

## 36<sup>th</sup> 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 <b>H</b> 1.01																	2 <b>He</b> 4.00
3 <b>Li</b> 6.94	4 <b>Be</b> 9.01											5 <b>B</b> 10.81	6 <b>C</b> 12.01	7 <b>N</b> 14.01	8 <b>O</b> 16.00	9 <b>F</b> 19.00	10 <b>Ne</b> 20.18
11 <b>Na</b> 22.99	12 <b>Mg</b> 24.31											13 <b>Al</b> 26.98	14 <b>Si</b> 28.09	15 <b>P</b> 30.97	16 <b>S</b> 32.07	17 <b>Cl</b> 35.45	18 <b>Ar</b> 39.95
19 <b>K</b> 39.10	20 <b>Ca</b> 40.08	21 <b>Sc</b> 44.96	22 <b>Ti</b> 47.88	23 <b>V</b> 50.94	24 <b>Cr</b> 52.00	25 <b>Mn</b> 54.94	26 <b>Fe</b> 55.85	27 <b>Co</b> 58.93	28 <b>Ni</b> 58.69	29 <b>Cu</b> 63.55	30 <b>Zn</b> 65.39	31 <b>Ga</b> 69.72	32 <b>Ge</b> 72.61	33 <b>As</b> 74.92	34 <b>Se</b> 78.96	35 <b>Br</b> 79.90	36 <b>Kr</b> 83.80
37 <b>Rb</b> 85.47	38 <b>Sr</b> 87.62	39 <b>Y</b> 88.91	40 <b>Zr</b> 91.22	41 <b>Nb</b> 92.91	42 <b>Mo</b> 95.94	43 <b>Tc</b> 98.91	44 <b>Ru</b> 101.07	45 <b>Rh</b> 102.91	46 <b>Pd</b> 106.42	47 <b>Ag</b> 107.87	48 <b>Cd</b> 112.41	49 <b>In</b> 114.82	50 <b>Sn</b> 118.71	51 <b>Sb</b> 121.76	52 <b>Te</b> 127.60	53 <b>I</b> 126.90	54 <b>Xe</b> 131.29
55 <b>Cs</b> 132.91	56 <b>Ba</b> 137.3	57-71	72 <b>Hf</b> 178.49	73 <b>Ta</b> 180.95	74 <b>W</b> 183.84	75 <b>Re</b> 186.21	76 <b>Os</b> 190.23	77 <b>Ir</b> 192.22	78 <b>Pt</b> 195.08	79 <b>Au</b> 196.97	80 <b>Hg</b> 200.59	81 <b>Tl</b> 204.38	82 <b>Pb</b> 207.19	83 <b>Bi</b> 208.98	84 <b>Po</b> 208.98	85 <b>At</b> 209.99	86 <b>Rn</b> 222.02
87 <b>Fr</b> 223	88 <b>Ra</b> 226	89-103	104 <b>Rf</b> 261	105 <b>Db</b> 262	106 <b>Sg</b> 263	107 <b>Bh</b> 264	108 <b>Hs</b> 265	109 <b>Mt</b> 268									
			57 <b>La</b> 138.91	58 <b>Ce</b> 140.12	59 <b>Pr</b> 140.91	60 <b>Nd</b> 144.24	61 <b>Pm</b> 144.92	62 <b>Sm</b> 150.36	63 <b>Eu</b> 151.96	64 <b>Gd</b> 157.25	65 <b>Tb</b> 158.93	66 <b>Dy</b> 162.50	67 <b>Ho</b> 164.93	68 <b>Er</b> 167.26	69 <b>Tm</b> 168.93	70 <b>Yb</b> 173.04	71 <b>Lu</b> 174.97
			89 <b>Ac</b> 227	90 <b>Th</b> 232	91 <b>Pa</b> 231	92 <b>U</b> 238	93 <b>Np</b> 237	94 <b>Pu</b> 244	95 <b>Am</b> 243	96 <b>Cm</b> 247	97 <b>Bk</b> 247	98 <b>Cf</b> 251	99 <b>Es</b> 252	100 <b>Fm</b> 257	101 <b>Md</b> 258	102 <b>No</b> 259	103 <b>Lr</b> 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 <sup>-1</sup> mol <sup>-1</sup>	Faraday constant	F = 96485 C mol <sup>-1</sup>
Use as standard pressure:	p = 1.013·10 <sup>5</sup> Pa		
Use as standard temperature:	T = 25°C = 298.15 K		
Avogadro's number	N <sub>A</sub> = 6.022·10 <sup>23</sup> mol <sup>-1</sup>	Planck constant	h = 6.626·10 <sup>-34</sup> J s
Speed of light	c = 3.00·10 <sup>8</sup> m s <sup>-1</sup>		

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

$$\Delta G = -nEF$$

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

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

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

Arrhenius equation  $k = A \cdot e^{-\frac{E_a}{R \cdot T}}$

Ideal gas law  $pV = nRT$

Nernst equation  $E = E^0 + \frac{RT}{nF} \cdot \ln \frac{c_{ox}}{c_{red}}$

Bragg's law  $n\lambda = 2d \cdot \sin \theta$

Beer- Lambert Law  $A = \log \frac{P_0}{P} = \epsilon c \cdot d$

$\rho = \frac{F}{A}$   $F = ma$

V(cylinder) =  $\pi r^2 h$   $A(\text{sphere}) = 4\pi r^2$   $V(\text{sphere}) = \frac{4}{3} \pi r^3$

1 J = 1 N m

1 N = 1 kg m s<sup>-2</sup>

1 Pa = 1 N m<sup>-2</sup>

1 W = 1 J s<sup>-1</sup>

1 C = 1 A s

## Problem 1: Thermodynamics

(24 points)

For his 18<sup>th</sup> 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,  $25.0^\circ\text{C}$ ) 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.

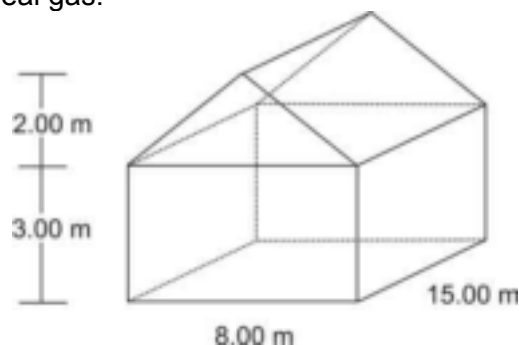
**1.2 The density of natural gas is  $0.740 \text{ g L}^{-1}$  ( $1.013 \cdot 10^5$  Pa,  $25.0^\circ\text{C}$ ) specified by PUC, the public utility company.**

**a) Calculate the amount of methane and ethane (in moles) in  $1.00 \text{ m}^3$  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  $1.00 \text{ m}^3$  of natural gas under standard conditions assuming that all products are gaseous. (If you do not have the amount from 1.2a) assume that  $1.00 \text{ m}^3$  natural gas corresponds to  $40.00 \text{ mol}$  natural gas.)**

**According to the PUC the combustion energy will be  $9.981 \text{ kWh}$  per  $\text{m}^3$  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  $3.00 \text{ m}$  wide,  $5.00 \text{ m}$  long and  $1.50 \text{ m}$  deep (below the floor). The tap water temperature is  $8.00^\circ\text{C}$  and the air temperature in the house (dimensions given in the figure below) is  $10.0^\circ\text{C}$ . 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 O<sub>2</sub>, 79.0% of N<sub>2</sub>) to 30.0°C at a pressure of 1.013·10<sup>5</sup> 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<sup>-1</sup> m<sup>-1</sup>.

**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 m<sup>3</sup> 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 <sup>-1</sup> ) <sup>-1</sup>	$S^0$ (J mol <sup>-1</sup> K <sup>-1</sup> ) <sup>-1</sup>	$C_p^0$ (J mol <sup>-1</sup> K <sup>-1</sup> ) <sup>-1</sup>
CO <sub>2</sub> (g)	0.0024	-393.5	213.8	37.1
N <sub>2</sub> (g)	0.0134	0.0	191.6	29.1
CH <sub>4</sub> (g)	0.9732	-74.6	186.3	35.7
C <sub>2</sub> H <sub>6</sub> (g)	0.0110	-84.0	229.2	52.5
H <sub>2</sub> O (l)	-	-285.8	70.0	75.3
H <sub>2</sub> O (g)	-	-241.8	188.8	33.6
O <sub>2</sub> (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  $\Delta t$

$d$  wall thickness

$\lambda_{\text{wall}}$  heat conductivity

$\Delta T$  difference in temperature between the inside and the outside of the house

## Problem 2: Kinetics at catalyst surfaces

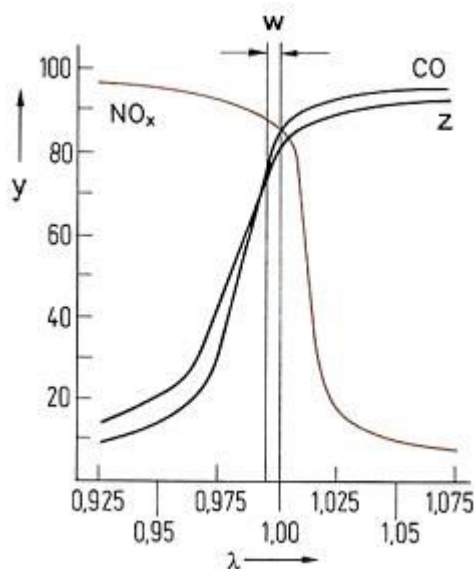
(23 points)

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  $\lambda$ -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:  $\lambda$ -window  
y: conversion efficiency (%)  
z: Hydrocarbons

### 2.2 Decide the questions on the answer sheet concerning the $\lambda$ 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  $\theta$  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  $K = 0.85 \text{ kPa}^{-1}$ .

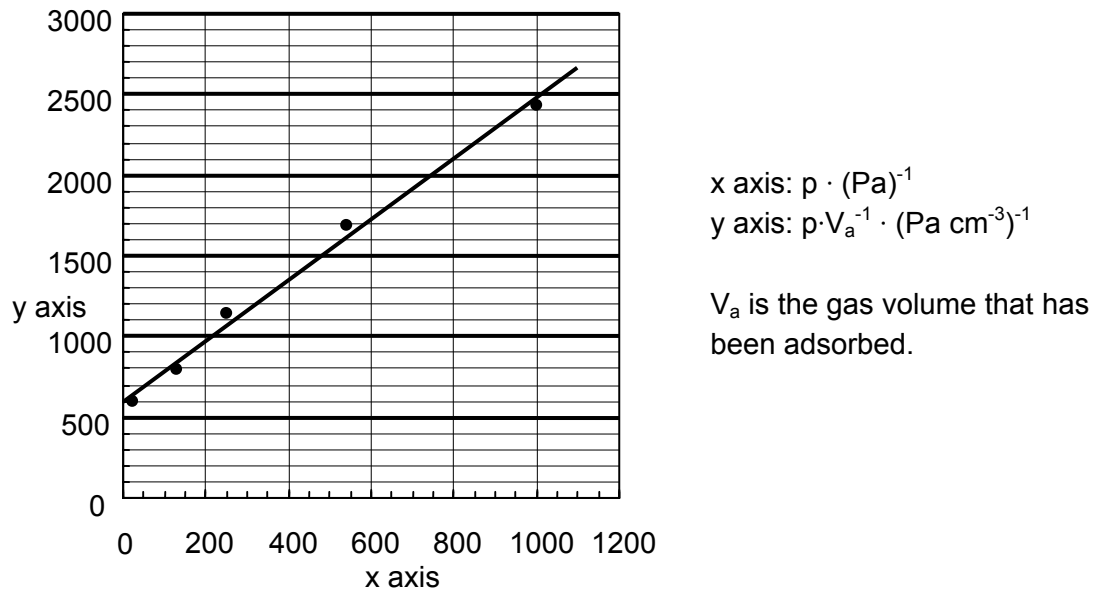
2.3 a) Determine the surface coverage  $\theta$  at a pressure of 0.65 kPa.

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  $\theta$  (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)

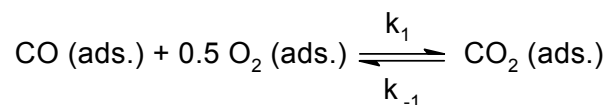


**If the Langmuir isotherm can be applied, determine the gas volume  $V_{a,max}$  needed for a complete coverage of the metal surface and the product  $K \cdot V_{a,max}$ .**

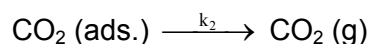
**Hint: Set  $\theta = V_a / V_{a,max}$ .**

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  $CO_2(g)$  - 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  $\text{CaCl}_2$  to  $\text{CaCl}$  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  $\text{CaCl}$ .**

After an attempt to reduce  $\text{CaCl}_2$  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  $\text{CaCl}_2$  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  $\text{CaCl}_2$  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  $\text{Mg}_2\text{C}_3$ .

**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  $\text{CaCl}_2$  with carbon?**

**(Provided that monovalent calcium does not exist.)**

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

It is the radius ratio of cation  $r(\text{M}^{m+})$  and anion  $r(\text{X}^{x-})$  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 $\Delta_L H^0$ for CaCl
3	Triangular	0.155-0.225	BN	- 663.8 kJ mol <sup>-1</sup>
4	Tetrahedral	0.225-0.414	ZnS	- 704.8 kJ mol <sup>-1</sup>
6	Octahedral	0.414-0.732	NaCl	- 751.9 kJ mol <sup>-1</sup>
8	Cubic	0.732-1.000	CsCl	- 758.4 kJ mol <sup>-1</sup>

$\Delta_L H^0(\text{CaCl})$  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?**

[ $r(\text{Ca}^+) \approx 120$  pm (estimated),  $r(\text{Cl}^-) \approx 167$  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 <sup>-1</sup>
ionization enthalpy	$\Delta_{1. \text{IE}} H(\text{Ca})$	$\text{Ca} \longrightarrow \text{Ca}^+$	589.7 kJ mol <sup>-1</sup>
ionization enthalpy	$\Delta_{2. \text{IE}} H(\text{Ca})$	$\text{Ca}^+ \longrightarrow \text{Ca}^{2+}$	1145.0 kJ mol <sup>-1</sup>
heat of vaporization	$\Delta_{\text{vap}} H^0(\text{Ca})$		150.0 kJ mol <sup>-1</sup>
dissociation energy	$\Delta_{\text{diss}} H(\text{Cl}_2)$	$\text{Cl}_2 \longrightarrow 2 \text{Cl}$	240.0 kJ mol <sup>-1</sup>
enthalpy of formation	$\Delta_f H^0(\text{CaCl}_2)$		-796.0 kJ mol <sup>-1</sup>
electron affinity	$\Delta_{\text{EA}} H(\text{Cl})$	$\text{Cl} + \text{e}^- \longrightarrow \text{Cl}^-$	- 349.0 kJ mol <sup>-1</sup>

To decide whether CaCl is thermodynamically stable to disproportionation into Ca and CaCl<sub>2</sub> the standard enthalpy of this process has to be calculated. (The change of the entropy  $\Delta S$  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  $\text{Ag}_2\text{S}$  and  $\text{H}_2\text{S}$ . 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 ( $\text{cm}^{-1}$ )
c	speed of light
k	force constant, indicating the strength of the bond ( $\text{N m}^{-1} = \text{kg s}^{-2}$ )
$\mu$	reduced mass in $\text{AB}_4$ , 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  $3030.00 \text{ cm}^{-1}$ . The vibrational frequency of the Z-analogue of methane is known to be  $2938.45 \text{ cm}^{-1}$ . 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.**

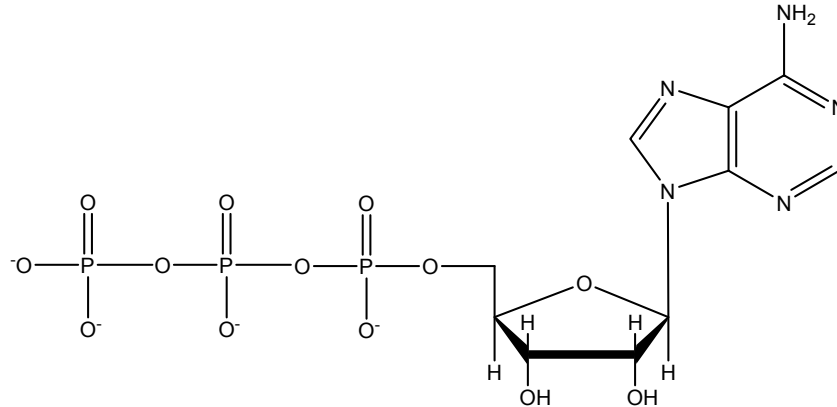
**Determine the atomic mass of Z from this information.**

**Give the chemical symbol of Z**

## Problem 5: Biochemistry with Thermodynamics

(18 points)

### Structure of ATP<sup>4-</sup>



### 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:

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

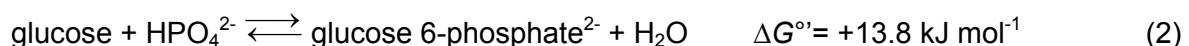
Free energy stored in ATP can be released according to the following reaction:



As the pH is close to 7 in most living cells, biochemists use  $\Delta G^{\circ'}$  instead of  $\Delta G^{\circ}$ . 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  $\text{H}^+$  is therefore omitted. Standard concentration is  $1 \text{ mol L}^{-1}$ .

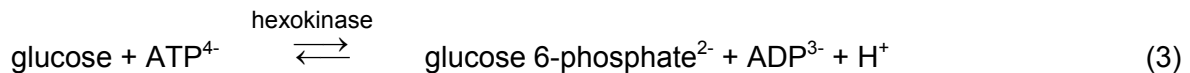
#### 5.1 Calculate the actual $\Delta G'$ of reaction (1) in the red blood cell at 25°C and pH = 7.

In living cells many so-called “anabolic” reactions take place, which are at first sight thermodynamically unfavourable because of a positive  $\Delta G$ . 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  $\text{pH} = 7$ .**

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  $\text{pH} = 7$ ?**

### 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  $-52 \text{ kJ mol}^{-1}$  for reaction (1), and a molecular weight of  $503 \text{ g mol}^{-1}$  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.**

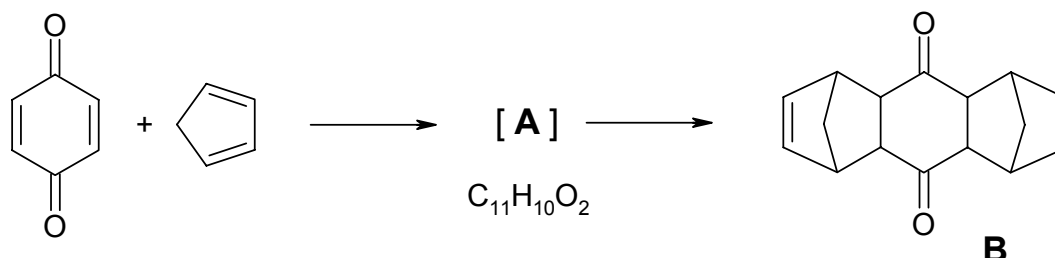
In animals the energy obtained by the oxidation of food is used to pump protons out of specialized membrane vesicles, the mitochondria. ATP-synthase, an enzyme, will allow protons to re-enter the mitochondria if ATP is simultaneously synthesized from ADP and phosphate.

- 5.5 a) How many protons ( $\text{H}^+$ ) are in a spherical mitochondrion with a diameter of  $1 \mu\text{m}$  at  $\text{pH} = 7$ ?**
- 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

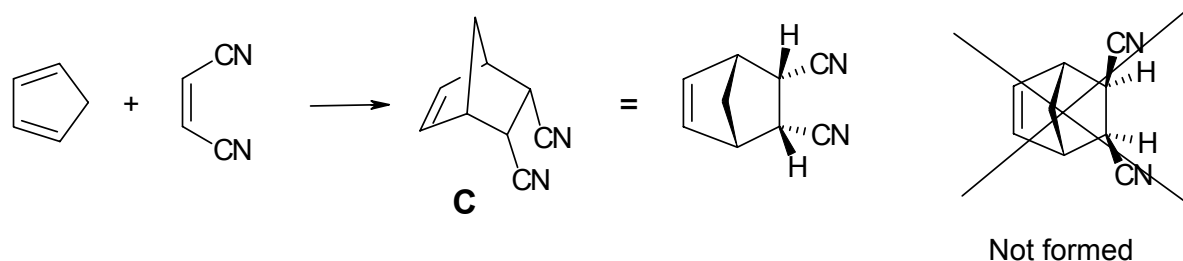
(20 points)

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



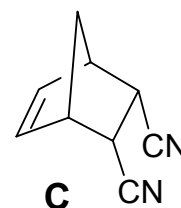
If you use the *E*-isomer of the alkene instead, you will obtain two other stereoisomers **D1** and **D2**.

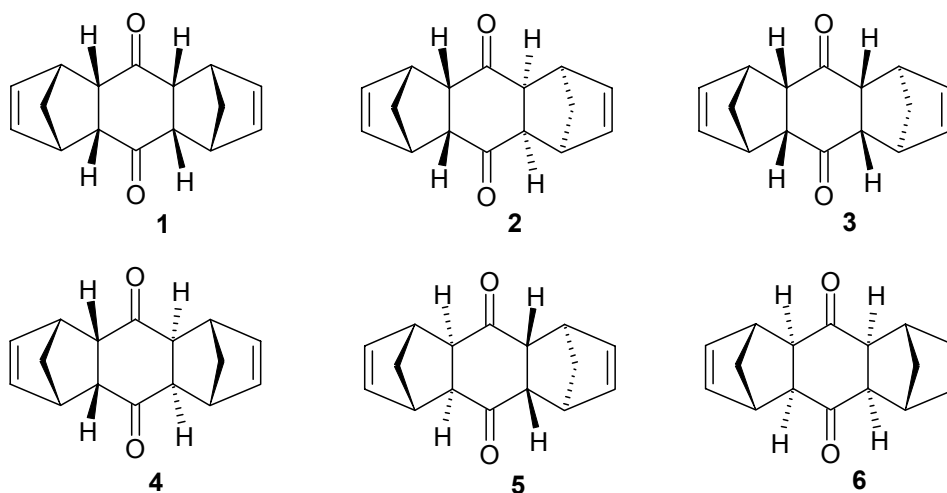
**6.2 Give the structures of D1 and D2.**

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:

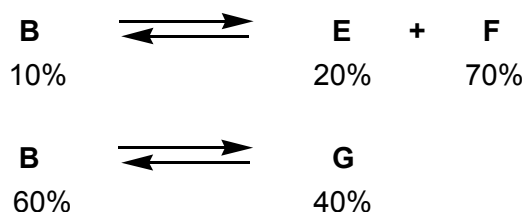
- keep the stereospecific formation of **C** in mind and
- the sterically less hindered isomer forms.





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

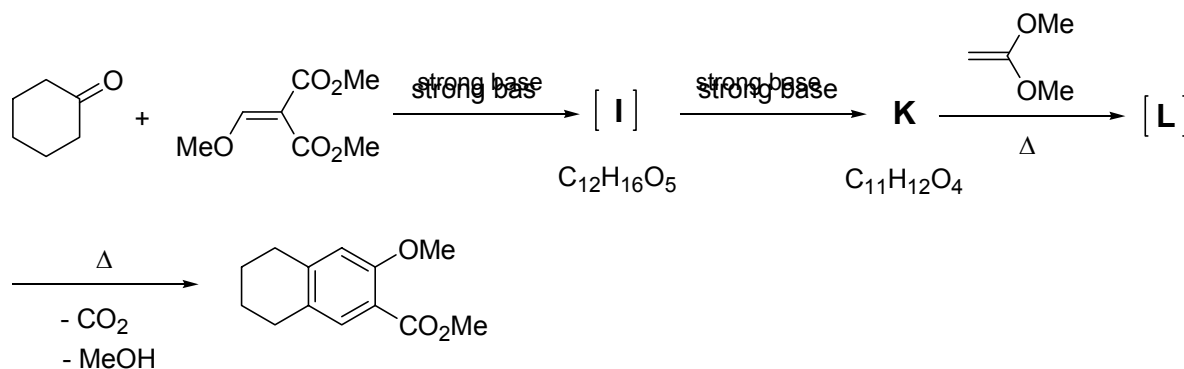
After prolonged heating (15h, 120°C) of the originally isolated stereoisomer **B** (melting point mp: 157°C), Diels and Alder obtained two new stereoisomers **E** (mp: 153°C) and **F** (mp: 163°C). Equilibration of **B** with a catalytic amount of a strong base at 25°C gave a further stereoisomer **G**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

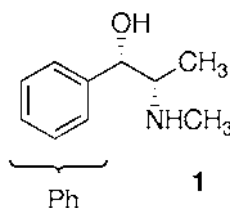
## Problem 7: Stereochemistry in Drugs

(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.



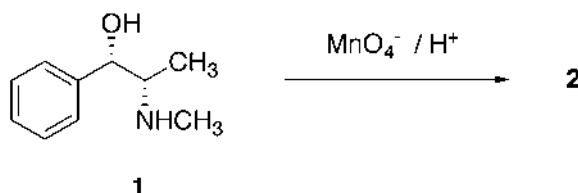
**7.2 Mark the stereocenters in 1 with an \* on the answer sheet.**

**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.**

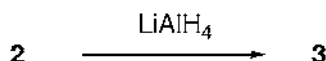
**Draw a Fischer representation of 1.**

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  $\text{LiAlH}_4$  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  $\text{CaCl}_2$  with a concentration of  $1.780 \text{ g L}^{-1}$ .

Solution B is an aqueous solution of  $\text{Na}_2\text{CO}_3$  with a concentration of  $1.700 \text{ g L}^{-1}$ .

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

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

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

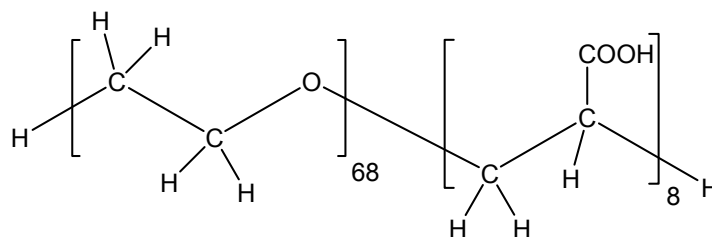
100 mL of solution A and 100 mL of solution B are mixed to form solution C. Solution C is adjusted to pH 10. A precipitate forms.

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

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

**8.2 Show by calculation for each of the compounds  $\text{Ca}(\text{OH})_2$  and  $\text{CaCO}_3$  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).

$$(\text{p}K_a(\text{COOH, copolymer}) = 4.88)$$

**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.*

<b>Modification</b>	<b>density</b>
Calcite	$2.71 \text{ g cm}^{-3}$
Vaterite	$2.54 \text{ g cm}^{-3}$
Aragonite	$2.95 \text{ g cm}^{-3}$