cycle:



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

$$\begin{aligned}\Delta_f H^0(\text{CaCl}) &= \Delta_{\text{subl}} H^0(\text{Ca}) + \Delta_{1, \text{IE}} H(\text{Ca}) + \frac{1}{2} \Delta_{\text{diss}} H(\text{Cl}_2) + \Delta_{\text{EA}} H(\text{Cl}) + \Delta_{\text{L}} H(\text{CaCl}) \\ &= (159.3 + 589.7 + 120 - 349.0 - 751.9) \text{ kJ mol}^{-1} \\ &= -231.9 \text{ kJ mol}^{-1}\end{aligned}$$

3.6 Stability to disproportionation:



$$\Delta H = \Delta_f H^0(\text{CaCl}_2) - 2 \Delta_f H^0(\text{CaCl}) = -796.0 \text{ kJ mol}^{-1} + 463.8 \text{ kJ mol}^{-1} = -332.2 \text{ kJ mol}^{-1}$$

Disproportionation:	yes	no	no decision possible, more information needed
	<input type="checkbox"/>	<input checked="" type="checkbox"/>	<input type="checkbox"/>

PROBLEM 4**Determining atomic masses**

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 dm^3 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 $\mu = \frac{3 m(\text{A}) m(\text{B})}{3 m(\text{A}) + 4 m(\text{B})}$

$m(\text{A}), m(\text{B})$ - 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.

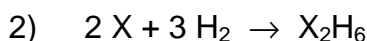
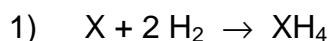
Estimate the force constant k of a Z-H bond, assuming that there is a linear proportionality between force constant and bond enthalpy.

Determine the atomic mass of Z from this information.

Give the chemical symbol of Z.

SOLUTION

4.1 Atomic mass of X, symbol of X, structures:



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

ii) $5.628 \text{ g} =$

$$= n_1(\text{XH}_4) \times [M(X) + 4 \times 1.01 \text{ g mol}^{-1}] + n_2(\text{X}_2\text{H}_6) \times [2 M(X) + 6 \times 1.01 \text{ g mol}^{-1}]$$

iii) $n_1(\text{XH}_4) = 2 n_2(\text{X}_2\text{H}_6)$

iii,i) \rightarrow i') $2 n_1(X) \times M(X) = 5.0 \text{ g}$

iii,ii) \rightarrow ii') $n_1(X) \times [2M(X) + 7.07 \text{ g mol}^{-1}] = 5.628 \text{ g}$

i',ii') \rightarrow vi) $(5.0 \text{ g}) \times [2 M(X)]^{-1} = (5.628 \text{ g}) \times [2 M(X) + 7.07 \text{ g mol}^{-1}]^{-1}$

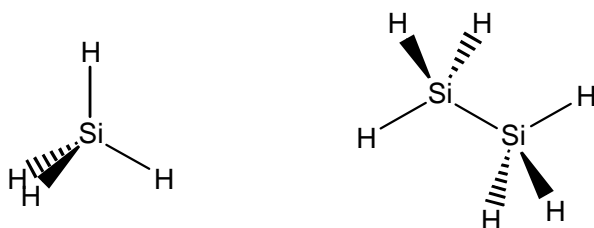
$$M(X) = 3.535 \text{ g mol}^{-1} \times (5.628 \text{ g})^{-1} \times [(5.0 \text{ g})^{-1} - (5.628 \text{ g})^{-1}]^{-1}$$

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

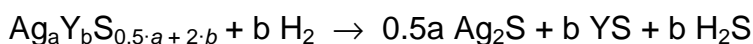
Atomic mass of X: $M(X) = 28.14 \text{ g mol}^{-1}$

Chemical symbol of X: Si

3D structures of the two products:



4.2 Atomic mass of Y and empirical formula of Argyrodite:



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

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

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

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

ii,i) \rightarrow ii')

$$b \times 10 \text{ g} \times (8.871 \cdot 10^{-3} \text{ mol})^{-1} =$$

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

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

iii,ii') \rightarrow iv)

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

$$b \cdot 1127 \text{ g mol}^{-1} =$$

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

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

Chemical symbol of Y: Ge

Empirical formula of Argyrodite: Ag_8GeS_6

4.3 The force constants of a C-H bond:

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

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

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

The force constants of a Z-H bond:

$k(\text{Z-}$

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

$$= 491.94 \text{ N m}^{-1} \cdot 450.2 \text{ kJ mol}^{-1} \cdot [438.4 \text{ kJ mol}^{-1}]^{-1} = 505.18 \text{ N m}^{-1}$$

The atomic mass and symbol of Z:

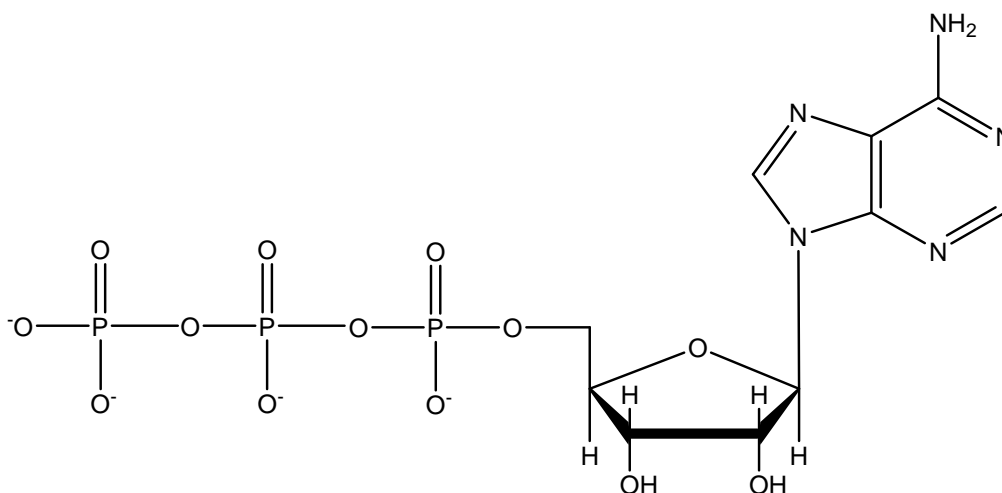
$$\frac{3 M(\text{Z}) \times M(\text{H})}{3 M(\text{Z}) + 4 M(\text{H})} = \frac{k(\text{Z-H}) \times N_A}{[2\pi c \tilde{\nu}(\text{Z-H})]^2}$$

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

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

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

Chemical symbol of Z: Ge

PROBLEM 5**Biochemistry with Thermodynamics**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:

$$c(\text{ATP}^{4-}) = 2.25 \text{ mmol dm}^{-3}$$

$$c(\text{ADP}^{3-}) = 0.25 \text{ mmol dm}^{-3}$$

$$c(\text{HPO}_4^{2-}) = 1.65 \text{ mmol dm}^{-3}$$

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 ΔG° instead of ΔG° . The standard state of ΔG° is defined as having a constant pH of 7. In equations with ΔG° and K for reactions at $pH = 7$ the concentration of H^+ is therefore omitted. Standard concentration is 1 mol dm^{-3} .

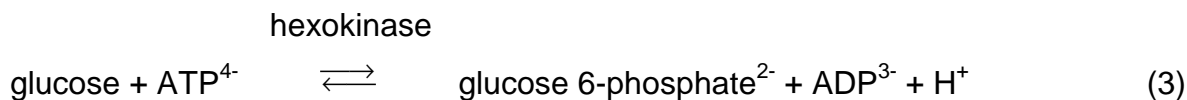
5.1 Calculate the actual $\Delta G'$ of reaction (1) in the red blood cell at 25 °C and $pH = 7$.

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 ΔG° 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 μm 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.

SOLUTION

5.1 Actual $\Delta G'$ of reaction (1):

$$\begin{aligned}\Delta G' &= \Delta G^{\circ'} + R T \ln \frac{[ADP^{3-}][HPO_4^{2-}]}{[ATP^{4-}]} \\ &= -30500 \text{ J mol}^{-1} + 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K} \times \ln \frac{0.00025 \times 0.00165}{0.00225} \\ &= -30.5 \text{ kJ mol}^{-1} - 21.3 \text{ kJ mol}^{-1} = -51.8 \text{ kJ mol}^{-1}\end{aligned}$$

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

$$\begin{aligned}\Delta G^{\circ'} &= -R T \ln K' \\ K' &= e^{-\Delta G^{\circ'}/RT} = e^{-13800 \text{ J/mol} / (8.314 \text{ J/(mol K)} \cdot 298.15 \text{ K})} = 0.0038 \\ K' &= \frac{[\text{glucose 6-phosphate}]}{[\text{glucose}][HPO_4^{2-}]} \\ \frac{[\text{glucose 6-phosphate}]}{[\text{glucose}]} &= K' \cdot [HPO_4^{2-}] \\ &= 0.0038 \cdot 0.00165 \\ &= 6.3 \cdot 10^{-6}\end{aligned}$$

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

$$\Delta G^{\circ}(3) = \Delta G^{\circ}(1) + \Delta G^{\circ}(2) = -30.5 \text{ kJ mol}^{-1} + 13.8 \text{ kJ mol}^{-1} = -16.7 \text{ kJ mol}^{-1}$$

$$\begin{aligned}\Delta G^{\circ} &= -R T \ln K' \\ K' &= e^{-\Delta G^{\circ}/RT} = e^{16700 \text{ J/mol} / (8.314 \text{ J/(mol K)} \cdot 298.15 \text{ K})} = 843\end{aligned}$$

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

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

$$= 843 \times (2.25 \text{ mmol dm}^{-3} / 0.25 \text{ mmol dm}^{-3}) = 7587$$

5.4 a) Mass of ATP produced per day:

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

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

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

Mass of ATP produced: $76.9 \text{ mol day}^{-1} \times 503 \text{ g mol}^{-1} = 38700 \text{ g day}^{-1}$

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

b) Mass of ATP in the human body:

Average lifetime: 1 day = 1440 min 1 min = 1440^{-1} day

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

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

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

- 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.

5.5 a) How many protons are in a spherical mitochondrion with a diameter of 1 μm at $\text{pH} = 7$?

$$V = 4/3 \pi r^3 = 4/3 \pi (0.5 \times 10^{-6} \text{ m})^3 = 5.2 \times 10^{-19} \text{ m}^3 = 5.2 \times 10^{-16} \text{ dm}^3$$

$$c = 1 \times 10^{-7} \text{ mol dm}^{-3}$$

$$n = V c \cdot N_A = 5.2 \times 10^{-16} \text{ dm}^3 \times 1 \times 10^{-7} \text{ mol dm}^{-3} \times 6.022 \times 10^{23} \text{ mol}^{-1} = 31$$

b) How many protons have to enter a mitochondrion?

Number of ATP molecules:

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

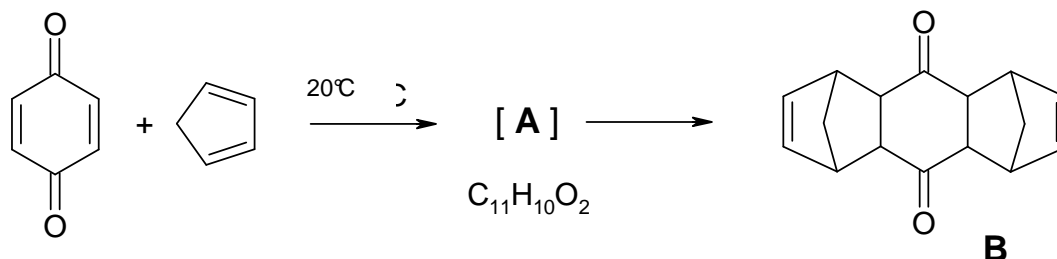
$$\text{Number of H}^+ \text{ per cell: } n(\text{H}^+_{\text{per cell}}) = n(\text{ATP}) \times 3 = 718300$$

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

PROBLEM 6

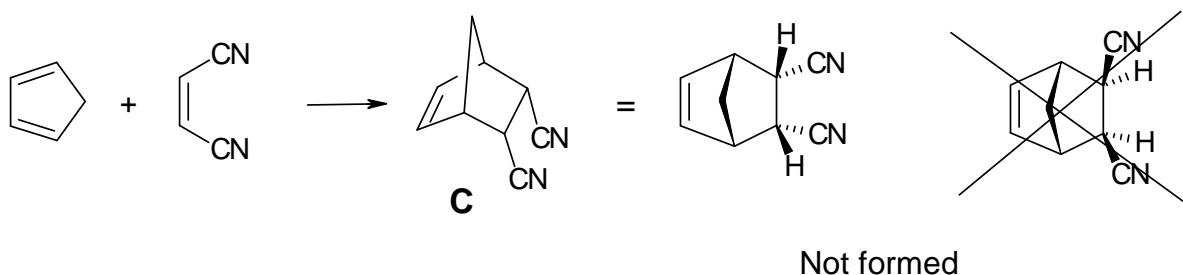
Diels-Alder Reactions

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



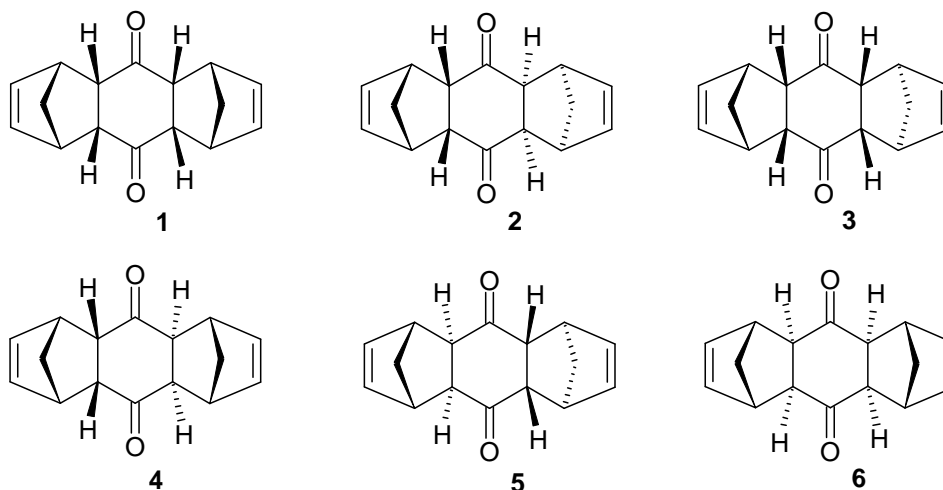
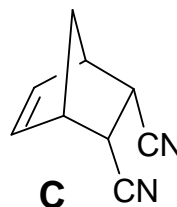
If you use the *E*-isomer of the alkene instead, you will obtain two other stereoisomers **D1** and **D2**.

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).

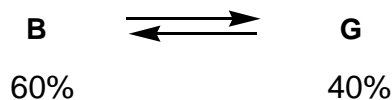
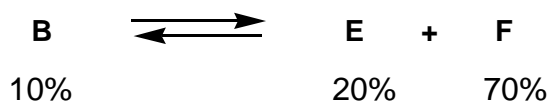
Hints:

- 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?

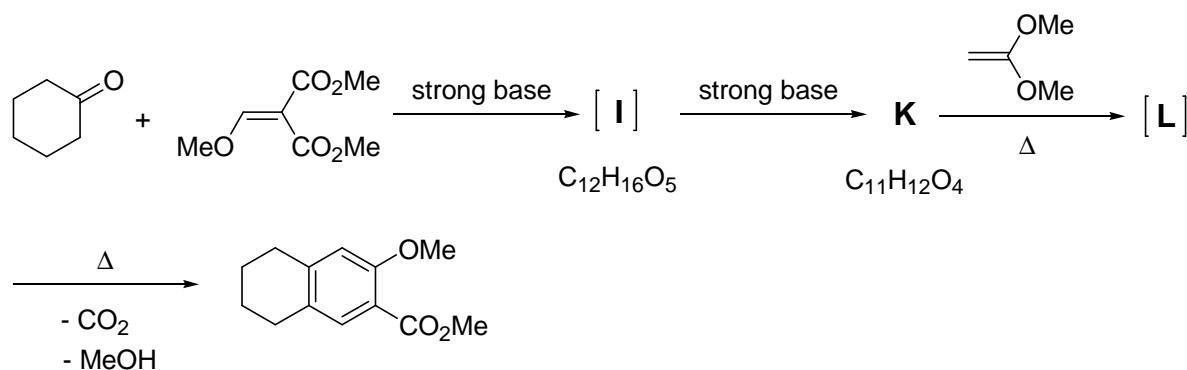
After prolonged heating (15h, 120 °C) of the originally isolated stereoisomer **B** (melting point mp: 157 °C), Diels and Alder obtained two new stereoisomers **E** (mp: 153 °C) and **F** (mp: 163 °C). Equilibration of **B** with a catalytic amount of a strong base at 25 °C gave a further stereoisomer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



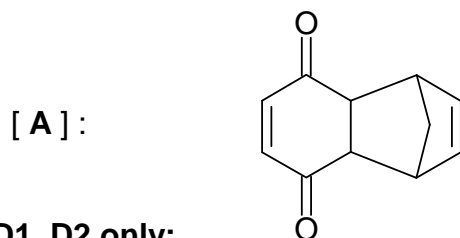
6.5 Draw the structures for **I**, **K** and **L**.

Hints: - **K** has only one methyl group.

- **L** is the Diels-Alder adduct of **K** and the alkene shown.

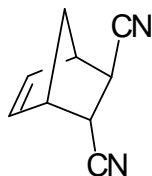
SOLUTION

6.1 Structure of **A** only:

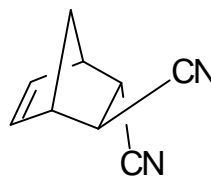


6.2 Structures of **D1**, **D2** only:

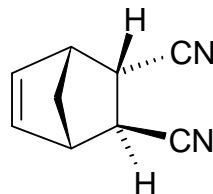
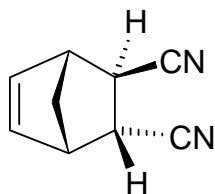
D1:



D2:



alternatively, the following structures are also correct:



Note: The two compounds are enantiomers

6.3 Correct structure of **B** (circle only one):

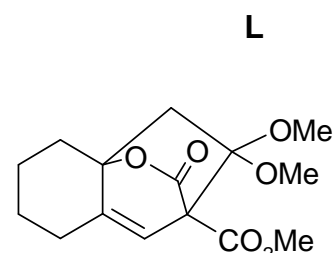
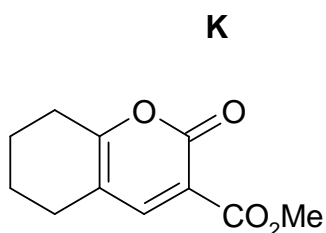
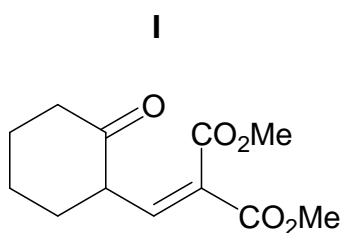
1 2 3 4 5 6

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.

6.4 Decide the questions concerning the Diels-Alder reaction.

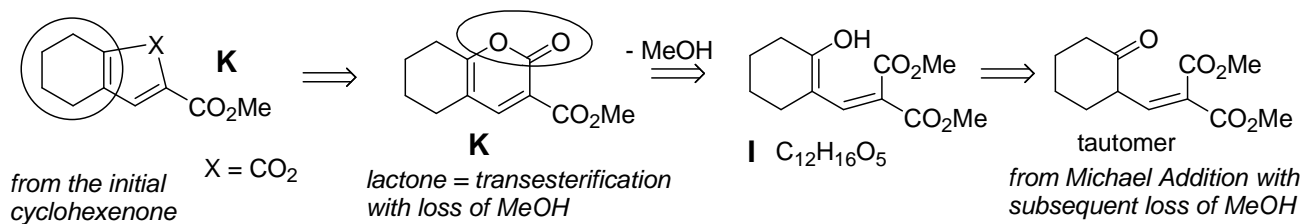
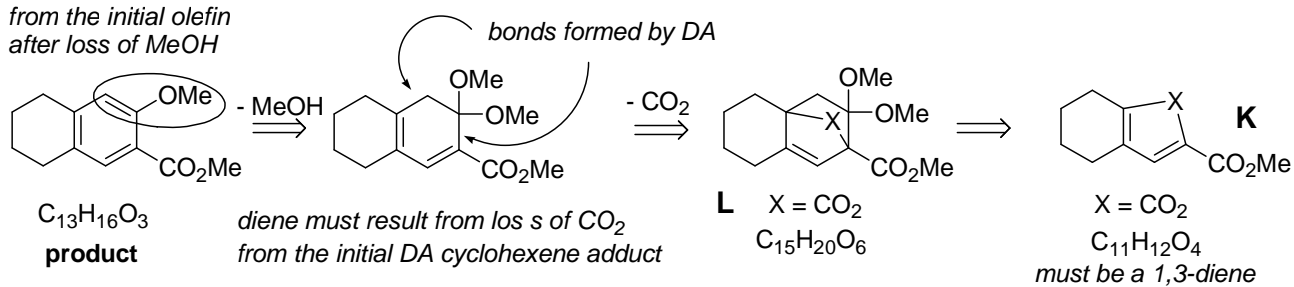
	true	false	no decision possible
• The Diels-Alder reaction is reversible	<input checked="" type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
• The formation of B in the original reaction is thermodynamically controlled	<input type="checkbox"/>	<input checked="" type="checkbox"/>	<input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

6.5 Structures of **I**, **K**, **L** only:



Notes:

from the initial olefin
after loss of MeOH



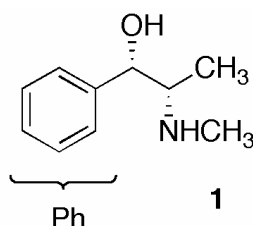
PROBLEM 7

Stereochemistry in Drugs

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.



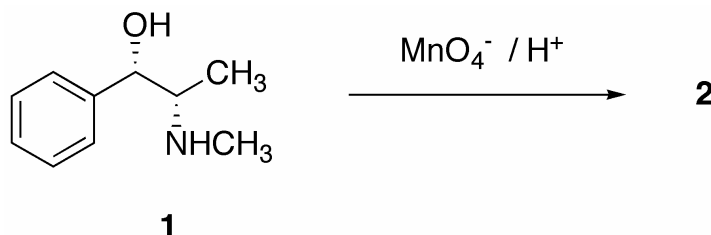
- 7.2 Mark the stereocenters in **1** with an asterisk * on the answer sheet.

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**.

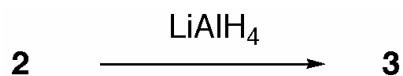
Draw a Fischer representation of **1**.

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



- 7.4 Draw the stereochemically correct structure of compound **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.

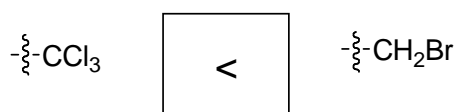
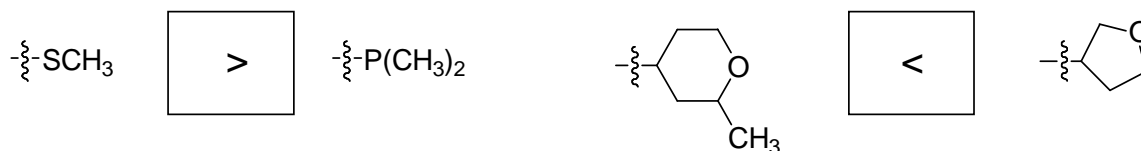
The treatment of **2** with LiAlH_4 results exclusively in compound **3**, which differs from **1** in its melting point.



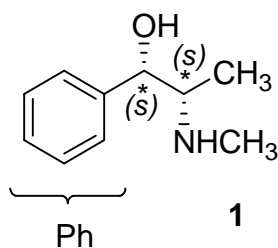
- 7.5** a) Draw the stereochemically correct structure of **3**.
 b) Decide the statements on the answer sheet concerning isomers.
 c) Draw a structural model to rationalize the exclusive formation of **3** from **2**.

SOLUTION

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

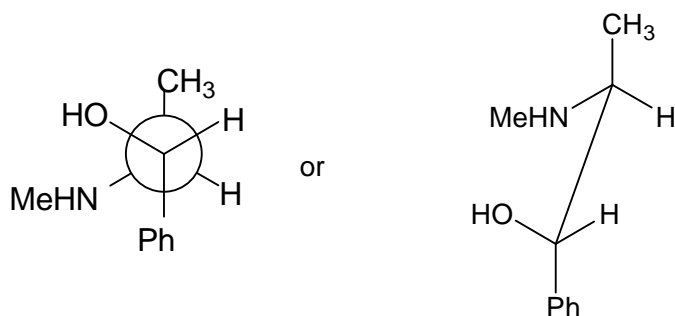


7.2



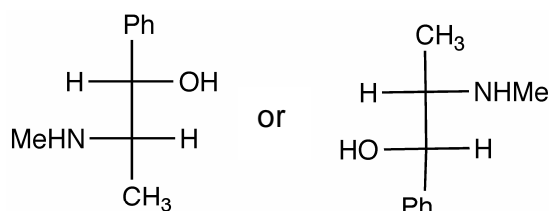
highest priority			lowest priority
OH	CH(NHCH ₃)CH ₃	Ph	H
NHCH ₃	CH(OH)Ph	CH ₃	H

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



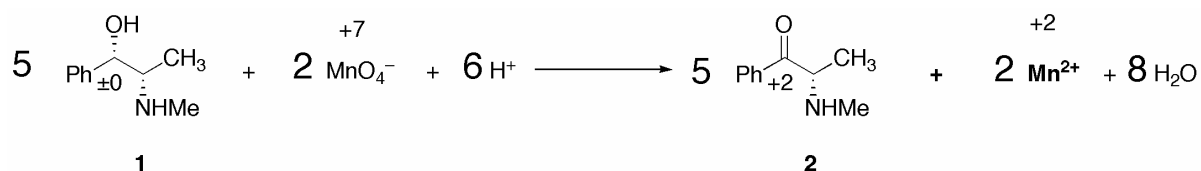
(Me = CH₃)

Fischer projection of **1**:

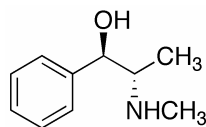


(Me = CH₃)

7.4 Equation with oxidation numbers and stereochemically correct structure of **2**:



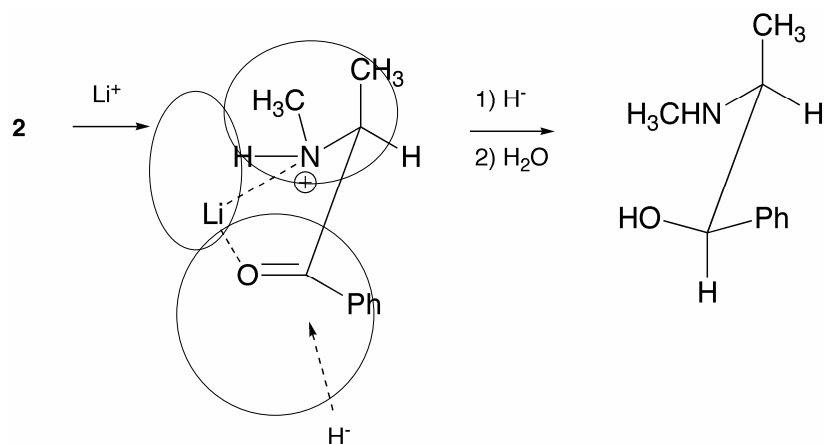
7.5 a) Structure of **3** (correct stereochemistry):



b) Statements concerning isomers:

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

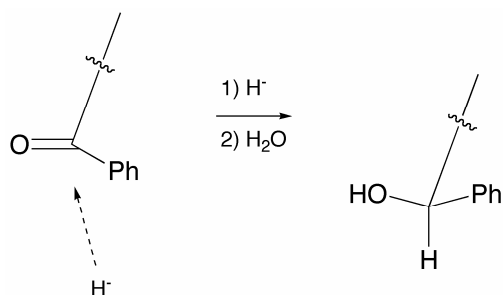
- c) Draw a structural model to rationalize the exclusive formation of **3** from **2**



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.



PROBLEM 8**Colloids**

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.

($T = 298.15$ K throughout whole problem)

Solution **A** is an aqueous solution of CaCl_2 with a concentration of 1.780 g dm^{-3} .

Solution **B** is an aqueous solution of Na_2CO_3 with a concentration of 1.700 g dm^{-3} .

$$pK_{a1}(\text{H}_2\text{CO}_3) = 6.37$$

$$pK_{a2}(\text{HCO}_3^-) = 10.33$$

8.1 Calculate the pH of solution **B** using reasonable assumptions.

100 cm^3 of solution **A** and 100 cm^3 of solution **B** are mixed to form solution **C**.

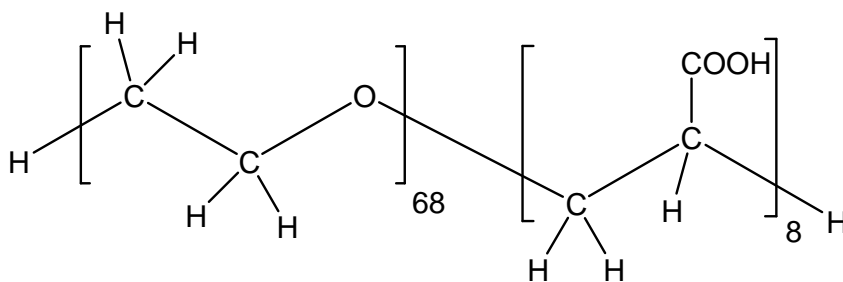
Solution **C** is adjusted to pH 10. A precipitate forms.

$$K_{sp}(\text{Ca}(\text{OH})_2) = 6.46 \times 10^{-6}$$

$$K_{sp}(\text{CaCO}_3) = 3.31 \times 10^{-9}$$

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 cm^3 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 cm³ of an aqueous NaOH solution ($c(\text{NaOH}) = 0.19 \text{ mol dm}^{-3}$). The solution is diluted by the addition of 200 cm³ 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). ($pK_a(\text{COOH}, \text{copolymer}) = 4.88$)

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

SOLUTION

8.1 pH of solution B:

$$K_{b2} = \frac{c(\text{HCO}_3^-)/(1 \text{ mol dm}^{-3}) \times c(\text{OH}^-)/(1 \text{ mol dm}^{-3})}{c(\text{CO}_3^{2-})/(1 \text{ mol dm}^{-3})} \quad K_{b2} = \frac{10^{-14}}{10^{-10.33}}$$

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

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

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

$$c(\text{HCO}_3^-) = c(\text{OH}^-) = x \quad \text{and} \quad c(\text{CO}_3^{2-}) = c_0(\text{CO}_3^{2-}) - x$$

$$c_0(\text{Na}_2\text{CO}_3) = \frac{1.700 \text{ g dm}^{-3}}{105.99 \text{ g mol}^{-1}}$$

$$c_0(\text{Na}_2\text{CO}_3) = c_0(\text{CO}_3^{2-}) = 0.016 \text{ mol dm}^{-3}$$

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

$$pH = 11.2$$

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

$$M(\text{CaCl}_2) = 110.98 \text{ g mol}^{-1} \quad pH = 10, \quad c(\text{OH}^-) = 1 \times 10^{-4} \text{ mol dm}^{-3}$$

$$c_0(\text{Na}_2\text{CO}_3) = \frac{1.700 \text{ g cm}^{-3}}{105.99 \text{ g mol}^{-1} \times 2} \quad c(\text{CaCl}_2) = \frac{1.780 \text{ g dm}^{-3}}{110.98 \text{ g mol}^{-1} \times 2}$$

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

Calculations for Ca(OH)₂:

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

Calculations for CaCO₃:

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

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

$$2.14 \times c(\text{CO}_3^{2-}) + c(\text{CO}_3^{2-}) = 8.0 \times 10^{-3} \text{ mol dm}^{-3}$$

$$\text{Initial concentration of CO}_3^{2-} \text{ in solution } \mathbf{C}: \quad c(\text{CO}_3^{2-}) = 2.55 \times 10^{-3} \text{ mol dm}^{-3}$$

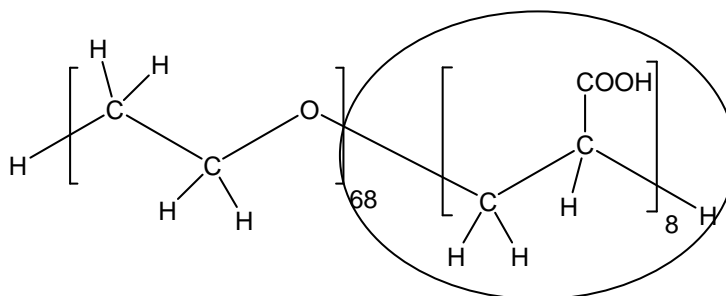
$$\text{Initial concentration of Ca}^{2+} \text{ in solution } \mathbf{C}: \quad c(\text{Ca}^{2+}) = 8.0 \times 10^{-3} \text{ mol dm}^{-3}$$

hence $c(\text{CO}_3^{2-}) \times c(\text{Ca}^{2+}) = 2.04 \times 10^{-5} > 3.3 \times 10^{-9} = K_{sp}(\text{CaCO}_3)$ precipitate

$\text{Ca}(\text{OH})_2$ will be found in the precipitate yes no

CaCO_3 will be found in the precipitate yes no

8.3 Circle the block that attaches to the CaCO_3 crystal:



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?



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

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

$$c_0(\text{OH}^-) = \frac{50 \text{ cm}^3}{250 \text{ cm}^3} \cdot 0.19 \text{ mol dm}^{-3} \quad c_0(\text{OH}^-) = 0.038 \text{ mol dm}^{-3}$$

$$c(\text{OH}^-) = 10^{-1.7} \text{ mol dm}^{-3} = 0.02 \text{ mol dm}^{-3} \quad x = 0.018 \text{ mol dm}^{-3}$$

$$K_b = \frac{(c_0(\text{COOH}) - x) / (1 \text{ mol dm}^{-3}) \times c(\text{OH}^-) / (1 \text{ mol dm}^{-3})}{x / (1 \text{ mol dm}^{-3})}$$

$$c_0(\text{COOH}) = \frac{K_b \cdot x \times (1 \text{ mol dm}^{-3})}{c(\text{OH}^-)} + x$$

$$c_0(\text{COOH}) = \left(\frac{0.018 \times 10^{-9.12}}{0.02} + 0.018 \right) \text{ mol dm}^{-3}$$

$$c_0(\text{COOH}) = 0.018 \text{ mol dm}^{-3}$$

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

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

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

$$m(\text{polymer}) = c(\text{polymer}) \times V \times M(\text{polymer})$$

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

8.5 Modification of CaCO_3 :

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

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

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

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

The number of polymers per particle indicates the mass of polymer per particle.

Thus, the mass of the calcium carbonate particle can be calculated:

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

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

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

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

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

calculated:

$$\begin{aligned}\rho(\text{CaCO}_3) &= \frac{m(\text{CaCO}_3 \text{ particle})}{V(\text{CaCO}_3 \text{ particle})} = \frac{3 m(\text{CaCO}_3 \text{ particle})}{4 \pi r^3} \\ &= \frac{3 (M (\text{total particle}) - N_{\text{polymer}} M(\text{polymer}))}{N_A 4 \pi r^3} \\ &= \frac{3 \times 8.01 \times 10^8 \text{ g mol}^{-1}}{N_A \cdot 4 \pi (5 \times 10^{-6} \text{ cm})^3} = 2.54 \text{ g cm}^{-3}\end{aligned}$$

The modification of calcium carbonate is Calcite Vaterite Aragonite

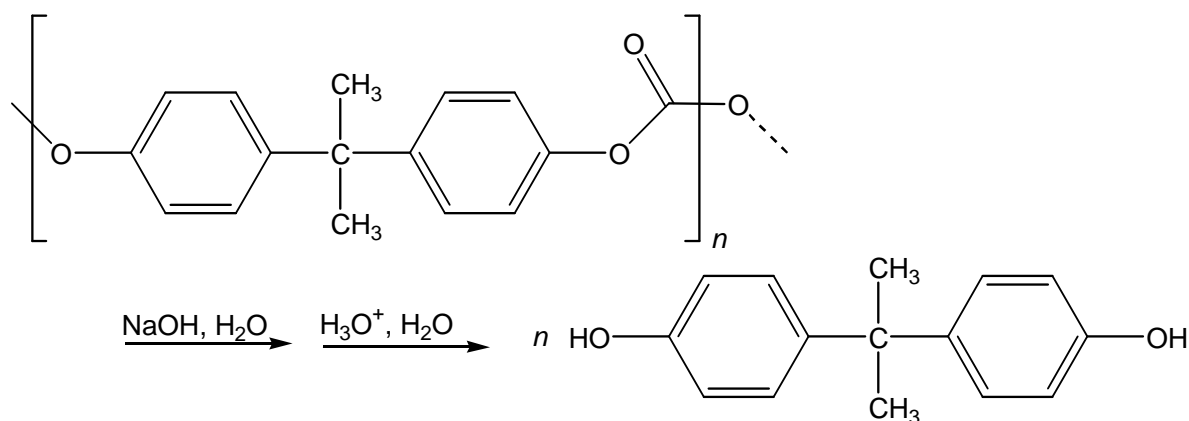
PRACTICAL PROBLEMS

PROBLEM 1 (Practical)

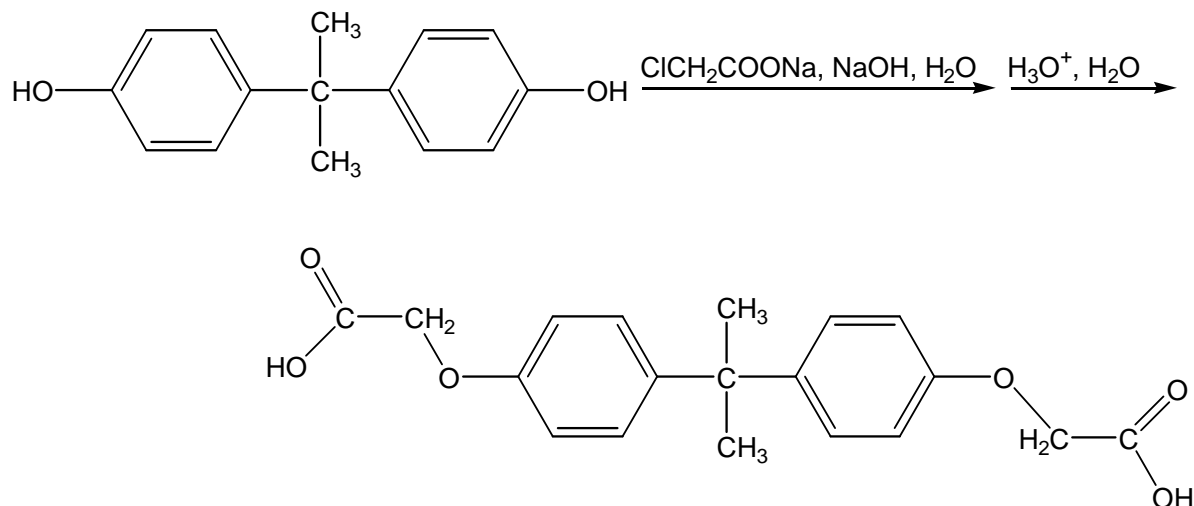
Two-Step Organic Synthesis of 2,2-Bis(*p*-phenyleneoxyacetic acid)propane (Bisphenol A bis(carboxymethyl)ether)

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 cm³ of demineralized water into a 100 cm³ 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 cm³ 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 cm³ of demineralized water and transfer the reaction mixture into a 400 cm³ beaker. Rinse the Erlenmeyer flask with 25 cm³ of demineralized water and add this to the contents of the beaker.
- Finally, fill up to 150 cm³ 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 cm³ 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 cm³ 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 cm³ Erlenmeyer flask with ground-glass joint.
- Add 10 cm³ of an aqueous sodium-hydroxide solution (No. **6**), 1 cm³ 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 cm³ 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 cm³ 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 cm³ of ethanol (No. 2). The precipitate is washed twice with 10 cm³ 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 cm³ 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 cm³ 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 cm³ 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.

SOLUTION

- 1.1 You started with 2.54 g of polycarbonate. Determine the theoretical yield of bisphenol A in g.

$$M_1(\text{polycarbonate}) = M_1(\text{C}_{16}\text{H}_{14}\text{O}_3)_n\text{H}_2 \approx M_1(\text{C}_{16}\text{H}_{14}\text{O}_3) = 254.30 \text{ g mol}^{-1}$$

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

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

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

Theoretical yield of bisphenol A: 2.28 g

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

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

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

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

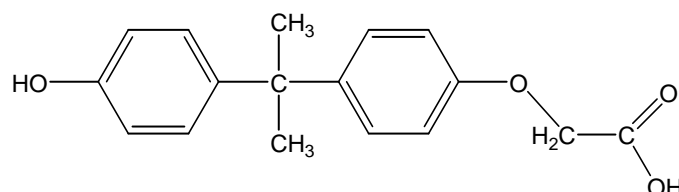
$$m_3 = m_2 \times M_2^{-1} \times M_3$$

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

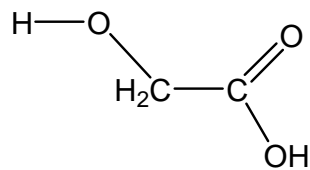
1.3

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

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



2. Alkaline hydrolysis of sodium chloroacetate:



PROBLEM 2 (Practical)

Qualitative and Quantitative Analysis of a Superconductor

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 cm^3 of perchloric acid (No. **22**) by heating the mixture. Add 5 cm^3 of demineralized water afterwards.

Cool down the solution until it is lukewarm.

Add about 5 cm^3 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 cm^3 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 cm^3 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 cm^3 . From now on this solution is called "parent solution".

2.2 *Quantitative determination of the total content of lanthanum and copper*

Transfer 25.00 cm^3 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 cm³. The *pH*-value has to be about **pH 6** before the determination, otherwise add more sodium acetate.

Titrate the solution with Na₂-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 cm³ of your parent solution (No. 13) into the 100 cm³ volumetric flask and fill up with demineralized water to a volume of 100.0 cm³. For each titration, transfer 25.00 cm³ 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 cm³ 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.

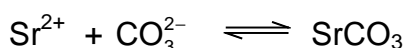
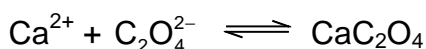
Repeat this procedure as many times as necessary.

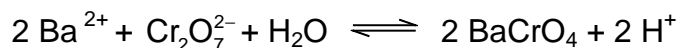
SOLUTION

2.1 Which alkaline earth metal(s) can be found in the superconductor? Mark only one box!

- | | | | | | |
|------------------|--------------------------|-----------|--------------------------|-----------|-------------------------------------|
| Ca | <input type="checkbox"/> | Sr | <input type="checkbox"/> | Ba | <input checked="" type="checkbox"/> |
| Ca and Sr | <input type="checkbox"/> | Ca and Ba | <input type="checkbox"/> | Sr and Ba | <input type="checkbox"/> |
| Ca and Sr and Ba | <input type="checkbox"/> | | | | |

Complete the following reaction equations:





2.2 Quantitative determination of the total content of lanthanum and copper.

Appropriate consumption of 0.1000 mol dm⁻³ EDTA solution: $V = 11.60 \text{ cm}^3$

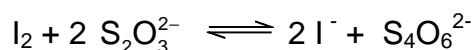
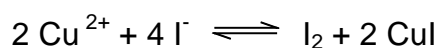
(according to 100 cm³ of superconductor solution)

2.3 Quantitative determination of the copper content.

Appropriate consumption of 0.01000 mol dm⁻³ Na₂S₂O₃ solution: $V = 10.50 \text{ cm}^3$

(according to 100 cm³ of superconductor solution)

Complete the following reaction equations:



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

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

Amount of copper:

$$10.50 \text{ cm}^3 \times 0.01 \text{ mol dm}^{-3} \times 4 \times 10 \times 63.55 \text{ g mol}^{-1} = 266.9 \text{ mg}$$

Amount of lanthanum:

$$[11.60 - (10.50 / 10 \times 4)] \text{ cm}^3 \times 0.1 \text{ mol dm}^{-3} \times 10 \times 138.91 \text{ g mol}^{-1} = 1028 \text{ mg}$$

$$\text{Mass Cu: } m(\text{Cu}) = 266.9 \text{ mg}$$

$$\text{Mass La: } m(\text{La}) = 1028 \text{ mg}$$

2.5 Assume a fictive consumption of 39.90 cm³ of 0.1000 mol dm⁻³ EDTA solution and 35.00 cm³ of 0.01000 mol dm⁻³ 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

Consumption for lanthanum = $[39.90 - (35.00/10 \times 4)] \text{ cm}^3 = 25.90 \text{ cm}^3$

Consumption for copper = $(39.90 - 25.90) \text{ cm}^3 = 14.00 \text{ cm}^3$

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

coefficient x: 1.85

formula: $\text{La}_{1.85}\text{Ba}_{0.15}\text{CuO}_4$
