

40th International
Chemistry Olympiad

Theoretical Problems

17 July 2008

Budapest, Hungary

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Instructions

- Write your name and code on each page.
- You have 5 hours to work on the problems. Begin only when the START command is given.
- Use only the pen and calculator provided.
- All results must be written in the appropriate boxes. Anything written elsewhere will not be graded. Use the reverse of the sheets if you need scratch paper.
- Write relevant calculations in the appropriate boxes when necessary. If you provide only correct end results for complicated problems, you receive no score.
- When you have finished the examination, you must put your papers into the envelope provided. Do not seal the envelope.
- You must stop your work immediately when the STOP command is given. A delay in doing this by 3 minutes may lead to cancellation of your exam.
- Do not leave your seat until permitted by the supervisors.
- This examination has 26 pages.
- The official English version of this examination is available on request only for clarification.

Constants and Formulae

Avogadro constant:	$N_A = 6.022 \cdot 10^{23} \text{ mol}^{-1}$	Ideal gas equation:	$pV = nRT$
Gas constant:	$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$	Gibbs energy:	$G = H - TS$
Faraday constant:	$F = 96485 \text{ C mol}^{-1}$	$\Delta_r G^\circ = -RT \ln K = -nFE_{\text{cell}}^\circ$	
Planck constant:	$h = 6.626 \cdot 10^{-34} \text{ J s}$	Nernst equation:	$E = E^\circ + \frac{RT}{zF} \ln \frac{c_{\text{ox}}}{c_{\text{red}}}$
Speed of light:	$c = 3.000 \cdot 10^8 \text{ m s}^{-1}$	Energy of a photon:	$E = \frac{hc}{\lambda}$
Zero of the Celsius scale:	273.15 K	Lambert-Beer law:	$A = \log \frac{I_0}{I} = \varepsilon cl$

In equilibrium constant calculations all concentrations are referenced to a standard concentration of 1 mol/dm^3 . Consider all gases ideal throughout the exam.

Periodic table with relative atomic masses

1 H 1.008																	18 He 4.003
3 Li 6.94	4 Be 9.01											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.30	3	4	5	6	7	8	9	10	11	12	13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.87	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.38	31 Ga 69.72	32 Ge 72.64	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.96	43 Tc -	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.90	54 Xe 131.29
55 Cs 132.91	56 Ba 137.33	57-71	72 Hf 178.49	73 Ta 180.95	74 W 183.84	75 Re 186.21	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po -	85 At -	86 Rn -
87 Fr -	88 Ra -	89-103	104 Rf -	105 Db -	106 Sg -	107 Bh -	108 Hs -	109 Mt -	110 Ds -	111 Rg -							

57 La 138.91	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm -	62 Sm 150.36	63 Eu 151.96	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.05	71 Lu 174.97
89 Ac -	90 Th -	91 Pa -	92 U -	93 Np -	94 Pu -	95 Am -	96 Cm -	97 Bk -	98 Cf -	99 Es -	100 Fm -	101 Md -	102 No -	103 Lr -

-	232.0 4	231.0 4	238.0 3	-	-	-	-	-	-	-	-	-	-	-
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Problem 1

total

6% of the

1a	1b	1c	1d	Task 1
4	2	8	8	22

The label on a bottle containing a dilute aqueous solution of an acid became damaged. Only its concentration was readable. A pH meter was nearby, and a quick measurement showed that the hydrogen ion concentration is equal to the value on the label.

- a) Give the formulae of four acids that could have been in the solution if the pH changed one unit after a tenfold dilution.

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Any univalent, strong acid (HCl, HBr, HI, HNO₃, HClO₄) is acceptable. HF is not!

- b) Could it be possible that the dilute solution contained sulfuric acid?

Sulfuric acid: $pK_{a2} = 1.99$

Yes No

If yes, calculate the pH (or at least try to estimate it) and show your work.

No, the first dissociation step can be regarded as complete in aqueous solutions, thus $[H^+] > C_{acid}$.

2 points are given for 'No'.

No text or calculations are needed later, and no pts will be given here.

pH:

Name:

Code: XXX-

c) Could it be possible that the solution contained acetic acid?

Acetic acid: $pK_a = 4.76$

Yes No

If yes, calculate the pH (or at least try to estimate it) and show your work.

Yes, but only in quite dilute solutions can this happen. 1 pt for ticking yes

$$c = [\text{HA}] + [\text{A}^-] = [\text{H}^+] \quad (1 \text{ pt})$$

$$[\text{H}^+] = [\text{A}^-] + [\text{OH}^-] \quad (1 \text{ pt})$$

This means that $[\text{HA}] = [\text{OH}^-]$

Formula:

$$K = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = \frac{[\text{H}^+]([\text{H}^+] - [\text{OH}^-])}{[\text{OH}^-]} = \frac{[\text{H}^+]^3}{K_w} - [\text{H}^+] \quad (2 \text{ pt})$$

} a sum of 4 pts

The pH of the solution must be acidic, but close to 7.

6.5 is a good guess. (1 pt for reasonable guess – between 6 and 7)

A good approximation is: $[\text{H}^+] = \sqrt[3]{(KK_w)}$

The full equation can be solved through iteration: $[\text{H}^+] = \sqrt[3]{(K + [\text{H}^+])K_w}$

Starting with a neutral solution two cycles of iteration give identical results:

$5.64 \cdot 10^{-7} \text{ mol/dm}^3$ as the required concentration. Exact pH is 6.25. 3 pts

pH:

Name:

Code: XXX-

- d) Could it be possible that the solution contained EDTA (ethylene diamino tetraacetic acid)? You may use reasonable approximations.

EDTA: $pK_{a1} = 1.70$, $pK_{a2} = 2.60$, $pK_{a3} = 6.30$, $pK_{a4} = 10.60$

Yes No

If yes, calculate the concentration.

Yes (1 pt)

We can suppose that this solution would be quite acidic, so the 3rd and 4th dissociation steps can be disregarded. (1 pt) The following equations are thus true:

$$c = [H_4A] + [H_3A^-] + [H_2A^{2-}] = [H^+] \quad (1 \text{ pt})$$

$$[H^+] = [H_3A^-] + 2[H_2A^{2-}] \quad (1 \text{ pt})$$

This means that $[H_4A] = [H_2A^{2-}]$ (1 pt)

$$K_1 K_2 = \frac{[H^+]^2 [H_2A^{2-}]}{[H_4A]} = [H^+]^2 \quad (\text{or } \text{pH} = (\text{p}K_1 + \text{p}K_2) / 2 = 2.15) \quad (2 \text{ pts})$$

$$c = 0.0071 \text{ mol/dm}^3 \quad (1 \text{ pt})$$

©EDTA:

Name:

Code: XXX-

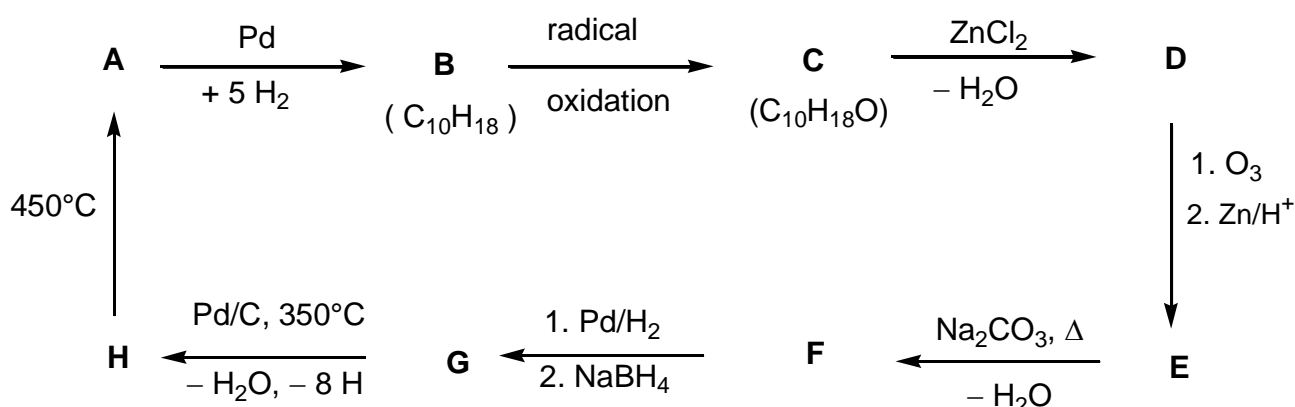
Problem 2

total

7% of the

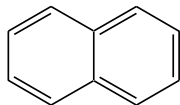
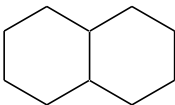
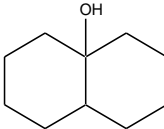
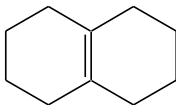
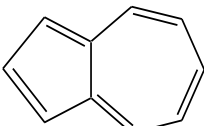
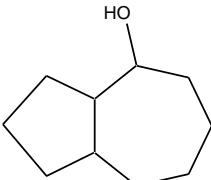
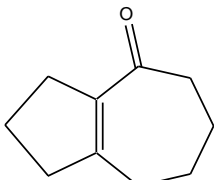
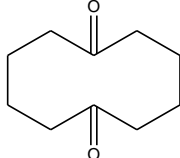
Task 2
18

Determine the structure of the compounds **A-H** (stereochemistry is not expected), based on the information given in the following reaction scheme:



Hints:

- **A** is a well-known aromatic hydrocarbon.
- A hexane solution of **C** reacts with sodium (gas evolution can be observed), but **C** does not react with chromic acid.
- ^{13}C NMR spectroscopy shows that **D** and **E** contain only two kinds of CH_2 groups.
- When a solution of **E** is heated with sodium carbonate an unstable intermediate forms at first, which gives **F** on dehydration.

A 	B 	C 	D 
H 	G 	F 	E 

2 pts each, 4 pts for **F**

Name:

Code: XXX-

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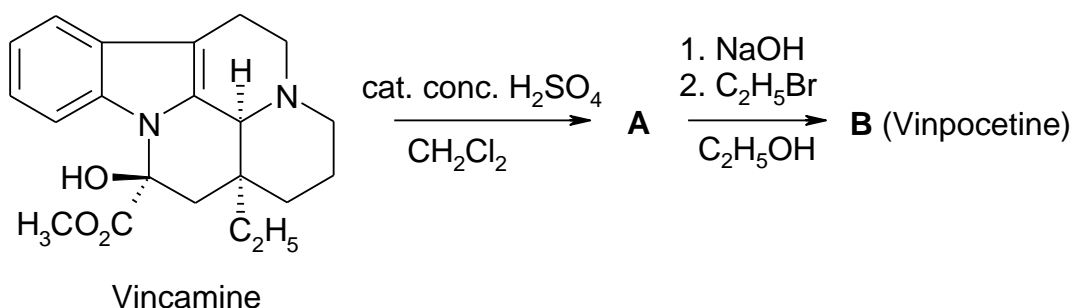
Problem 3

total

6% of the

3a	3b	3c	Task 3
4	8	2	14

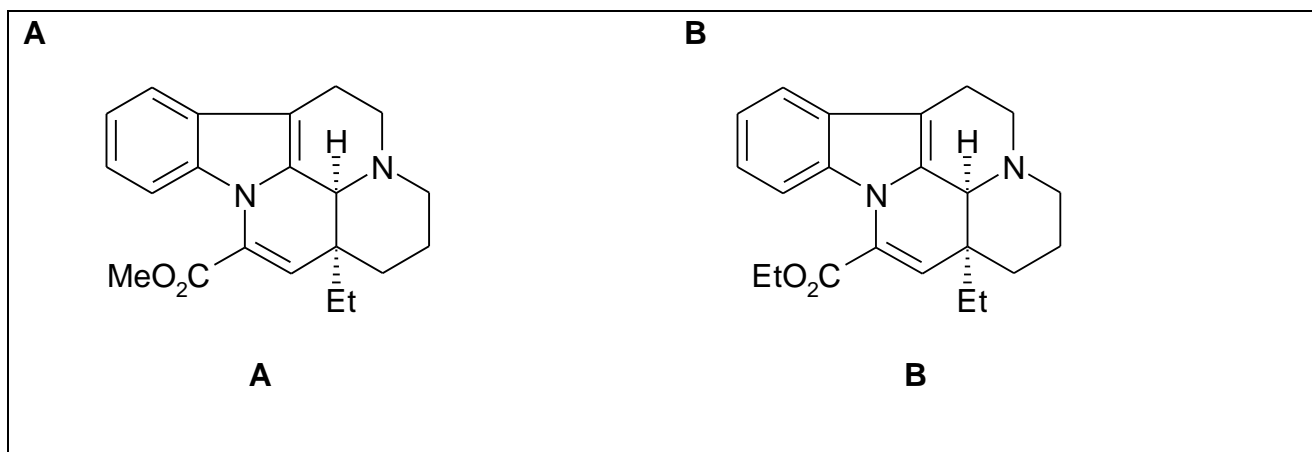
Vinpocetine (Cavinton®, Calan®) is one of the best selling original drugs developed in Hungary. Its preparation relies on a natural precursor, (+)-vincamine ($C_{21}H_{26}N_2O_3$), which is isolated from the vine plant, *vinca minor*. The transformation of (+)-vincamine to vinpocetine is achieved in two steps depicted below.



All compounds (**A** to **F**) are enantiomerically pure compounds.

- The elementary composition of **A** is: C 74.97%, H 7.19%, N 8.33%, O 9.55%.
- **B** has 3 other stereoisomers.

a) Propose structures for the intermediate **A** and vinpocetine (**B**).



A study of the metabolism of any drug forms a substantial part of its documentation. There are four major metabolites each formed from vinpocetine (**B**): **C** and **D** are formed in hydrolysis or hydration reactions, while **E** and **F** are oxidation products.

Name:

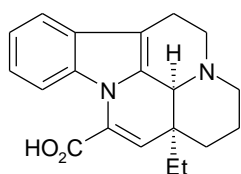
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Hints:

- The acidity of the metabolites decreases in the order **C** >> **E** >> **D**. **F** does not contain an acidic hydrogen.
- **C** and **E** each have 3 other stereoisomers, while **D** and **F** each have 7 other stereoisomers.
- **F** is a pentacyclic zwitterion and it has the same elementary analysis as **E**:
C 72.11%, H 7.15%, N 7.64%, O 13.10%.
- The formation of **E** from **B** follows an electrophilic pattern.
- The formation of **D** from **B** is both regio- and stereoselective.

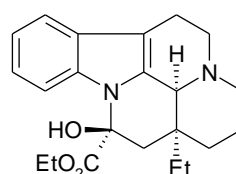
b) Propose one **possible** structure for each of the metabolites **C**, **D**, **E** and **F**!

C



C apovincaminic acid

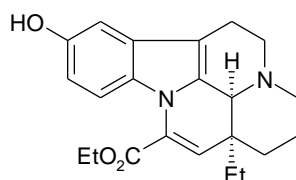
D



D ethyl vincamate

Both stereoisomers around the new chiral center are acceptable.

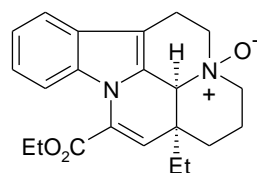
E



E 10-hydroxyvinpocetine

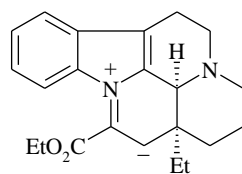
All aromatic positions for the OH are acceptable in **E**.

F



F vinpocetine N-oxide

c) Draw a resonance structure for **B** that explains the regioselective formation of **D** and the absence of the alternate regioisomer in particular.



Problem 4

total

6% of the

4a	4b	4c	4d	4e	Task 4
6	2	6	8	6	28

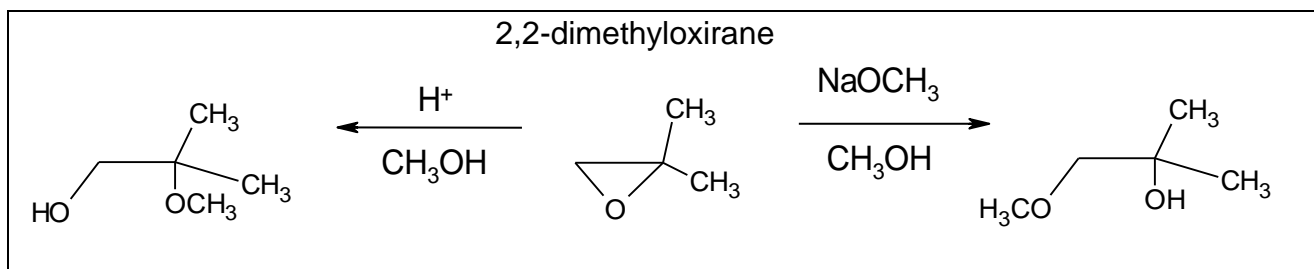
A major transformation route for oxiranes (epoxides) is ring opening. This may be accomplished in various ways.

On acid catalysis the reactions proceed through cation-like (carbenium ion-like) species. For substituted oxiranes the direction of ring opening (which C–O bond is cleaved) depends on the stability of the intermediate carbenium ion. The more stable the intermediate carbenium ion the more probable its formation. However, an open carbenium ion (with a planar structure) only forms if it is tertiary, benzylic or allylic.

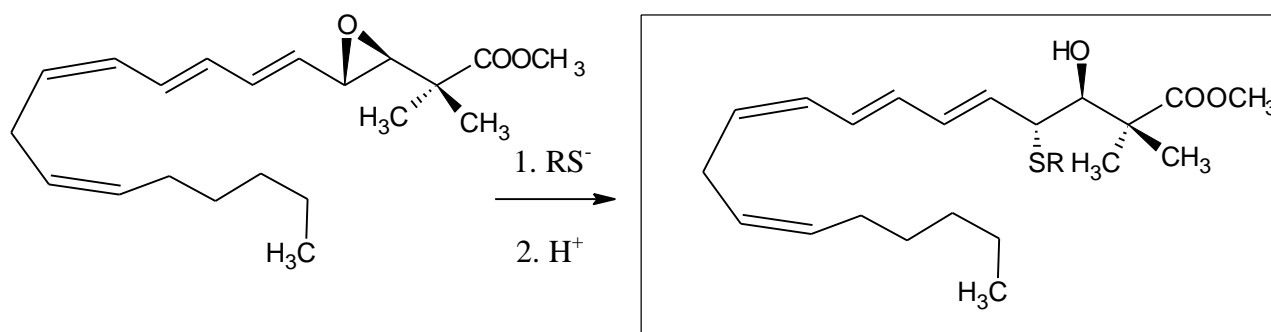
On base catalysis the sterically less hindered C–O bond is cleaved predominantly.

Keep stereochemistry in mind throughout the whole problem. To depict stereochemistry use only the \blacktriangleleft \cdots — bond symbols and nothing else where necessary.

- a) Draw the structure of the reactant and the predominant products when 2,2-dimethyloxirane (1,2-epoxy-2-methylpropane) reacts with methanol at low temperatures, catalysed by
- sulfuric acid
 - NaOCH_3 .



- b) Draw the structure of the predominant product when the epoxide ring of the following leukotriene derivative is opened with a thiolate (RS^-).



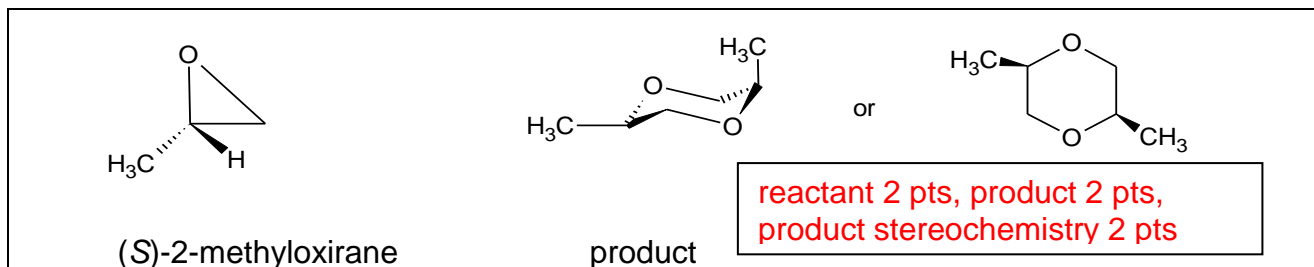
Different porous **acidic** aluminosilicates can also be used to catalyse the transformation of alkyl oxiranes. In addition to ring opening, cyclic dimerisation is found to be the main

Name:

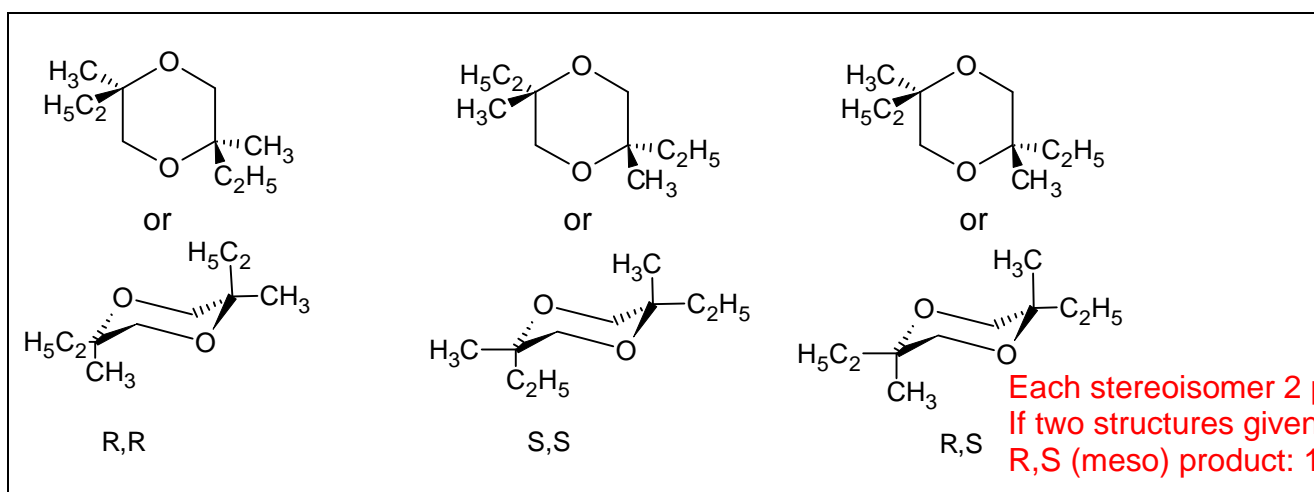
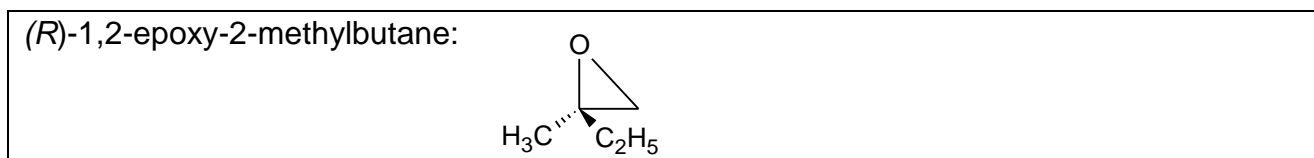
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reaction pathway producing mainly 1,4-dioxane derivatives (six-membered saturated rings with two oxygen atoms in positions 1,4).

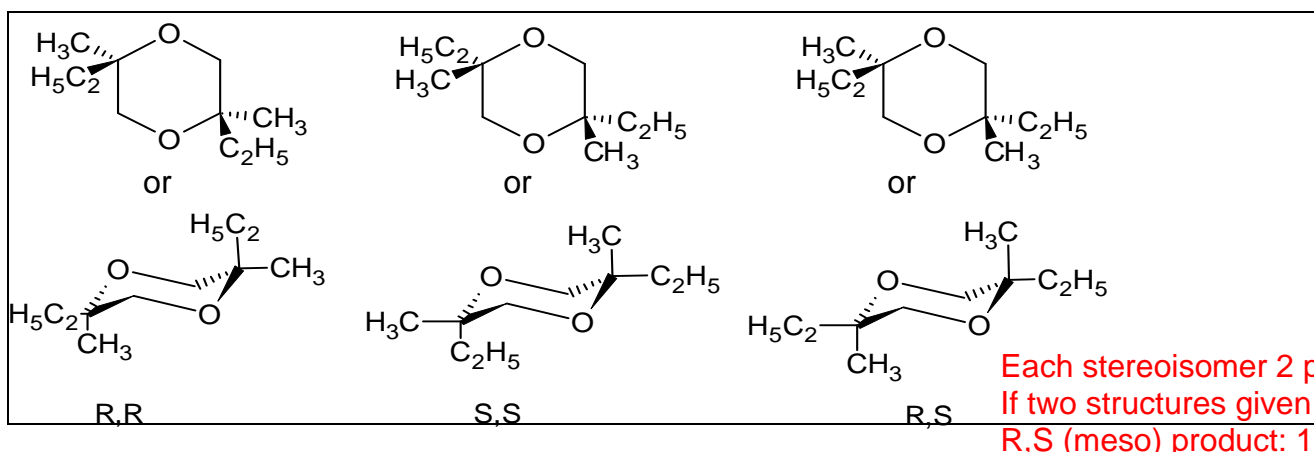
- c) Draw the structure(s) of the most probable 1,4-dioxane derivative(s) when the starting compound is (*S*)-2-methyloxirane ((*S*)-1,2-epoxypropane). Give the structure of the reactant as well.



- d) Draw the structure(s) of the substituted 1,4-dioxane(s) when the epoxide reacting is (*R*)-1,2-epoxy-2-methylbutane ((*R*)-2-ethyl-2-methyloxirane). Give the structure of the reactant as well.



- e) Give the structure(s) of the substituted 1,4-dioxane(s) when this reaction is carried out with racemic 1,2-epoxy-2-methylbutane (2-ethyl-2-methyloxirane).



Name:

Code: XXX-

Problem 5

total

7% of the

5a	5b	Task 5
67	33	100

A and **B** are white crystalline substances. Both are highly soluble in water and can be moderately heated (up to 200 °C) without change but both decompose at higher temperatures. If an aqueous solution of 20.00 g **A** (which is slightly basic, pH ≈ 8.5-9) is added to an aqueous solution of 11.52 g **B** (which is slightly acidic, pH ≈ 4.5-5) a white precipitate **C** forms that weighs 20.35 g after filtering, washing and drying. The filtrate is essentially neutral and gives a brown colour reaction with an acidified KI solution. When boiled, the filtrate evaporates without the appearance of any residue.

The white solid **D** can be prepared by the heating of **A** in the absence of air. The exothermic reaction of **D** with water gives a colourless solution. This solution, if kept in an open container, slowly precipitates a white solid **E** and leaves water. Upon prolonged exposure to air at room temperature, solid **D** is transformed into **E** as well. However, heating **D** in air at 500 °C produces a different white substance **F**, which is barely soluble in water and has a mass of only 85.8% of the **E** formed from the same amount of **D**. **F** gives a brown colour reaction with an acidified solution of KI.

E can be converted back into **D** but ignition above 1400 °C is required for this purpose. The reaction of **B** and **D** in water forms the precipitate **C** and is accompanied by a characteristic odour.

a) Give the formulae of the substances A - F

A	Ba(NO₂)₂ 8 pts	B	(NH₄)₂SO₄ 8 pts	C	BaSO₄ 4 pts	25 bonus points if both A and B are identified correctly.
D	BaO 4 pts	E	BaCO₃ 4 pts	F	BaO₂ 14 pts	

b) Write balanced equations for all the reactions mentioned. (The equation for the thermal decomposition of **B** is not required.)

Equations:

Suggestions for the treatment of some errors:

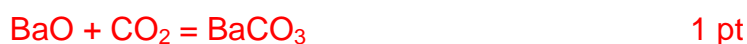
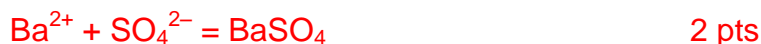
If the student chooses Ca or Sr for the cation in **A**, the solution may be qualitatively partly correct but it contradicts the stoichiometric data. In this case the student loses the points for the Ba containing species but gets full points for all otherwise correct equations, with the obvious exception of the peroxide formation. The choice of any other metal nullifies the points for all formulae and equations featuring the metal. The choice of HPO₄²⁻ for the anion of **B** is treated similarly. Minor errors in the equations (charges, coefficients etc.) will be penalized with 1p each (but obviously no negative score for any item).

Name:

Code: XXX-



(Remark: NH_4HSO_4 boils without further decomposition at 490°C . This is not a widely taught fact and its knowledge cannot be expected from the students.)



Detailed solution:

The problem contains quite a number of clues to the identification of the compounds. It is clear that **A**, **D**, **E**, and **F** all contain the same element; with a water-soluble solid compound stable at 1400°C , probably a metal. The aqueous solution of a metal compound giving a precipitate and pure water upon standing in the air strongly hints at the formation of a carbonate, possibly from a soluble hydroxide. A likely conclusion is that **D** is an oxide, limiting the choice of the metal to Sr or Ba. (One might also consider Li, Ca, or Tl which are less satisfactory because $\text{Ca}(\text{OH})_2$ is poorly soluble while the solubilities of Li_2CO_3 and Tl_2CO_3 are quite significant.) If **E** is an alkaline earth metal carbonate, then the molar mass of **F** could be either $M_{\text{Ca}} + 45.8$, or $M_{\text{Sr}} + 39.05$, or $M_{\text{Ba}} + 32$. Since **F** is formed by heating the oxide in air, the former two do not make any sense while the latter is consistent with BaO_2 . This is confirmed by the oxidative capability of **F**.

The odour appearing in the reaction of **B** with $\text{Ba}(\text{OH})_2$ indicates that the former might be an ammonium salt. Assuming that the reaction of **A** and **B** is a simple precipitation between a barium salt and an ammonium salt, we get an equivalent mass of 48 for the anion of the precipitate. This might be either SO_4^{2-} or HPO_4^{2-} but the acidity of **B** is consistent with the former and, in addition, $(\text{NH}_4)_2\text{HPO}_4$ would not give the same BaHPO_4 precipitate with $\text{Ba}(\text{OH})_2$ as with $\text{Ba}(\text{NO}_2)_2$. If we accept that **B** is $(\text{NH}_4)_2\text{SO}_4$, we obtain an equivalent mass of 46 for the anion of **A**. This and the surrounding chemistry are consistent with the nitrite ion.

Problem 6

total

7% of the

6a	6b	6c	6d	6e	6f	6g	Task 6
3	5	3	6	6	12	10	45

A feathery, greenish solid precipitate can be observed if chlorine gas is bubbled into water close to its freezing point. Similar precipitates form with other gases such as methane and noble gases. These materials are interesting because vast quantities of the so-called methane-hydrates are supposed to exist in nature (comparable in quantity with other natural gas deposits).

These precipitates all have related structures. The molecules of water just above its freezing point form a hydrogen-bonded structure. The gas molecules stabilize this framework by filling in the rather large cavities in the water structure forming clathrates.

The crystals of chlorine and methane clathrates have the same structure. Their main characteristics are dodecahedra formed from 20 water molecules. The unit cell of the crystal can be thought as a body-centered cubic arrangement built from these dodecahedra which are almost spherical objects. The dodecahedra are connected via additional water molecules located on the faces of the unit cell. Two water molecules can be found on each face of the unit cell. The unit cell has an edge dimension of 1.182 nm.

There are two types of cavities in this structure. One is the internal space in the dodecahedra (**A**). These are somewhat smaller than the other type of voids (**B**), of which there are 6 for each unit cell.

- a) How many type **A** cavities can be found in a unit cell?

2

- b) How many water molecules are there in a unit cell?

$46 = 20 \times 2$ (dodecahedra) + $6 \times 2 / 2$ (faces)

- c) If all cavities contain a guest molecule, what is the ratio of the number of water to the number of guest molecules?

$46:8 = 5.75$

- d) Methane hydrate is formed with the structure in **c**) at temperatures between 0-10 °C. What is the density of the clathrate?

A unit cell has a volume of $1.182^3 \text{ nm}^3 = 1.651 \text{ nm}^3$. 2 pt
 It contains 8 methane and 46 water molecules with a mass of $957 \text{ g mol}^{-1} / N_A = 1.589 \cdot 10^{-21} \text{ g}$. 2 pt
 The density is $1.589 / 1.651 = 0.962 \text{ g/cm}^3$. 2 pt

Name:

Code: XXX-

Density:

- e) The density of chlorine hydrate is 1.26 g/cm^3 . What is the ratio of the number of water and guest molecules in the crystal?

The mass of a unit cell with this density is: $1.651 \text{ nm}^3 \cdot 1.26 \text{ g/cm}^3 = 2.081 \cdot 10^{-21} \text{ g}$, meaning 1253 g/mol for the contents.

Subtracting the waters, this means 424.3 g/mol for the chlorine atoms, giving 11.97 chlorine atoms in a unit cell. 2 pts

The ratio is then 6 (5.98) chlorine molecules for the 46 waters, or a ratio of 7.68. 1 pts

It is expected that only the 6 larger B type cavities contain chlorine. 3 pts

Ratio:

Which cavities are likely to be filled in a perfect chlorine hydrate crystal? Mark one or more.

- Some **A** Some **B** All **A** All **B**

Covalent radii reflect atomic distances when the atoms are covalently bonded. Nonbonded or van der Waals radii give a measure of the atomic size when they are not bonded covalently (modeled as hard spheres).

Atom	Covalent radius (pm)	Nonbonded radius (pm)
H	37	120
C	77	185
O	73	140
Cl	99	180

Name:

Code: XXX-

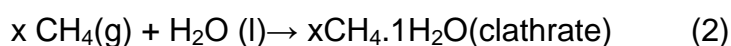
- f) Based on the covalent and nonbonded radii of these atoms estimate lower and upper bounds for the average radii of the cavities where possible. Show your reasoning.

Methane fits in both cavities, its radius is appr. $37 + 77 + 120 \text{ pm} = 234 \text{ pm}$. 3 pts
 The chlorine molecule, with a radius of $180 + 99 \text{ pm} = 279 \text{ pm}$, fits only in **B**. 3 pts
 Thus $234 \text{ pm} < r(\mathbf{A}) < 279 \text{ pm}$ and $279 \text{ pm} < r(\mathbf{B})$
 2 pts 2 pts 2 pts

$< r(\mathbf{A}) <$

$< r(\mathbf{B})$

Let us consider the following processes



- g) What are the signs of the following molar quantities referring to these reactions in the given direction at $4 \text{ }^\circ\text{C}$? Mark with a -, 0 or +.

	sign
$\Delta G_m(1)$	
$\Delta G_m(2)$	
$\Delta H_m(1)$	
$\Delta H_m(2)$	
$\Delta S_m(1)$	
$\Delta S_m(2)$	
$\Delta S_m(2) - \Delta S_m(1)$	
$\Delta H_m(2) - \Delta H_m(1)$	

+, -, -, -, -, -, -, -,

Under these conditions, methane clathrate forms, while ice melts to water, so the Gibbs energy changes are of opposite signs.

Freezing is an exothermic process with an entropy decrease in both cases.

The entropy decrease of the clathrate formation is larger in magnitude, as it involves a gas-solid transition.

The relation of the reaction enthalpies can be inferred from these facts:

$$\Delta G_m(1) > \Delta G_m(2)$$

$$\Delta H_m(1) - T \Delta S_m(1) > \Delta H_m(2) - T \Delta S_m(2)$$

$$T(\Delta S_m(2) - \Delta S_m(1)) > \Delta H_m(2) - \Delta H_m(1)$$

$$\text{a negative quantity} > \Delta H_m(2) - \Delta H_m(1)$$

1 pt each, the last 3 pts.

Problem 7

total

8% of the

7a	7b	7c	7d	7e	7f	7g	7h	Task 7
2	1	4	2	8	5	8	12	42

The dithionate ion ($\text{S}_2\text{O}_6^{2-}$) is a rather inert inorganic ion. It can be prepared by bubbling sulphur-dioxide continuously into ice-cooled water to which manganese dioxide is added in small increments. Dithionate and sulphate ions are formed under these circumstances.

a) Write the balanced chemical equations for the two reactions.



After the reaction is complete, $\text{Ba}(\text{OH})_2$ is added to the mixture until the sulphate ions are fully precipitated. This is followed by the addition of Na_2CO_3 .

b) Write the balanced equation for the reaction that takes place upon addition of Na_2CO_3 .



Sodium dithionate is then crystallized by evaporating some of the solvent. The prepared crystals dissolve readily in water and do not give a precipitate with BaCl_2 solution. When the solid is heated and maintained at $130\text{ }^\circ\text{C}$, 14.88 % weight loss is observed. The resulting white powder dissolves in water and does not give a precipitate with BaCl_2 solution. When another sample of the original crystals is kept at $300\text{ }^\circ\text{C}$ for a few hours, 41.34 % weight loss occurs. The resulting white powder dissolves in water and gives a white precipitate with BaCl_2 solution.

c) Give the composition of the prepared crystals and write balanced equations for the two processes that occur during heating.

Formula:



Equation ($130\text{ }^\circ\text{C}$):



Equation ($300\text{ }^\circ\text{C}$):



Name:

Code: XXX-

Although dithionate ion is a fairly good reducing agent thermodynamically, it does not react with oxidants in solution at room temperature. At 75 °C, however, it can be oxidized in acidic solutions. A series of kinetic experiments were carried out with bromine as an oxidant.

- d) Write the balanced chemical equation for the reaction between bromine and dithionate ion.



The initial rates (v_0) of the reaction were determined in a number of experiments at 75 °C.

$[\text{Br}_2]_0$ (mmol/dm ³)	$[\text{Na}_2\text{S}_2\text{O}_6]_0$ (mol/dm ³)	$[\text{H}^+]_0$ (mol/dm ³)	v_0 (nmol dm ⁻³ s ⁻¹)
0.500	0.0500	0.500	640
0.500	0.0400	0.500	511
0.500	0.0300	0.500	387
0.500	0.0200	0.500	252
0.500	0.0100	0.500	129
0.400	0.0500	0.500	642
0.300	0.0500	0.500	635
0.200	0.0500	0.500	639
0.100	0.0500	0.500	641
0.500	0.0500	0.400	511
0.500	0.0500	0.300	383
0.500	0.0500	0.200	257
0.500	0.0500	0.100	128

- e) Determine the order of the reaction with respect to Br_2 , H^+ and $\text{S}_2\text{O}_6^{2-}$, the experimental rate equation, and the value and unit of the rate constant.

Reaction order for Br_2 :	for H^+ :	for $\text{S}_2\text{O}_6^{2-}$:
	0	1
	1	1
	(2 pts each)	
Experimental rate equation:	$v = k[\text{S}_2\text{O}_6^{2-}][\text{H}^+]$ (1 pt)	
k :	$k = 2.56 \cdot 10^{-5} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (1 pt: no point if unit is incorrect; unorthodox but correct unit acceptable)	

Name:

Code: XXX-

In similar experiments, chlorine, bromate ion, hydrogen peroxide and chromate ion have all been used as oxidizing agents at 75 °C. The rate equations for these processes are analogous to the one observed with bromine, the units of all rate constants are the same, the values are $2.53 \cdot 10^{-5}$ (Cl_2), $2.60 \cdot 10^{-5}$ (BrO_3^-), $2.56 \cdot 10^{-5}$ (H_2O_2), and $2.54 \cdot 10^{-5}$ ($\text{Cr}_2\text{O}_7^{2-}$).

Experiments were also carried out in acidic sodium dithionate solution without any oxidizing agent. When following the processes by UV spectrophotometry, the slow appearance of a new absorption band around 275 nm was observed. Although hydrogen sulphate ion is a detectable product of the reaction, it does not absorb any light above 200 nm.

- f) Give the formula of the major species causing the new absorption band and write the balanced equation of the chemical reaction occurring in the absence of oxidants.

Species:	SO_2 (or H_2SO_3) 3pts (2 pt for HSO_3^- or SO_3^{2-})
Reaction:	$\text{S}_2\text{O}_6^{2-} + \text{H}^+ \rightarrow \text{HSO}_4^- + \text{SO}_2$ 2pts (if sulfur(IV) product is different but consistent with the previous answer also 2 pts)

An experiment was carried out to follow the absorbance at 275 nm with initial concentrations: $[\text{Na}_2\text{S}_2\text{O}_6] = 0.0022 \text{ mol/dm}^3$, $[\text{HClO}_4] = 0.70 \text{ mol/dm}^3$, and the temperature was 75 °C. A pseudo first-order kinetic curve was found with a half-life of 10 hours and 45 minutes.

- g) Calculate the rate constant of the reaction.

k:	$t_{1/2} = 10 \text{ h } 45 \text{ min} = 3.87 \cdot 10^4 \text{ s}$ $k_{\text{obs}} = \ln 2 / t_{1/2} = 1.79 \cdot 10^{-5} \text{ s}^{-1}$ 2 pts $k = k_{\text{obs}} / [\text{H}^+] = 2.56 \cdot 10^{-5} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ 2 pts (other consistent units also acceptable)
----	--

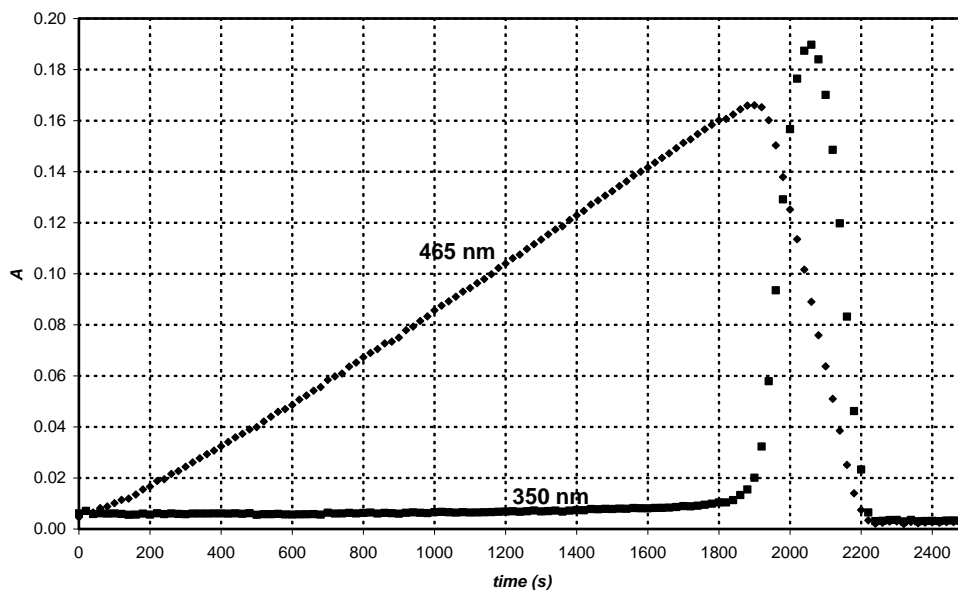
Suggest a balanced chemical equation for the rate determining step of the reactions that used an oxidizing agent.

Rate determining step:	$\text{S}_2\text{O}_6^{2-} + \text{H}^+ \rightarrow \text{HSO}_4^- + \text{SO}_2$ 4 pts
------------------------	---

When periodate ion (which is present as H_4IO_6^- in aqueous solution) was used as an oxidant for dithionate ion, the two kinetic curves depicted in the graph were detected at 75 °C in the same experiment at two different wavelengths. The initial concentrations were $[\text{H}_4\text{IO}_6^-] = 5.3 \cdot 10^{-4} \text{ mol/dm}^3$, $[\text{Na}_2\text{S}_2\text{O}_6] = 0.0519 \text{ mol/dm}^3$, $[\text{HClO}_4] = 0.728 \text{ mol/dm}^3$. At 465 nm, only I_2 absorbs and its molar absorption coefficient is $715 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$. At 350 nm, only I_3^- absorbs and its molar absorption coefficient is $11000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$. The optical path length was 0.874 cm.

Name:

Code: XXX-



- h) Write balanced chemical equations for the reactions that occur in the region where the absorbance increases at 465 nm, and in the region where the absorbance decreases at 465 nm.

Increase:



Decrease:



Calculate the expected time for the maximum absorbance of the kinetic curve measured at 465 nm.

$$t_{\max} = \frac{7}{2} \frac{[\text{H}_4\text{IO}_6^-]_0}{k[\text{S}_2\text{O}_6^{2-}]_0[\text{H}^+]_0} = \frac{7 \times 5.3 \times 10^{-4} \text{ M}}{2 \times 2.56 \times 10^{-5} \text{ M}^{-1}\text{s}^{-1} \times 0.0519 \text{ M} \times 0.728 \text{ M}} = 1900 \text{ s}$$

5 pts

 t_{\max} :

Estimate the expected ratio of the slopes of the increasing and decreasing regions in the kinetic curve measured at 465 nm

slope ratio: 1: -7 (it reflects the stoichiometry)
3 pts

Slope ratio:

Problem 8

total

7 % of the

8a	8b	8c	8d	8e	8f	8g	8h	8i	Task 8
3	3	4	2	3	2	7	3	5	32

Ms. Z was a bright student, whose research project was to measure the complexation of all lanthanide(III) ions with newly designed complexing ligands. One day she monitored the UV-vis absorption with Ce(III) and a particularly poor complexing ligand in a spectrophotometer. She noticed that some small bubbles had formed in the closed cell by the end of the 12-hour experiment. Soon she realized that the presence of the ligand is not necessary to see the bubble formation, and continued her experiments with an acidified CeCl₃ solution. Bubble formation never occurred when she just kept the solution in the spectrophotometer without turning on the instrument. Next, Ms. Z used a small quartz flask, in which she dipped a chloride ion selective electrode and could also withdraw samples regularly for spectrophotometric measurements. She calibrated the chloride ion selective electrode using two different NaCl solutions and obtained the following results:

c _{NaCl} (mol/dm ³)	E (mV)
0.1000	26.9
1.000	-32.2

- a) Give a formula to calculate the chloride ion concentration of an unknown sample based on the electrode voltage reading (E).

$$[\text{Cl}^-] = \boxed{[\text{Cl}^-] = 10^{-(E+32.2\text{mV})/59.1\text{mV}}}$$

Ms. Z also determined the molar absorption coefficient for Ce³⁺ ($\epsilon = 35.2 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) at 295 nm, and, as a precaution, also for Ce⁴⁺ ($\epsilon = 3967 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$).

- b) Give a formula to calculate the Ce³⁺ concentration from an absorbance reading at 295 nm (A) measured in a solution containing CeCl₃ (cuvette path length: 1.000 cm).

$$[\text{Ce}^{3+}] = \boxed{[\text{Ce}^{3+}] = \frac{A_{295\text{nm}}}{35.2 \text{ dm}^3 \text{ mol}^{-1}}}$$

Ms. Z prepared a solution which contained 0.0100 mol/dm³ CeCl₃ and 0.1050 mol/dm³ HCl, and began her experiment by turning on a quartz lamp. HCl does not absorb at 295 nm.

- c) What were the expected initial absorbance and voltage readings?

$$A_{295\text{nm}} = \boxed{[\text{Ce}^{3+}] = 0.0100 \text{ mol/dm}^3 \Rightarrow A_{295\text{nm}} = 0.352}$$

$$E = \boxed{[\text{Cl}^-] = 3 \cdot 0.0100 \text{ mol/dm}^3 + 0.1050 \text{ mol/dm}^3 = 0.1350 \text{ mol/dm}^3 \Rightarrow E = 19.2 \text{ mV}}$$

Name:

Code: XXX-

Before the quantitative experiment Ms. Z collected the gas formed into a carefully neutralized solution of methyl orange (acid-base and redox indicator). Although she saw bubbles going through the solution, the colour did not change or fade even after a day.

- d) Give the formula of two gases, comprised of elements in the illuminated sample, which could not be present given the results of this experiment.

HCl, Cl₂, (O₃, ClO₂) (no oxidation of indicator)

During her quantitative experiment she recorded the absorbance and voltage values regularly. The uncertainty of the spectrophotometric measurements is ± 0.002 and the accuracy of the voltage measurements is ± 0.3 mV.

time (min)	0	120	240	360	480
$A_{295\text{ nm}}$	0.3496	0.3488	0.3504	0.3489	0.3499
E (mV)	19.0	18.8	18.8	19.1	19.2

- e) Estimate the average rate of change in the concentrations of Ce³⁺, Cl⁻, and H⁺.

$$d[\text{Ce}^{3+}]/dt =$$

$$d[\text{Cl}^-]/dt =$$

$$d[\text{H}^+]/dt =$$

No significant change in either Cl⁻ or Ce³⁺ concentrations.
[H⁺] = [Cl⁻] - 3 [Ce³⁺], no significant change.
All three values zero. 1 pt each.

The following day, Ms. Z used an intense monochromatic light beam (254 nm) with an intensity of 0.0500 W. She passed this light through a 5-cm long quartz photoreactor filled with the same acidic CeCl₃ solution she had used before. She measured the molar absorption coefficient for Ce³⁺ ($\epsilon = 2400 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) at 254 nm.

- f) What percentage of the light is absorbed in this experimental setup?

$$A = 2400 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1} \cdot 5 \text{ cm} \cdot 0.0100 \text{ M} = 120 \Rightarrow (100 - 10^{-118})\% \approx 100\%$$

The equipment allowed her to lead the gas first through a drying tube that removed traces of water vapour and then into a closed chamber, whose volume was 68 cm³. The chamber was equipped with a high-precision manometer and an igniter. She first filled the chamber with dry argon to a pressure of 102165 Pa and then she turned on the lamp. In 18.00 hours, the pressure reached 114075 Pa. The temperature of the equipment was 22.0 °C.

Name:

Code: XXX-

g) Estimate the amount of substance of the gas collected in the chamber.

$$p_{\text{partial}} = p_{\text{final}} - p_{\text{initial}} = 114075 \text{ Pa} - 102165 \text{ Pa} = 11910 \text{ Pa}$$

$$n = p_{\text{partial}} V / (RT) = 11910 \text{ Pa} \cdot 0.000068 \text{ m}^3 / (8.314 \text{ J/mol/K} \cdot 295.15 \text{ K}) = 3.3 \cdot 10^{-4} \text{ mol}$$

2 pts

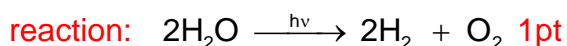
n_{gas} :

At this point, Ms. Z turned off the light and pressed the ignition button. When the chamber cooled down to the initial temperature, the final pressure was 104740 Pa.

Suggest the formula(s) of the gas(es) formed and collected, and give the balanced equation for the original chemical reaction taking place under illumination.

Gas(es):

identity of gases: H₂, O₂ 4 pts



Reaction:

h) What would be the final pressure after the ignition if the chamber was being filled for 24 hours before ignition?

Final pressure: 104740 Pa (saturated water vapour)

$p =$

i) Estimate the quantum yield of product formation in the Ce(III) solution.

Quantum yield:

$3.3 \cdot 10^{-4}$ mol gas formed altogether: $2.2 \cdot 10^{-4}$ mol H₂ and $1.1 \cdot 10^{-4}$ mol O₂.

Light beam intensity $0.0500 \text{ Js}^{-1} \Rightarrow \frac{0.0500 \text{ J/s } \lambda}{hcN_A} = 1.06 \cdot 10^{-7} \text{ mols}^{-1}$ photon

Total time 18.00 h = 64800 s

Total number of absorbed photons: $64800 \text{ s} \cdot 1.06 \cdot 10^{-7} \text{ mols}^{-1} = 6.87 \cdot 10^{-3} \text{ mol}$

Quantum yield for H₂ production: $\Phi = 2.2 \cdot 10^{-4} \text{ mol} / 6.87 \cdot 10^{-3} \text{ mol} = 0.032$

Quantum yield for O₂ production: $\Phi = 1.1 \cdot 10^{-4} \text{ mol} / 6.87 \cdot 10^{-3} \text{ mol} = 0.016$

Either value or the quantum yield of the gas production (0.048) is acceptable when demonstrated in a calculation.

Quantum yield:

Problem 9

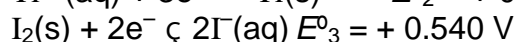
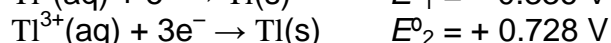
total

6 % of the

9a	9b	9c	9d	Task 9
12	21	15	9	57

Thallium exists in two different oxidation states: Tl^+ and Tl^{3+} . Iodide ions can combine with iodine to form tri-iodide ions (I_3^-) in aqueous solutions,

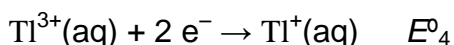
The standard redox potentials for some relevant reactions are:



The equilibrium constant for the reaction $I_2(s) + I^-(aq) \rightarrow I_3^-(aq)$: $K_1 = 0.459$.

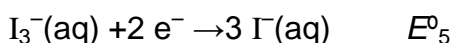
Use $T=25^\circ\text{C}$ throughout this problem.

a) Calculate the redox potential for the following reactions:



$$E_4^\circ = \frac{3E_2^\circ - E_1^\circ}{2} = 1.26 \text{ V} \quad 6 \text{ pts}$$

$E_4^\circ =$



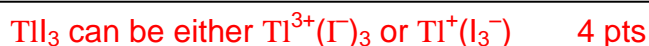
$$E_5^\circ = E_3^\circ + 0.059/2 \lg(1/K_1) = 0.550 \text{ V} \quad 6 \text{ pts}$$

$E_5^\circ =$

b) Write empirical formulae for all theoretically possible neutral compounds that contain one thallium ion and any number of iodide and/or tri-iodide ion(s) as anion(s).



There is an empirical formula that could belong to two different compounds. Which one?



Name:

Code: XXX-

Based on the standard redox potentials, which of the two isomers mentioned above is the stable one at standard conditions? Write the chemical reaction for the isomerisation of the other isomer of thallium iodide.

More stable:	$Tl^+(I_3^-)$ as $E^{\circ}_4 > E^{\circ}_5$ or E°_3 , 6 pts
Isomerisation:	$Tl^{3+} + 3I^- = Tl^+ + I_3^-$ 6 pts 3 pts for $TlI_3 = Tl(I_3)$; 0 pts for $Tl^{3+} + 3I^- = Tl^+ + I_2$

Complex formation can shift this equilibrium. The cumulative complex formation constant for the reaction $Tl^{3+} + 4I^- \rightarrow TlI_4^-$ is $\beta_4 = 10^{35.7}$

- c) Write the reaction that takes place when a solution of the more stable isomer of thallium iodide is treated with an excess of KI. Calculate the equilibrium constant for this reaction.

Reaction:	$Tl^+ + I_3^- + I^- \rightarrow TlI_4^-$ 3 pts
<p>This reaction could be regarded as sum of three reactions:</p> <p>$Tl^+(aq) \rightarrow Tl^{3+}(aq) + 2e^-$ $-E^{\circ}_4 = -1.26$ V, thus $\Delta_r G_4^{\circ} = nFE_4^{\circ} = 243.1$ kJ/mol</p> <p>$I_3^-(aq) + 2e^- \rightarrow 3I^-(aq)$ $E^{\circ}_5 = 0.550$ V, thus $\Delta_r G_5^{\circ} = -nFE_5^{\circ} = -106.1$ kJ/mol</p> <p>$Tl^{3+} + 4I^- \rightarrow TlI_4^-$ $\beta_4 = 10^{35.7}$ thus $\Delta_r G_6^{\circ} = -RT \ln \beta_4 = -203.8$ kJ/mol</p> <p>The net free enthalpy change is $\Delta_r G_7^{\circ} = \Delta_r G_4^{\circ} + \Delta_r G_5^{\circ} + \Delta_r G_6^{\circ} = -66.8$ kJ/mol</p> <p>Thus $K_2 = \exp\left(-\frac{\Delta_r G_7^{\circ}}{RT}\right) = 4.96 \cdot 10^{11}$</p> <p>3 pts each for $\Delta_r G^{\circ}_{(4-6)}$ and for K_2.</p>	
K_2 :	

If the solution of the more stable isomer is treated with a strong basic reagent precipitation of a black substance can be observed. After the water content of the precipitate is removed, the remaining material contains 89.5% thallium (by mass).

- d) What is the empirical formula of this compound? Show your calculations. Write a balanced equation for its formation.

<p>Supposing that the substance contains TI and an anion, the formula of the compound is $Tl_a X_b$ and the following equation holds:</p> $\frac{a \cdot 204.4}{a \cdot 204.4 + bM_x} = 0.895$ <p>From the values $b = 1, 3$ and $a = 1, 2, 3$ only $b = 3, a = 2$ gives a realistic $M_x = 16.0$ g/mol.</p> <p>X is oxygen. 4 pts</p>

Name:

Code: XXX-

Formula:

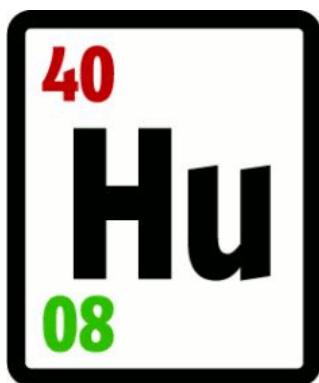
Tl_2O_3 . 2 pts

Equation:

$2 \text{TlI}_3 + 6 \text{OH}^- \rightarrow \text{Tl}_2\text{O}_3 + 6 \text{I}^- + 3 \text{H}_2\text{O}$ 3 pts
2 pts if H^+ or H_3O^+ ions are written at the right side of the equation.

Name:

Code: XXX-



40th International
Chemistry Olympiad

Practical tasks

15 July 2008
Budapest, Hungary

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Instructions

- This examination has **10** pages and **5** pages of answer sheets (8+4 for Task 1-2, 2+1 for Task 3).
- You have **3 hours** to complete **Tasks 1 and 2**. After that you will have to leave the laboratory for a short **break** while the assistants exchange your glassware and chemicals. You will then have **2 hours** to work on **Task 3**.
- Begin only when the **START** command is given. You must stop your work immediately when the **STOP** command is given after each part. A delay in doing this by 3 minutes will lead to cancellation of your experimental exam.
- Follow **safety rules** given in the IChO regulations. At all times while you are in the laboratory you must wear **safety glasses** or your own glasses if they have been approved, and use the **pipette filler bulb** provided. Use **gloves** when handling the organic liquids.
- You will receive only **ONE WARNING** from the laboratory supervisor if you break safety rules. On the second occasion you will be dismissed from the laboratory with a resultant zero score for the entire experimental examination.
- Do not hesitate to ask a demonstrator if you have any questions concerning safety issues or if you need to leave the room.
- Use only the pen and calculator provided.
- Write your **name and code on each answer sheet**. Do not attempt to separate the sheets.
- All results must be written in the appropriate areas on the answer sheets. Anything written elsewhere will not be graded. Use the reverse of the sheets if you need scratch paper.
- You will need to reuse some glassware during the exam. Clean them carefully at the sink closest to you.
- Use the labeled **waste containers** under the hood for the disposal of organic liquids from Task 1 and all liquids from Task 3.
- The number of **significant figures** in numerical answers must conform to the rules of evaluation of experimental errors. Mistakes will result in penalty points, even if your experimental technique is flawless.
- Chemicals and laboratory ware are not supposed to be **refilled or replaced**. Each such incident (other than the first, which you will be allowed) will result in the **loss of 1 point** from your 40 practical points.
- When you have finished a part of the examination, you must put your answer sheets into the envelope provided. Do not seal the envelope.
- The official English version of this examination is available on request only for clarification.

Apparatus

For common use in the lab:
Heating block preadjusted to 70 °C under the hood
Distilled water (H ₂ O) in jugs for refill
Latex gloves (ask for a replacement if allergic to latex)
Labeled waste containers for Task 1 (organic liquids) and Task 3 (all liquids)
Container for broken glass and capillaries
On each desk:
Goggles
Heat gun
Permanent marker
Pencil and ruler
Stopwatch, ask supervisor about operation if needed. (You can keep it.)
Tweezers
Spatula
Glass rod
Ceramic tile
Paper tissue
Spray bottle with distilled water
9 Eppendorf vials in a foam stand
TLC plate in labeled ziplock bag
Plastic syringe (100 cm ³) with polypropylene filter disc
Pipette bulb
14 graduated plastic Pasteur pipettes
Petri dish with etched competitor code
Burette
Stand and clamp
Pipette (10 cm ³)
2 beakers (400 cm ³)
Beaker and watchglass lid with filter paper piece for TLC
10 capillaries
2 graduated cylinders (25 cm ³)
3 Erlenmeyer flasks (200 cm ³)
Beaker (250 cm ³)
2 beakers (100 cm ³)
Funnel
Volumetric flask (100 cm ³)
30 test tubes in stand*
Indicator paper pieces and pH scale in ziplock bag*
Wooden test tube clamp*
2 plugs for test tubes*

* Only handed out for Task 3

Chemicals

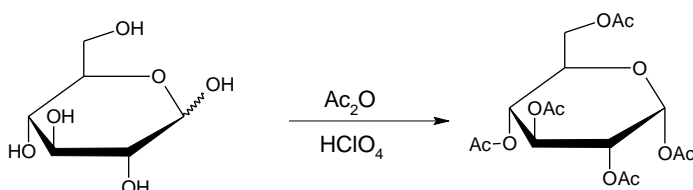
Sets for 4-6 people	R phrases	S phrases
0.025 mol/dm ³ ferroin solution	52/53	
0.2 % diphenylamine, (C ₆ H ₅) ₂ NH solution in conc. H ₂ SO ₄	23/24/25-33-35-50/53	26-30-36/37-45-60-61
0.1 mol/dm ³ K ₃ [Fe(CN) ₆] solution	32	
Pumice stone		
On each desk:		
50 mg anhydrous ZnCl ₂ in a small test tube (in the foam stand, labeled with code)	22-34-50/53	36/37/39-26-45-60-61
100 mg β-D-glucopyranose pentaacetate (labelled as BPAG)		
3.00 g anhydrous glucose, C ₆ H ₁₂ O ₆ , preweighed in vial		
(CH ₃ CO) ₂ O in Erlenmeyer flask (12 cm ³)	10-20/22-34	26-36/37/39-45
(CH ₃ CO) ₂ O in vial (10 cm ³)	10-20/22-34	26-36/37/39-45
CH ₃ COOH in vial (15 cm ³)	10-35	23-26-45
CH ₃ OH in vial (10 cm ³)	11-23/24/25-39	7-16-36/37-45
30 % HClO ₄ in CH ₃ COOH in vial (1 cm ³)	10-35	26-36/37/39-45
1:1 isobutyl acetate – isoamyl acetate in vial (20 cm ³), labeled as ELUENT	11-66	16-23-25-33
solid K ₄ [Fe(CN) ₆].3H ₂ O sample with code in small flask	32	22-24/25
ZnSO ₄ solution labeled with code and concentration (200 cm ³)	52/53	61
0.05136 mol/dm ³ Ce ⁴⁺ solution (80 cm ³)	36/38	26-36
1.0 mol/dm ³ H ₂ SO ₄ solution (200 cm ³)	35	26-30-45
Sample solutions for Task 3 (to be handed out at the start of Task 3)	1-26/27/28-32-35-50/53	24/25-36/39-61

Risk and Safety Phrases

Indication of Particular Risks			
1	Explosive when dry	33	Danger of cumulative effects
10	Flammable	34	Causes burns
11	Highly Flammable	35	Causes severe burns
22	Harmful if swallowed	39	Danger of very serious irreversible effects
32	Contact with concentrated acids liberates very toxic gas		
Combination of Particular Risks			
20/22	Harmful by inhalation and if swallowed	36/38	Irritating to eyes and skin
23/24/25	Toxic by inhalation, in contact with skin and if swallowed	50/53	Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment
26/27/28	Very Toxic by inhalation, in contact with skin and if swallowed	52/53	Harmful to aquatic organisms, may cause long-term adverse effects in the aquatic environment
Indication of Safety Precautions			
7	Keep container tightly closed	30	Never add water to this product
16	Keep away from sources of ignition - No smoking	33	Take precautionary measures against static discharges
22	Do not breathe dust	36	Wear suitable protective clothing
23	Do not breathe fumes/vapour	45	In case of accident or if you feel unwell, seek medical advice immediately (show label where possible)
25	Avoid contact with eyes	60	This material and/or its container must be disposed of as hazardous waste
26	In case of contact with eyes, rinse immediately with plenty of water and seek medical advice	61	Avoid release to the environment.
Combination of Safety Precautions			
24/25	Avoid contact with skin and eyes	36/37/39	Wear suitable protective clothing, gloves and eye/face protection
36/37	Wear suitable protective clothing and gloves		

Task 1

Synthesis of α -D-glucopyranose pentaacetate

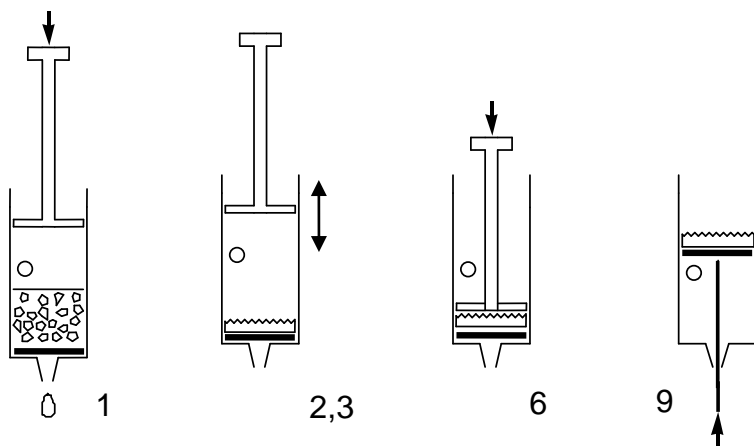


Caution: Use gloves while manipulating acetic acid and acetic anhydride. Let the lab supervisors know if any is spilled.

Add and mix 12 cm³ of pure acetic acid to 12 cm³ of acetic anhydride (provided in an Erlenmeyer flask) and add 3.00 g glucose (acetic anhydride is used in excess). Add with a Pasteur-pipette 5 drops of 30% HClO₄ dissolved in acetic acid. After the addition of the catalyst the solution might warm up considerably.

Let the mixture rest covered for 10 minutes and swirl it from time to time. Pour the reaction mixture into 100 cm³ of water in a beaker. Scratch the wall of the beaker with a glass rod to initiate crystallization, and let it crystallize for 10 minutes. Filter and wash the product two times with 10 cm³ of water using the syringe and the porous polypropylene filter disc.

Filtration using a plastic syringe



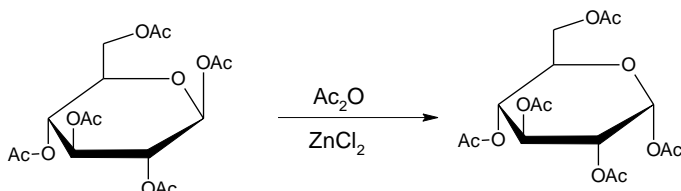
1. Pull out the piston. Fill the syringe from above with the suspension to be filtered. The syringe can be filled to the level of the hole. Replace piston.
2. Cover the hole with your finger and press in the piston as far as the hole.
3. Open the hole and draw the piston back. Do not draw in air through the filter.
4. Repeat steps 2-3 a few times to expel the liquid.
5. Repeat steps 1-4 until all solids are on the filter.
6. Press the piston against the filter cake and squeeze out the liquid.
7. Wash the product twice with 10 cm³ of water repeating steps 1-4.
8. Press the piston against the filter cake and squeeze out the water.
9. Pull the piston out with the hole closed to lift out the filter cake. (Pushing with the end of the spatula can help.)

- a) Place your product in the open Petri dish marked with your code. Leave it on your table. The organizers will dry it, weigh it and check it for purity.

- b) Calculate the theoretical yield (mass) of your product in g. ($M(\text{C}) = 12 \text{ g/mol}$, $M(\text{O}) = 16 \text{ g/mol}$, $M(\text{H}) = 1.0 \text{ g/mol}$)

Synthesis of α -D-glucopyranose pentaacetate from β -D-glucopyranose pentaacetate

An alternative synthesis of α -D-glucopyranose pentaacetate starts from readily available β -D-glucopyranose pentaacetate. In this experiment we will study the kinetics of this reaction with thin layer chromatography.



Add 1.5 cm^3 acetic anhydride to 50 mg of anhydrous ZnCl_2 (preweighed in a test tube). Add 100 mg of pure β -D-glucopyranose pentaacetate (BPAG) and swirl until dissolved. Take three drops from this mixture into an Eppendorf tube, add 0.5 cm^3 methanol and save it.

Place the test tube in the heating apparatus under the hood closest to your desk. Place the test tube in the heating block preadjusted to 70°C . Mix the contents of the test tube from time to time. During the reaction take three drops of sample from the mixture with a Pasteur pipet after 2, 5, 10, and 30 minutes. Mix immediately each sample with 0.5 cm^3 of methanol to stop the reaction in an Eppendorf tube.

Prepare a silica TLC plate with the collected samples to study the reaction kinetics. Apply the necessary reference compounds as well to help identification of the spots on the plate. Mark the spots with a pencil, and develop the plate in isobutyl acetate/ isoamyl acetate (1:1) eluent. Heat the plates with a heat-gun (under the hood!) to visualise the spots (the colour is stable). You can ask for a second plate without penalty points if needed for proper evaluation.

- c) Copy your plate on the answer sheet and place your plate in the labeled ziplock bag.
- d) Interpret your experimental findings answering the questions on the answer sheet.

Task 2

Insert this remark in your translation if your students do not know this kind of pipette.

Hint: The pipette has two graduation marks. Stop at the second mark to measure out exact volumes. Do not let all the solution to run out.

When potassium hexacyanoferrate(II), $K_4[Fe(CN)_6]$ is added to a solution containing zinc ions, an insoluble precipitate forms immediately. Your task is to find out the composition of the stoichiometric precipitate that contains no water of crystallization.

The precipitation reaction is quantitative and so quick that it can be used in a titration. The end point can be detected using redox indication, but first the concentration of the potassium hexacyanoferrate(II) solution has to be determined.

Preparation of $K_4[Fe(CN)_6]$ solution and determination of its exact concentration

Dissolve the solid $K_4[Fe(CN)_6] \cdot 3H_2O$ ($M = 422.41$ g/mol) sample in the small Erlenmeyer flask and quantitatively transfer it into the 100.00 cm³ volumetric flask. Take 10.00 cm³ portions of the hexacyanoferrate(II) solution. Add 20 cm³ 1 mol/dm³ sulfuric acid and two drops of the ferroin indicator solution to each sample before titration. Titrate with the 0.05136 mol/dm³ Ce^{4+} solution. Repeat titration as necessary. Cerium(IV) is a strong oxidant under acidic conditions forming $Ce(III)$.

- Report the Ce^{4+} solution volumes consumed.
- Give the equation for the titration reaction. What was the mass of your $K_4[Fe(CN)_6] \cdot 3H_2O$ sample?

The reaction between zinc ions and potassium hexacyanoferrate(II)

Take 10.00 cm³ of the hexacyanoferrate(II) solution and add 20 cm³ 1 mol/dm³ sulfuric acid. Add three drops of indicator solution (diphenyl amine) and two drops of $K_3[Fe(CN)_6]$ solution. The indicator only works if the sample contains some hexacyanoferrate(III), $[Fe(CN)_6]^{3-}$. Titrate slowly with the zinc solution. Continue until a bluish violet colour appears. Repeat titration as necessary.

- Report the zinc solution volumes consumed.
- Interpret the titration answering the questions on the answer sheet.
- Determine the formula of the precipitate.

Caveat: Best marks are not necessarily awarded to measurements reproducing theoretically expected values.

Task 3

Caution: Handle all unknown solutions as if they were toxic and corrosive. Discard them only in the appropriate waste container.

The heat gun heats the expelled air up to 500 °C. Do not direct the stream towards combustible materials or body parts. Be careful with the hot nozzle.

Always place a single piece of pumice into liquids before heating to avoid bumping. Never point the mouth of a heated test tube towards a person.

You have eight unknown aqueous solutions. Each solution contains only one compound. The same ion may appear in more than one solution. Every compound formally consists of one type of cation and one type of anion from the following list:

Cations: H^+ , NH_4^+ , Li^+ , Na^+ , Mg^{2+} , Al^{3+} , K^+ , Ca^{2+} , Cr^{3+} , Mn^{2+} , Fe^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Sr^{2+} , Ag^+ , Sn^{2+} , Sn^{4+} , Sb^{3+} , Ba^{2+} , Pb^{2+} , Bi^{3+}

Anions: OH^- , CO_3^{2-} , HCO_3^- , CH_3COO^- , $\text{C}_2\text{O}_4^{2-}$, NO_2^- , NO_3^- , F^- , PO_4^{3-} , HPO_4^{2-} , H_2PO_4^- , SO_4^{2-} , HSO_4^- , S^{2-} , HS^- , Cl^- , ClO_4^- , MnO_4^- , Br^- , I^-

You have test tubes and heating but no additional reagents apart from distilled water and pH paper.

Identify the compounds in the solutions **1-8**. You can use the solubility table for some of the anions on the next page. If you are unable to identify an ion exactly, give the narrowest selection possible.

Remarks:

The unknown solutions may contain minor impurities arising from their exposure to air. The concentration of all solutions is around 5 % by mass so you can expect clearly observable precipitates from the main components. In some cases, precipitation does not occur instantaneously; some substances may remain in an oversaturated solution for a while. Don't draw negative conclusions too hastily, wait 1-2 minutes where necessary. Always look carefully for all signs of a reaction.

Keep in mind that heating accelerates all processes, increases the solubility of most substances, and may start reactions that do not take place at room temperature.

Name:

Code: XXX-

Solubility Table at 25 °C

	NH ₄ ⁺	Li ⁺	Na ⁺	Mg ²⁺	Al ³⁺	K ⁺	Ca ²⁺	Cr ³⁺	Mn ²⁺	Fe ²⁺	Fe ³⁺	Co ²⁺	Ni ²⁺	Cu ²⁺	Zn ²⁺	Sr ²⁺	Ag ⁺	Sn ²⁺	Sn ⁴⁺	Sb ³⁺	Ba ²⁺	Pb ²⁺	Bi ³⁺
CH ₃ COO ⁻														HR			1.0	↓	↓	↓			↓
C ₂ O ₄ ²⁻			3.6	↓			↓		↓	↓ (Y)	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓
NO ₂ ⁻	HR				HR			HR		↓ R				HR	↓		0.41 (Y)	↓ R	↓	↓			↓
NO ₃ ⁻																							
F ⁻		0.13		↓	0.5		↓	4.0	1.0	↓ (W)	↓ (W)	1.4	2.6	↓	1.6	↓					0.16	↓	↓
SO ₄ ²⁻							0.21									↓	0.84		↓		↓	↓	
PO ₄ ³⁻	HR	↓		↓	↓		↓	↓	↓	↓ (W)	↓	↓ (P)	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓
HPO ₄ ²⁻		↓		↓	↓		↓	↓	↓	↓ (W)	↓ (W)	↓ (P)	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓	↓
H ₂ PO ₄ ⁻					HR		1.0	HR	HR		↓ (W)	HR		↓	↓	HR	↓ (Y)	↓	↓	↓	HR	↓	↓
ClO ₄ ⁻						2.1																	
MnO ₄ ⁻	HR							HR	↓ R	R		HR					0.91	R		R		↓ R	
Br ⁻																	↓ (Y)					0.98	
I ⁻											R			↓ R			↓ (Y)	1.0				↓ (Y)	↓ (B)

No entry: Soluble compound ↓: Insoluble compound **R:** Redox reaction at room temperature

HR: Soluble at room temperature. In hot solution a reaction with an observable effect (not necessarily a precipitate) takes place.
Solubilities in g (substance) / 100 g water. Accurately known values between 0.1 and 4 are shown only.

Precipitates whose colour significantly differs from that of their hydrated ions: **(B)** = black, **(P)** = purple, **(W)** = white, **((Y))** = pale yellow, **(Y)** = yellow.

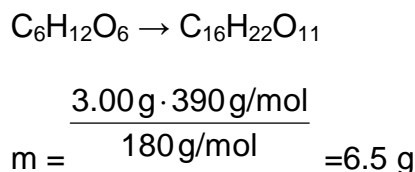
Task 1**10% of the total**

1a	1b	1c	1d	Task 1
30	2	12	4	48

a) Yield of the product in g, measured by the organizer:

The samples are dried by the organizers. Full pts for a 60-100% yield, linear scale between 0-60% yield. The typical yield is 70%.
 Purity is checked by solubility (acetone) and TLC. If there is no insoluble material and no impurity is detectable by TLC, the full points for the yield are received.
 If there is a considerable (easily visible) amount of insoluble material or impurity on the TLC plate, then 0 point is received for the yield (only possible in case of intentional contamination).
 5 points off if filter disc is submitted.

b) Calculate the theoretical yield of your product in g.



Theoretical yield:

c) Sketch your developed TLC plate and leave on your desk to be evaluated,

If both standards and all samples are present and labeled: 5 pts
 If any sample is missing: 2 pts, if more than one is missing: 0 pt.
 Loading of the plate: if over- or underloading does not interfere with the evaluability: 4 pts, if interfering, but evaluation is still possible: 2 pts, if evaluation is not possible: 0 pt
 If the development is appropriate (minor tilting is acceptable): 3 pts. If erratically developed, but still evaluable (the two isomers separate): 1 pt, otherwise 0 pt.

Name:

Code: XXX-

d) **Interpret your experiment** and choose the correct answer.

The acetylation reaction of glucose is exothermic.

- a) Yes
- b) No
- c) Cannot be decided based on these experiments

The isomerisation reaction of β -D-glucopyranose pentaacetate can be used for the preparation of pure α -D-glucopyranose pentaacetate.

- a) Yes
- b) No
- c) Cannot be decided based on these experiments

Solutions: a, a (2 pts. each)

Name:

Code: XXX-

Task 2

15 % of the total

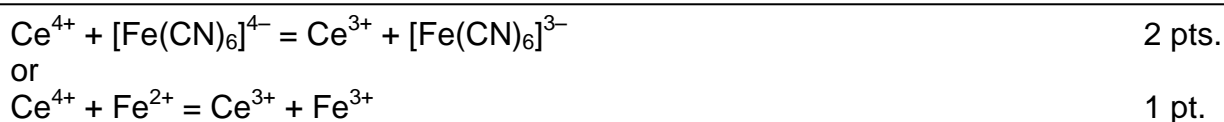
2a	2b	2c	2d	2e	Task 2
25	4	25	6	5	65

a) Ce^{4+} consumptions:

Full marks (25 pts.) if V_1 is within 0.15 cm^3 of the expected value recalculated from the $\text{K}_4[\text{Fe}(\text{CN})_6]$ mass. Zero marks if deviation is more than 0.50 cm^3 . Linear scale is applied in between.

Average volume consumed (V_1):

b) The titration reaction:



Calculation of sample mass:

$$m = c_{\text{Ce}} V_1 10 \cdot M \quad 2 \text{ pts.}$$

Actual sample masses will be distributed with the exam copies.

$\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$ mass (m):

c) Zinc consumptions:

Full marks (25 pts.) if V_2 is within 0.15 cm^3 of the expected value recalculated from $\text{K}_4[\text{Fe}(\text{CN})_6]$ mass, zinc concentrations and empirical ratio. Zero marks if the deviation is more than 0.50 cm^3 . Linear scale is applied in between.

Average volume consumed (V_2):

d) Mark the correct answer.

The diphenyl amine indicator changes in colour at the end point

- a) because the concentration of the Zn^{2+} ions increases.
- b) because the concentration of the $[\text{Fe}(\text{CN})_6]^{4-}$ ions decreases.
- c) because the concentration of the $[\text{Fe}(\text{CN})_6]^{3-}$ ions increases.
- d) because the indicator is liberated from its complex.

Name:

Code: XXX-

Which form of the indicator is present before the end point?

- a) Oxidized
 b) Reduced
 c) Complexed to a metal ion

At the beginning of the titration the redox potential for the hexacyanoferrate(II) - hexacyanoferrate(III) system is lower than the redox potential of the diphenyl amine indicator.

- a) True
 b) False

Solutions: b, b, a (2 pts. each)

e) Determine the formula of the precipitate. Show your work.

The mole ratio of the zinc:hexacyanoferrate(II) in the precipitate can be evaluated as:

$$n_{\text{Zn}}/n_{\text{Fe}(\text{CN})_6} = \frac{10c_{\text{Zn}}V_2M}{m}$$

Values for c_{Zn} are distributed according to country color (found on seating plan)

Red/Pink: 0.0500 Green: 0.0450 Blue: 0.0475 Yellow/Ivory: 0.0525

The empirical ratio obtained from the experiments is 1.489.

Calculating the zinc/hexacyanoferrate(II) ratio: 3 pts.

Cations are needed to make the precipitate neutral and only potassium is present.

The precipitate is $\text{K}_2\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$. 2 pts.

Any other reasonable calculation giving the same result is accepted.

Hydrogen instead of potassium ($\text{H}_2\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$ or $\text{KHZn}_3[\text{Fe}(\text{CN})_6]_2$) is also acceptable.

Mistakes in units, dilution factors, significant figures (not 3 or 4 in 2b) carry a penalty of 1 pt. in each calculation.

The formula of the precipitate:

Name:

Code: XXX-

Items replaced or refilled:

Student signature:

Supervisor signature:

Name:

Code: XXX-

Task 3**15 % of the total**

Task 3
108

Only fill out this table when you are ready with all your assignments.

	1	2	3	4	5	6	7	8
Cation								
Anion								

6 pts for each correctly identified ion except for HCO_3^- and HS^- which are worth 12 pts, bringing up the total to 108 points.

Partial points will be awarded in the following cases:

Anions:

AgNO_3 : Full points if NO_3^- is the only anion shown. 3 pts for ClO_4^- only. 3 pts if fluoride appears together with nitrate and/or perchlorate. Otherwise 0 pt.

$\text{Pb}(\text{CH}_3\text{COO})_2$: 3 pts if NO_3^- and/or ClO_4^- appear together with CH_3COO^- . 1 pt for nitrate and/or perchlorate on their own. Otherwise 0 pt.

3 pts for CO_3^{2-} instead of HCO_3^- , and for S^{2-} instead of HS^- .

Cations:

In the case of all alkali metal compounds, 2 pts for an incorrect alkali metal.

1 pt for Ca^{2+} or Sr^{2+} instead of Ba^{2+} .

Solution

The solutions received by the students contain the following compounds. The country colours can be found on the laboratory seating plan.

Country colour	1	2	3	4	5	6	7	8
Blue	AgNO ₃	KHCO ₃	NH ₄ ClO ₄	NaOH	NaHS	Pb(OAc) ₂	BaI ₂	MgSO ₄
Green	Pb(OAc) ₂	NH ₄ ClO ₄	NaOH	NaHS	MgSO ₄	KHCO ₃	AgNO ₃	BaI ₂
Ivory	NH ₄ ClO ₄	Pb(OAc) ₂	KHCO ₃	BaI ₂	AgNO ₃	MgSO ₄	NaHS	NaOH
L.Blue	NaHS	MgSO ₄	BaI ₂	NH ₄ ClO ₄	Pb(OAc) ₂	AgNO ₃	NaOH	KHCO ₃
L.Green	BaI ₂	NaHS	MgSO ₄	AgNO ₃	NaOH	NH ₄ ClO ₄	KHCO ₃	Pb(OAc) ₂
Pink	MgSO ₄	NaOH	AgNO ₃	Pb(OAc) ₂	KHCO ₃	BaI ₂	NH ₄ ClO ₄	NaHS
Red	NaOH	BaI ₂	Pb(OAc) ₂	KHCO ₃	NH ₄ ClO ₄	NaHS	MgSO ₄	AgNO ₃
Yellow	KHCO ₃	AgNO ₃	NaHS	MgSO ₄	BaI ₂	NaOH	Pb(OAc) ₂	NH ₄ ClO ₄

The problem can be approached in many ways. Intuition is very helpful in the tentative assignment of some compounds in the early phases of the work. A systematic solution is given here for the blue Country colour.

All solutions are colourless (NaHS may be slightly yellowish because of polysulfide impurity). Solutions **1**, **3**, **6**, **7**, and **8** are practically neutral (pH paper reading about 5-6). Solution **2** is basic (pH = 9) while solutions **4** and **5** are very strongly basic (pH > 11).

We can exclude all ions that only form coloured compounds in aqueous solutions: Cr³⁺, Fe²⁺, Fe³⁺, Co²⁺, Ni²⁺, Cu²⁺, and MnO₄⁻. (In principle we should also exclude Mn²⁺ but its solutions have a very light pink colour that might be mistaken for colourless. The yellowish solution is strongly basic hence its colour cannot be attributed to iron.) The compounds of H⁺, Sn²⁺, Sn⁴⁺, Sb³⁺, Bi³⁺, and HSO₄⁻ with the possible counter-ions could only exist in markedly acidic solutions; therefore they can also be safely excluded.

Thus the list of possible ions is:

Cations: NH₄⁺, Li⁺, Na⁺, Mg²⁺, Al³⁺, K⁺, Ca²⁺, Mn²⁺, Zn²⁺, Sr²⁺, Ag⁺, Ba²⁺, Pb²⁺.

Anions: OH⁻, CO₃²⁻, HCO₃⁻, CH₃COO⁻, C₂O₄²⁻, NO₂⁻, NO₃⁻, F⁻, PO₄³⁻, HPO₄²⁻, H₂PO₄⁻, SO₄²⁻, S²⁻, HS⁻, Cl⁻, ClO₄⁻, Br⁻, I⁻.

The unknown solutions react with each other as follows (\downarrow = precipitate; \uparrow = volatile product; “no change” means even when boiled, unless indicated otherwise):

	1 AgNO ₃	2 KHCO ₃	3 NH ₄ ClO ₄	4 NaOH	5 NaHS	6 Pb(OAc) ₂	7 BaI ₂	8 MgSO ₄
1 AgNO ₃	—	—	—	—	—	—	—	—
2 KHCO ₃	\downarrow light yellow \uparrow neutral, odourless	—	—	—	—	—	—	—
3 NH ₄ ClO ₄	no change	\downarrow white crystals (*)	—	—	—	—	—	—
4 NaOH	\downarrow brown-black	no change	boiling: \uparrow basic, odour of ammonia	—	—	—	—	—
5 NaHS	\downarrow black solution turns acidic	no change	boiling: \uparrow basic, odour of NH ₃ , H ₂ S	no change	—	—	—	—
6 Pb(OAc) ₂	\downarrow white crystals	\downarrow white \uparrow neutral, odourless	no change	\downarrow white	\downarrow black	—	—	—
7 BaI ₂	\downarrow yellow	\downarrow white \uparrow (**)	no change	no change	no change	\downarrow yellow	—	—
8 MgSO ₄	\downarrow white crystals	no change (***)	no change	\downarrow white	no change (****)	\downarrow white	\downarrow white	—

(*): upon boiling, the formation of NH₃ is detectable by its odour and by pH paper.

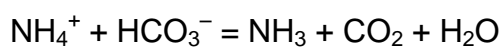
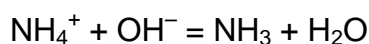
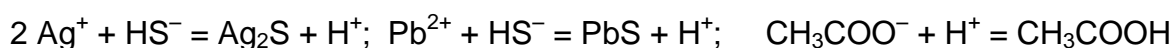
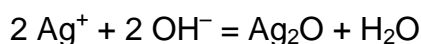
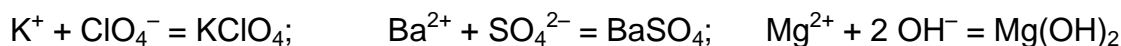
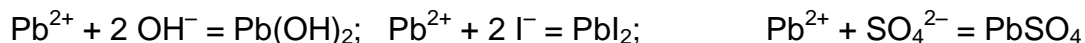
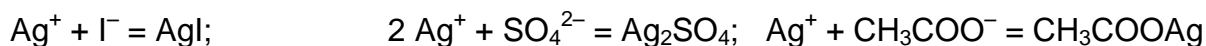
(**): gas bubbles are usually not observed when **2** is in excess.

(***): upon boiling, an odourless gas evolves and a white precipitate forms.

(****): upon boiling, a white precipitate forms and the odour of H₂S appears.



$\text{Mg}^{2+} + 2 \text{HCO}_3^- = \text{MgCO}_3 + \text{CO}_2 + \text{H}_2\text{O}$ (more accurately, basic carbonates of variable composition are formed)



Two groups of the observed phenomena give instant clues to the identification of some of the ions.

First, the reactions of **2** are often accompanied with the formation of a colourless and odourless gas that can only be CO_2 . Thus **2** contains CO_3^{2-} or HCO_3^- .

Second, there are only 3 dark precipitates that can form from the given ions: Ag_2O , Ag_2S , and PbS . This fact, together with the pH of the solutions, instantly identifies the cation of **1** as Ag^+ , the cation of **6** as Pb^{2+} , the anion of **4** as OH^- , and the anion of **5** as sulfide or hydrosulfide (confirmed by the distinct smell of the solution).

The choice between the latter two can be made by measuring the pH of the solution formed in the reaction of **5** with an excess of **1** or **6**. In the case of **1**, the reaction mixture is strongly acidic. Thus the anion of **5** is HS^- .

The evolution of CO_2 in the reaction with Ag^+ and Pb^{2+} also identifies the anion of **2** as HCO_3^- . (in accord with the moderately basic pH)

The reaction of **3** and **4** yields ammonia. **4** is obviously not a solution of NH_3 itself. Thus the cation of **3** is NH_4^+ .

2+4 do not form either a precipitate or ammonia. The cations of **2** and **4** are Na^+ or K^+ .

2+5 do not form either a precipitate or ammonia. The cation of **5** is an alkali metal.

3 is the only solution that does not give a precipitate with Ag^+ . Accordingly, it can be ammonium nitrate, fluoride, or perchlorate. But it does give a precipitate with **2**, a hydrocarbonate of Na^+ or K^+ . Thus the anion of **3** is ClO_4^- and the cation of **2** is K^+ .

4 does not give a precipitate with NH_4ClO_4 . The cation of **4** is Na^+ .

5 does not give a precipitate either with NH_4ClO_4 (K^+) or with a mixture of KHCO_3 and NaOH (Li^+). The cation of **5** is Na^+ .

7 forms no precipitate or ammonia with NaOH but gives a precipitate with KHCO_3 . **7** cannot be an alkali metal perchlorate because it forms yellow precipitates with **1** and **6**. Thus the cation of **7** is Ba^{2+} and the anion of **7** is I^- .

At room temperature **8** gives a precipitate with OH^- but not with HS^- which means it can only be a salt of a Group 2A metal. Thus the reaction of **8** with BaI_2 is obviously one

between Ba^{2+} and the anion of **8**. The latter is very likely SO_4^{2-} but HCO_3^- and H_2PO_4^- are also theoretically possible. The solution of **8** is unchanged upon boiling and gives a white precipitate with Ag^+ . This excludes both HCO_3^- and H_2PO_4^- . Thus the anion of **8** is SO_4^{2-} . This instantly identifies the cation of **8** as Mg^{2+} .

6 is a soluble compound of lead. The anion could be CH_3COO^- , NO_2^- , NO_3^- , or ClO_4^- . The slight odour of acetic acid might give a clue. Unlike **1**, the reaction of an excess of **6** with HS^- does not yield a markedly acidic solution which shows that **6** is a salt of a weak acid. If **6** were a nitrite, it would give a yellowish precipitate with Ag^+ . It would also react with NH_4ClO_4 upon heating with the evolution of N_2 (and nitrogen oxides from the reaction with HS^- would also be noticeable). The absence of these reactions indicates that the anion of **6** is CH_3COO^- .

Soluble salts of silver are even less numerous, the only choices are NO_3^- , F^- , and ClO_4^- . The anion can be examined if one removes the silver ions from the solution of **1** with an excess of NaOH . The Ag_2O precipitate quickly separates from the solution which can be easily poured off. This solution, containing the anion of **1**, does not give a precipitate with BaI_2 which rules out F^- . The solubility of KClO_4 is quite significant; therefore the absence of a precipitate with KHCO_3 is inconclusive. The anion of **1** is therefore either NO_3^- or ClO_4^- .