

40th International
Chemistry Olympiad

Theoretical Problems

17 July 2008

Budapest, Hungary

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40th International Chemistry Olympiad
Institute of Chemistry
Eötvös Loránd University
Pázmány Péter sétány 1/A
H-1117 Budapest
Hungary
E-mail: info@icho.hu or olimpia@chem.elte.hu
Web: www.icho.hu

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: $A = \log \frac{I_0}{I} = \epsilon c l$

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 232.04 | 91 Pa 231.04 | 92 U 238.03 | 93 Np - | 94 Pu - | 95 Am - | 96 Cm - | 97 Bk - | 98 Cf - | 99 Es - | 100 Fm - | 101 Md - | 102 No - | 103 Lr - |

Name:

Code: XXX-

Problem 1

6% of the total

| 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.

| | | | |
|--|--|--|--|
| | | | |
|--|--|--|--|

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)

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

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

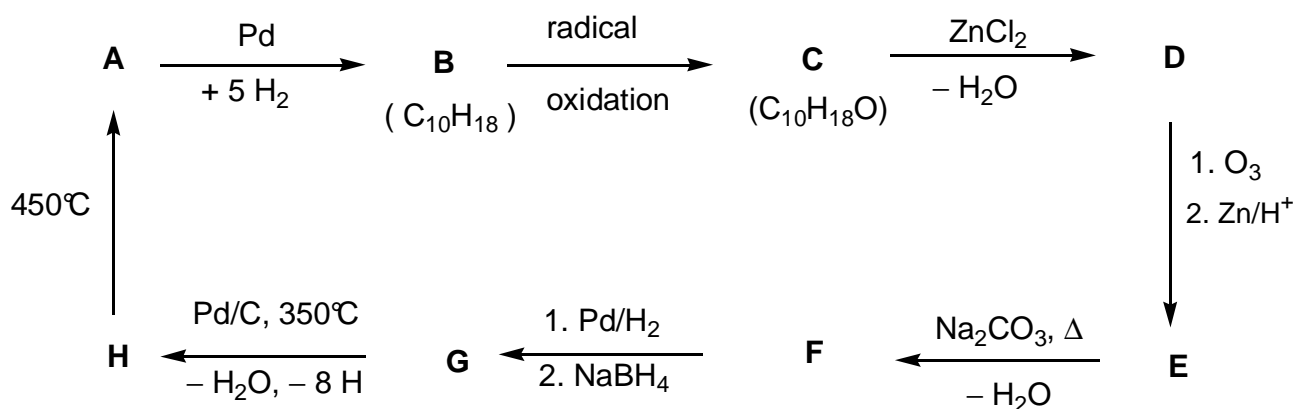
©EDTA:

Problem 2

7% of the total

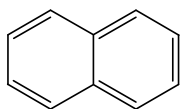
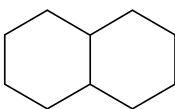
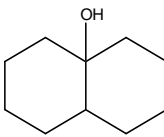
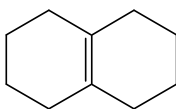
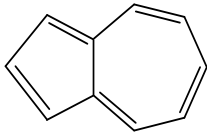
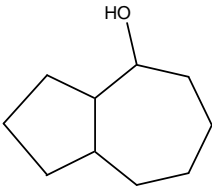
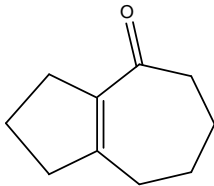
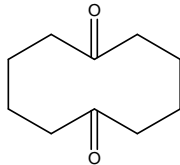
| |
|--------|
| Task 2 |
| 18 |
| |

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  |

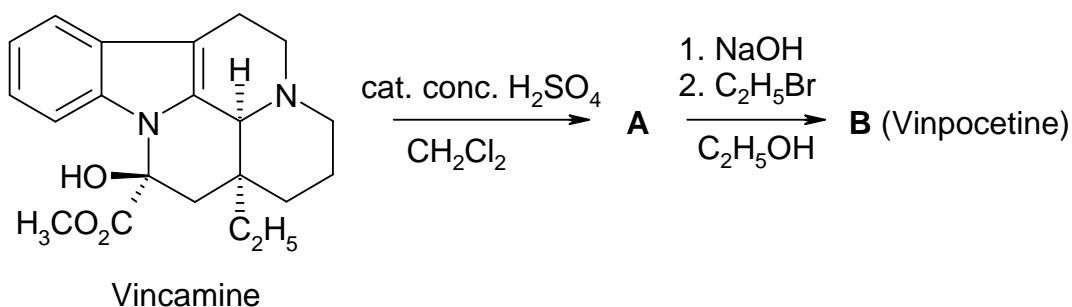
2 pts each, 4 pts for **F**

Problem 3

6% of the total

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

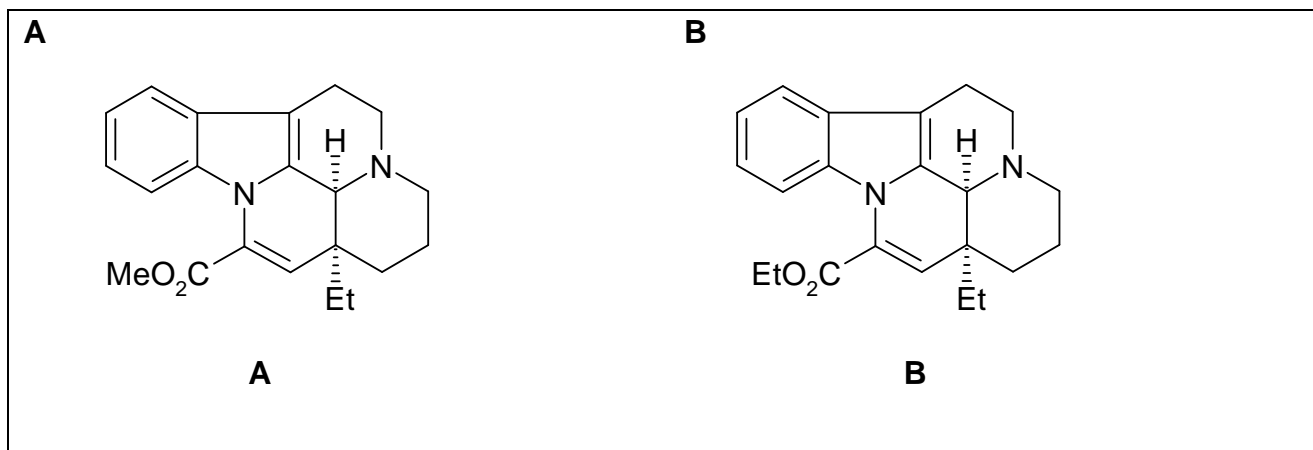
Vinpocetine (Cavinton®, Calan®) is one of the best selling original drugs developed in Hungary. Its preparation relies on a natural precursor, (+)-vincamine ($C_{21}H_{26}N_2O_3$), which is isolated from the vine plant, *vinca minor*. The transformation of (+)-vincamine to vinpocetine is achieved in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

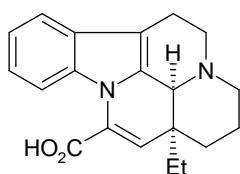
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Hints:

- 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.

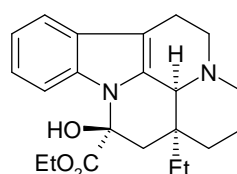
b) Propose one **possible** structure for each of the metabolites **C**, **D**, **E** and **F**!

C



C apovincaminic acid

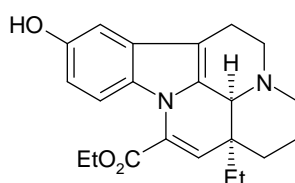
D



D ethyl vincamate

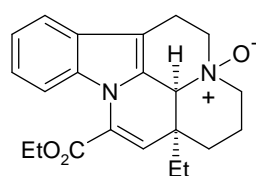
Both stereoisomers around the new chiral center are acceptable.

E



E 10-hydroxyvinpocetine

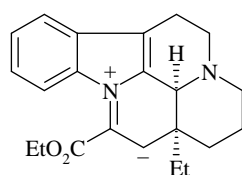
F



F vinpocetine N-oxide

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

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

6% of the total

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

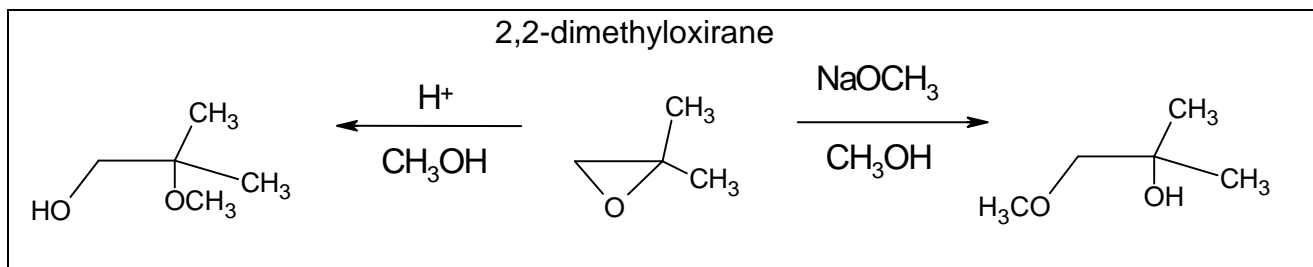
A major transformation route for oxiranes (epoxides) is ring opening. This may be accomplished in various ways.

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.

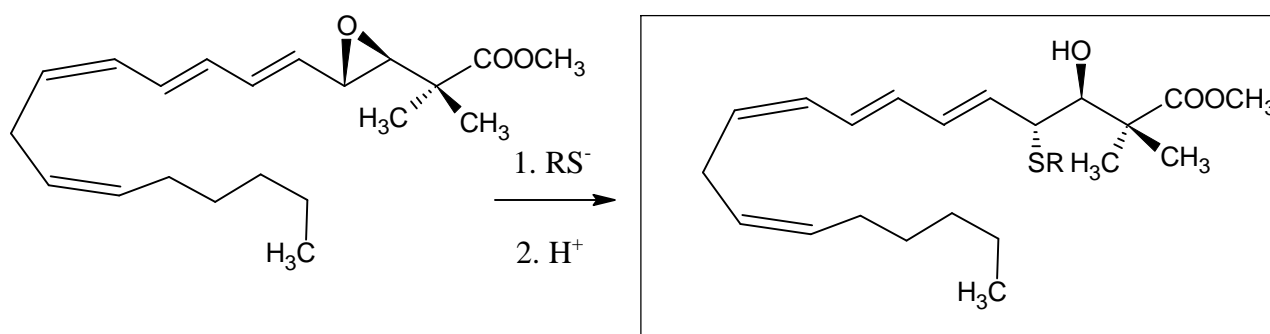
On base catalysis the sterically less hindered C–O bond is cleaved predominantly.

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^-).

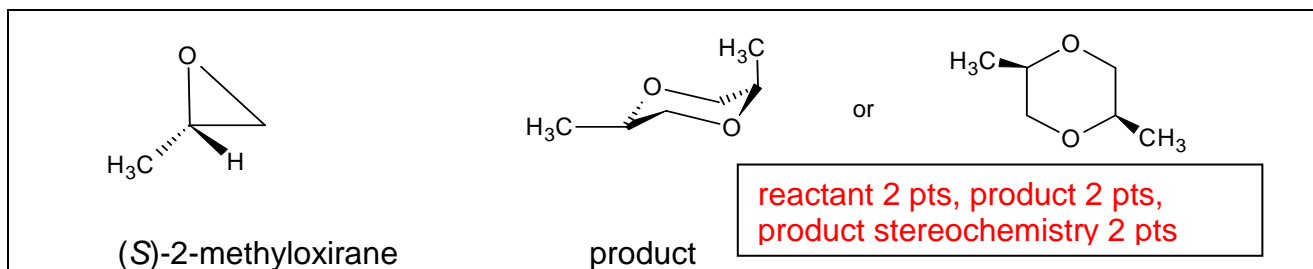


Different porous **acidic** aluminosilicates can also be used to catalyse the transformation of alkyl oxiranes. In addition to ring opening, cyclic dimerisation is found to be the main reaction pathway producing mainly 1,4-dioxane derivatives (six-membered saturated rings with two oxygen atoms in positions 1,4).

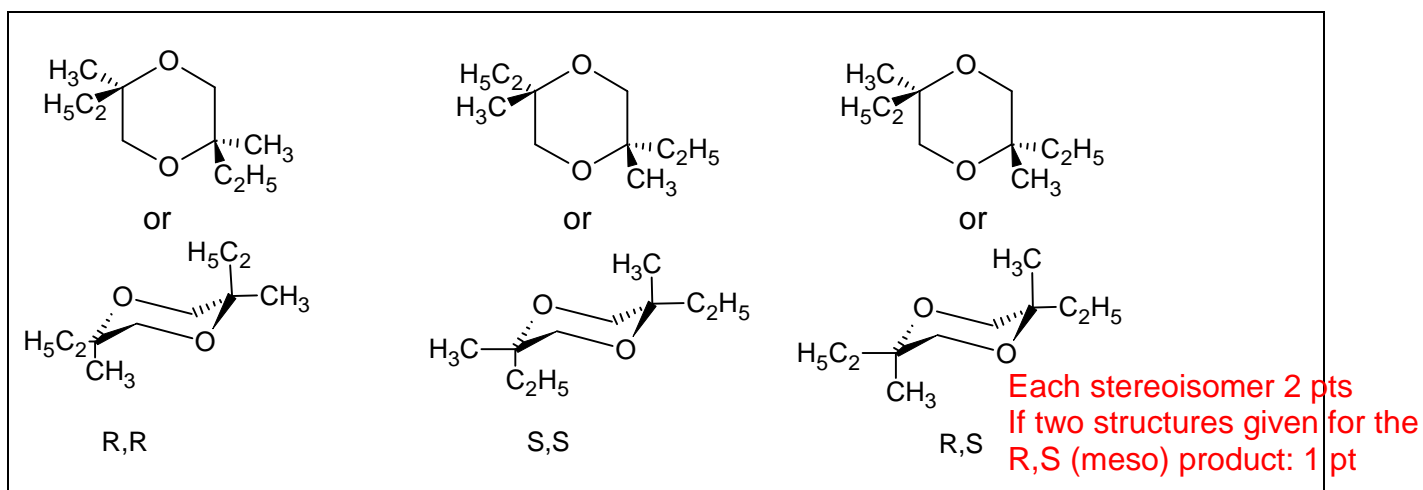
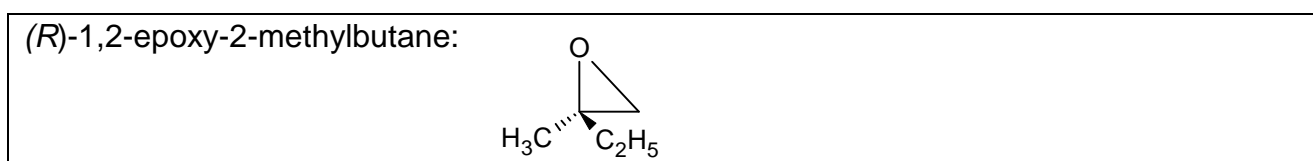
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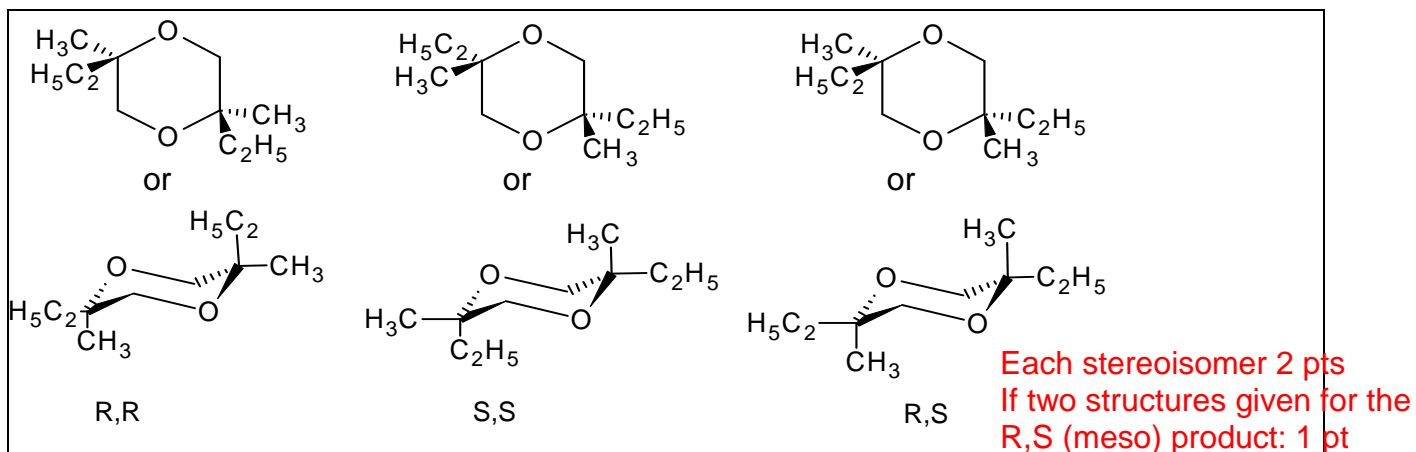
- c) Draw the structure(s) of the most probable 1,4-dioxane derivative(s) when the starting compound is (S)-2-methyloxirane ((S)-1,2-epoxypropane). Give the structure of the reactant as well.



- 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).



Problem 5

7% of the total

| | | |
|----|----|--------|
| 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(NO ₂) ₂ 8 pts | B | (NH ₄) ₂ SO ₄ 8 pts | C | BaSO ₄ 4 pts | 25 bonus points if both A and B are identified correctly. |
| D | BaO 4 pts | E | BaCO ₃ 4 pts | F | BaO ₂ 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

7% of the total

| | | | | | | | |
|----|----|----|----|----|----|----|--------|
| 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-

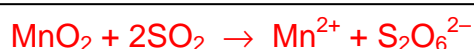
Problem 7

8% of the total

| 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 |
| Experimental rate equation: | (2 pts each) | |
| | $v = k[\text{S}_2\text{O}_6^{2-}][\text{H}^+]$ (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) |
|----|--|

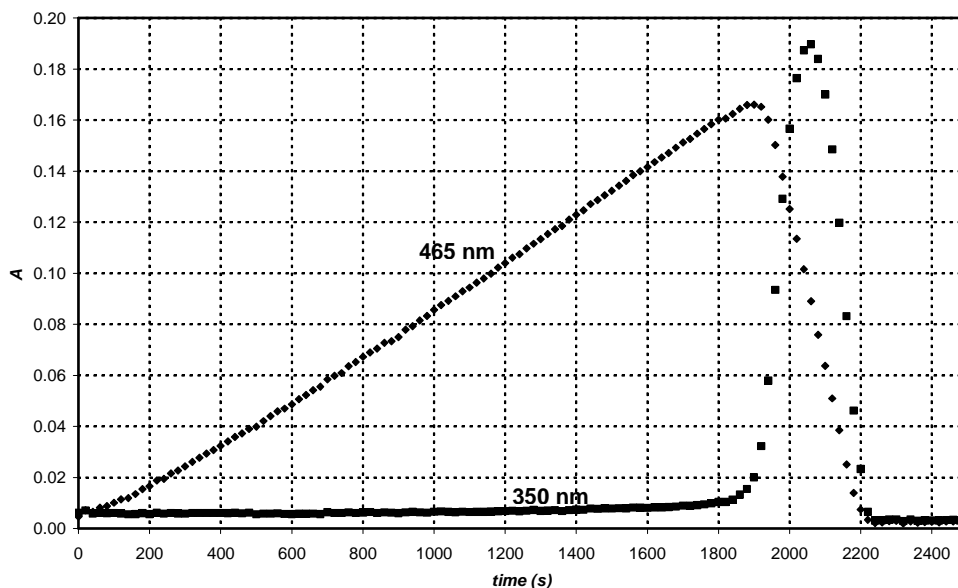
Suggest a balanced chemical equation for the rate determining step of the reactions that used an oxidizing agent.

| | |
|------------------------|---|
| 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 wavelenghts. 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

7 % of the total

| | | | | | | | | | |
|----|----|----|----|----|----|----|----|----|--------|
| 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 CeCl_3 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 Ce^{3+} ($\epsilon = 35.2 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) at 295 nm, and, as a precaution, also for Ce^{4+} ($\epsilon = 3967 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$).

- b) Give a formula to calculate the Ce^{3+} concentration from an absorbance reading at 295 nm (A) measured in a solution containing CeCl_3 (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 $0.0100 \text{ mol/dm}^3 \text{ CeCl}_3$ and $0.1050 \text{ mol/dm}^3 \text{ HCl}$, 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.

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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

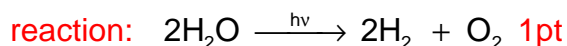
n_{gas} :

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: H_2, O_2 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:

$3.3 \cdot 10^{-4} \text{ mol}$ gas formed altogether: $2.2 \cdot 10^{-4} \text{ mol H}_2$ and $1.1 \cdot 10^{-4} \text{ mol O}_2$.

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 H_2 production: $\Phi = 2.2 \cdot 10^{-4} \text{ mol} / 6.87 \cdot 10^{-3} \text{ mol} = 0.032$

Quantum yield for O_2 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:

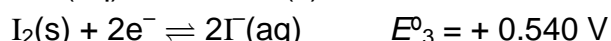
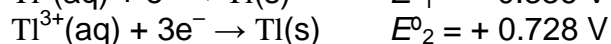
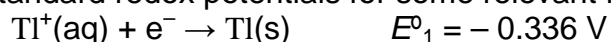
Problem 9

6 % of the total

| | | | | |
|----|----|----|----|--------|
| 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,

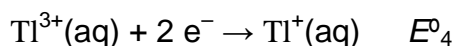
The standard redox potentials for some relevant reactions are:



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

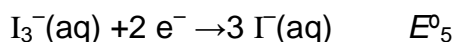
Use $T=25 \text{ }^{\circ}\text{C}$ throughout this problem.

a) Calculate the redox potential for the following reactions:



$$E^{\circ}_4 = \frac{3E^{\circ}_2 - E^{\circ}_1}{2} = 1.26 \text{ V} \quad \text{6 pts}$$

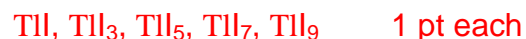
$E^{\circ}_4 =$



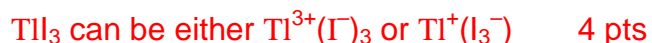
$$E^{\circ}_5 = E^{\circ}_3 + 0.059/2 \lg(1/K_1) = 0.550 \text{ V} \quad \text{6 pts}$$

$E^{\circ}_5 =$

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: $Tl^+(aq) \rightarrow Tl^{3+}(aq) + 2e^-$ $-E^{\circ}_4 = -1.26$ V, thus $\Delta_r G_4^{\circ} = nFE_4^{\circ} = 243.1$ kJ/mol $I_3^-(aq) + 2e^- \rightarrow 3I^-(aq)$ $E^{\circ}_5 = 0.550$ V, thus $\Delta_r G_5^{\circ} = -nFE_5^{\circ} = -106.1$ kJ/mol $Tl^{3+} + 4I^- \rightarrow TlI_4^-$ $\beta_4 = 10^{35.7}$ thus $\Delta_r G_6^{\circ} = -RT \ln \beta_4 = -203.8$ kJ/mol 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 Thus $K_2 = \exp\left(-\frac{\Delta_r G_7^{\circ}}{RT}\right) = 4.96 \cdot 10^{11}$ 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. 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.