40th International
Chemistry Olympiad

Theoretical Problems

17 July 2008
Budapest, Hungary

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

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																	18
1 H 1.008	2											13	14	15	16	17	2 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 -

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

<div style="color:red">
Any univalent, strong acid (HCl, HBr, HI, HNO_3, $HClO_4$) is acceptable. HF is not!
</div>

b) <u>Could</u> it be possible that the dilute solution contained sulfuric acid?

Sulfuric acid: pK_{a2} = 1.99

☐ Yes ☐ No

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

<div style="color:red">
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.
</div>

pH:

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

Acetic acid: $pK_a = 4.76$

☐ Yes ☐ No

If yes, <u>calculate</u> 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

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

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

This means that $[HA] = [OH^-]$ a sum of 4 pts

Formula:

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

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: $[H^+] = \sqrt[3]{(KK_w)}$

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

Starting with a neutral solution two cycles of iteration give identical results: $5.64 \cdot 10^{-7}$ mol/dm^3 as the required concentration. Exact pH is 6.25.   3 pts

pH:

d) <u>Could</u> 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, <u>calculate</u> 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:

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

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

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

$$K_1K_2 = \frac{[H^+]^2[H_2A^{2-}]}{[H_4A]} = [H^+]^2 \quad \text{(or pH} = (pK_1 + pK_2)/2 = 2.15\text{)} \qquad \text{(2 pts)}$$
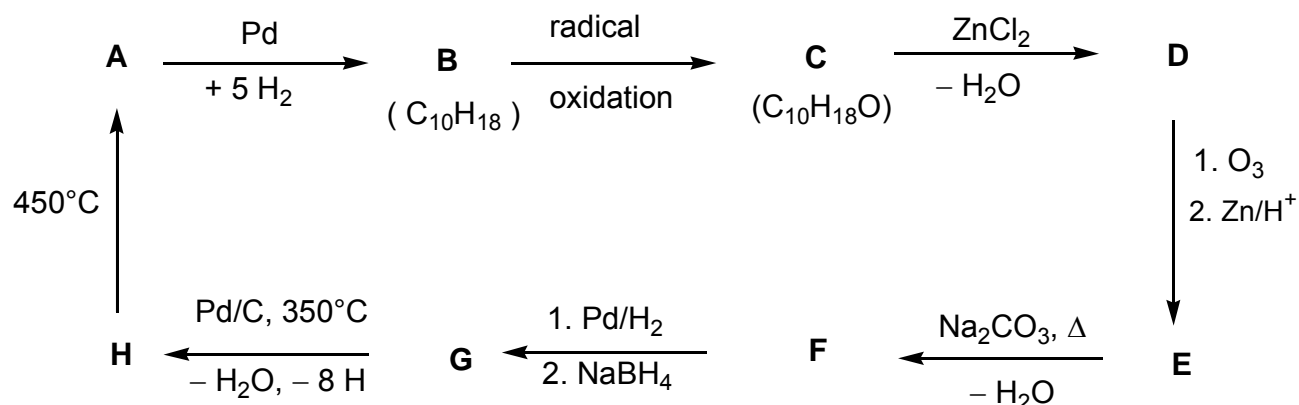
c = 0.0071 mol/dm^3 (1 pt)

c_{EDTA}:

Problem 2   7% of the total
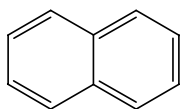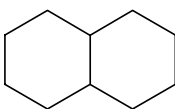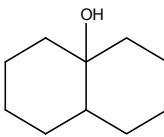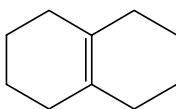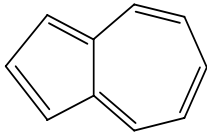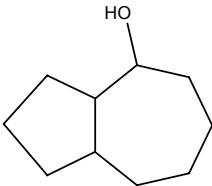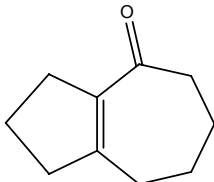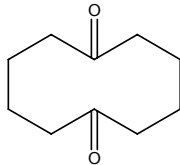
Task 2
18

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

$$\textbf{A} \xrightarrow[\text{+ 5 H}_2]{\text{Pd}} \textbf{B} \xrightarrow[\text{oxidation}]{\text{radical}} \textbf{C} \xrightarrow[\text{– H}_2\text{O}]{\text{ZnCl}_2} \textbf{D}$$

B ($C_{10}H_{18}$) C ($C_{10}H_{18}O$)

450°C (A ← H)

D → E : 1. O_3 2. Zn/H^+

$$\textbf{H} \xleftarrow[\text{– H}_2\text{O, – 8 H}]{\text{Pd/C, 350°C}} \textbf{G} \xleftarrow[\text{2. NaBH}_4]{\text{1. Pd/H}_2} \textbf{F} \xleftarrow[\text{– H}_2\text{O}]{\text{Na}_2\text{CO}_3, \Delta} \textbf{E}$$

Hints:

- **A** is a well-known aromatic hydrocarbon.

- A <u>hexane</u> 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
		OH	

H	G	F	E
	HO		
		2 pts each, 4 pts for **F**	

Problem 3   6% of the total

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

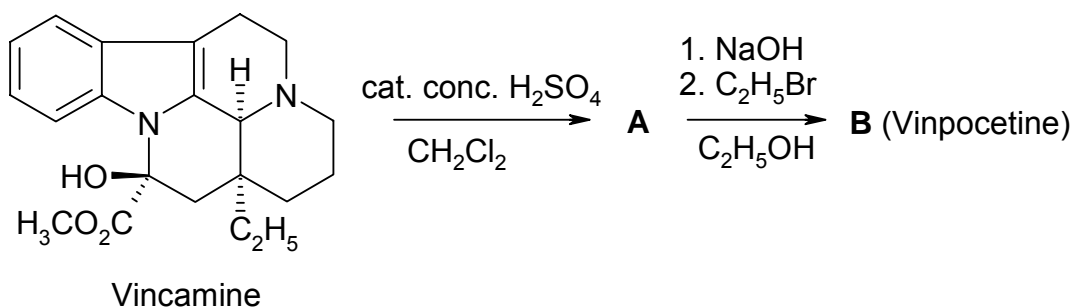Vinpocetine (Cavinton®, Calan®) is one of the best selling original drugs developed in Hungary. Its preparation relies on a natural precursor, (+)-vincamine ($C_{21}H_{26}N_2O_3$), which is isolated from the vine plant, *vinca minor*. The transformation of (+)-vincamine to vinpocetine is achieved in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

Vincamine

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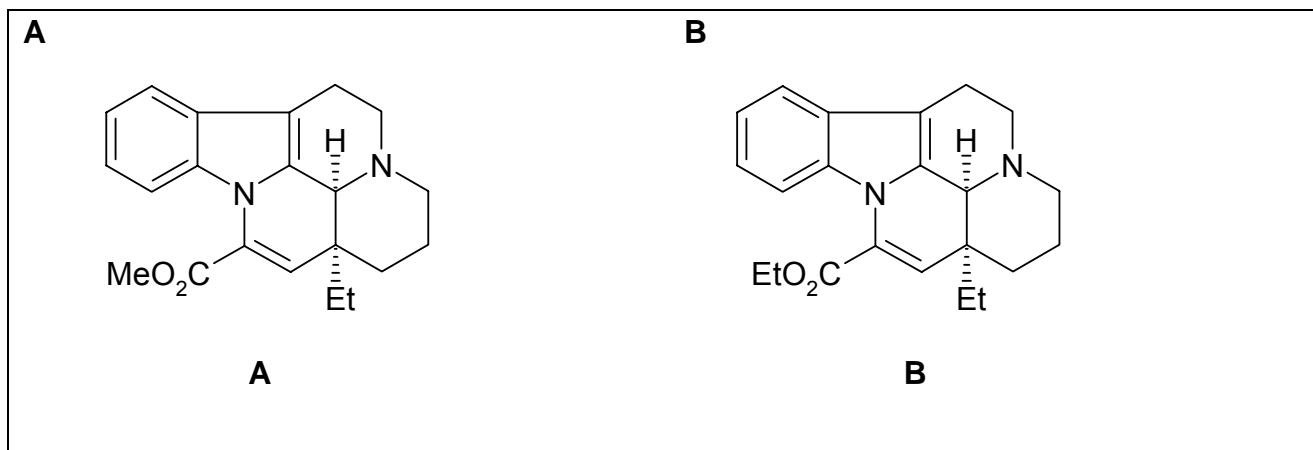
A study of the metabolism of any drug forms a substantial part of its documentation. There are four major metabolites each formed from vinpocetine (**B**): **C** and **D** are formed in hydrolysis or hydration reactions, while **E** and **F** are oxidation products.

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
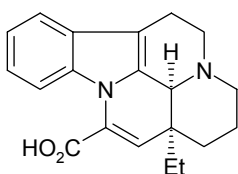
C apovincaminic acid

D
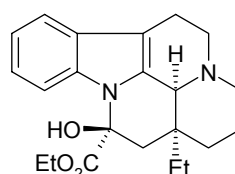
D ethyl vincaminate

Both stereoisomers around the new chiral center are acceptable.

E
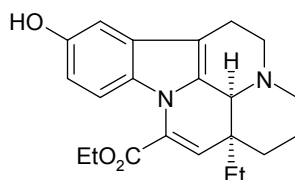
E 10-hydroxyvinpocetine

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.
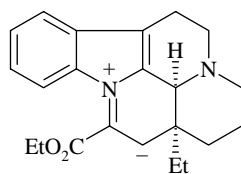
Problem 4   6% of the total

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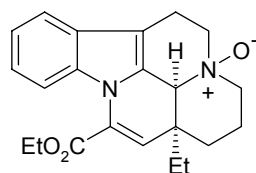
On base catalysis the sterically less hindered C–O bond is cleaved predominantly.

Keep stereochemistry in mind throughout the whole problem. To depict stereochemistry use only the ◄ ⸾⸾⸾⸾⸾‖‖ ——— bond symbols and nothing else where necessary.

a)   Draw the structure of the reactant and the predominant products when 2,2-dimethyl-oxirane (1,2-epoxy-2-methylpropane) reacts with methanol at low temperatures, catalysed by
     (i) sulfuric acid
     (ii) NaOCH$_3$.
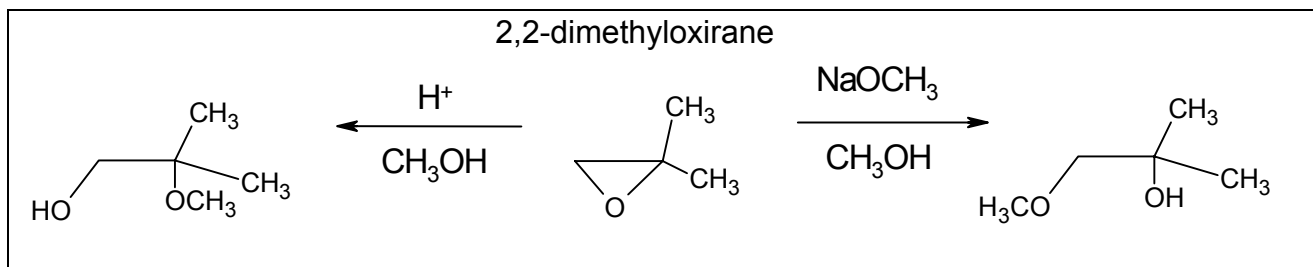
b)   Draw the structure of the predominant product when the epoxide ring of the following leukotriene derivative is opened with a thiolate (RS$^-$).
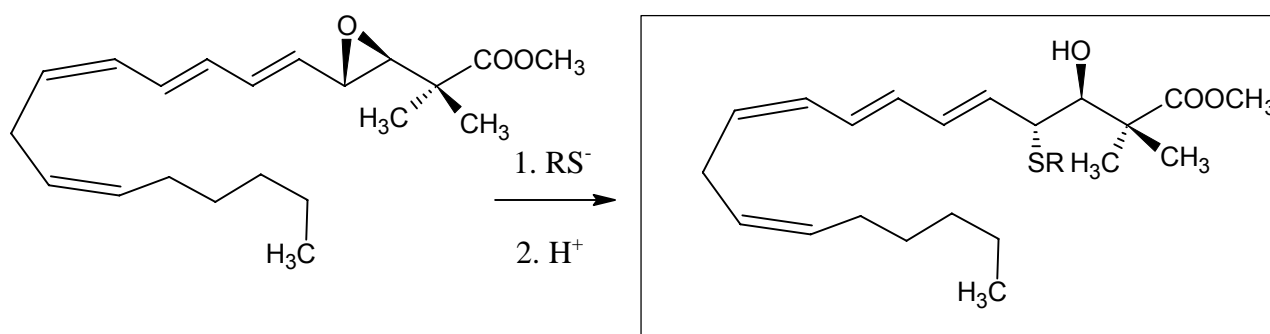
Different porous **acidic** aluminosilicates can also be used to catalyse the transformation of alkyl oxiranes. In addition to ring opening, cyclic dimerisation is found to be the main reaction pathway producing mainly 1,4-dioxane derivatives (six-membered saturated rings with two oxygen atoms in positions 1,4).

Name: **Code: XXX-**

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

(*S*)-2-methyloxirane   product

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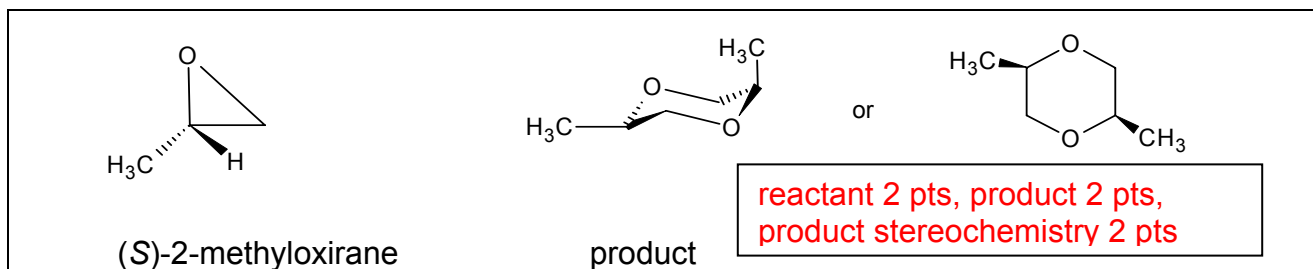
d) <u>Draw</u> the structure(s) of the substituted 1,4-dioxane(s) when the epoxide reacting is (*R*)-1,2-epoxy-2-methylbutane ((*R*)-2-ethyl-2-methyloxirane). <u>Give</u> the structure of the reactant as well.

(*R*)-1,2-epoxy-2-methylbutane:

R,R   S,S   R,S

Each stereoisomer 2 pts
If two structures given for the R,S (meso) product: 1 pt
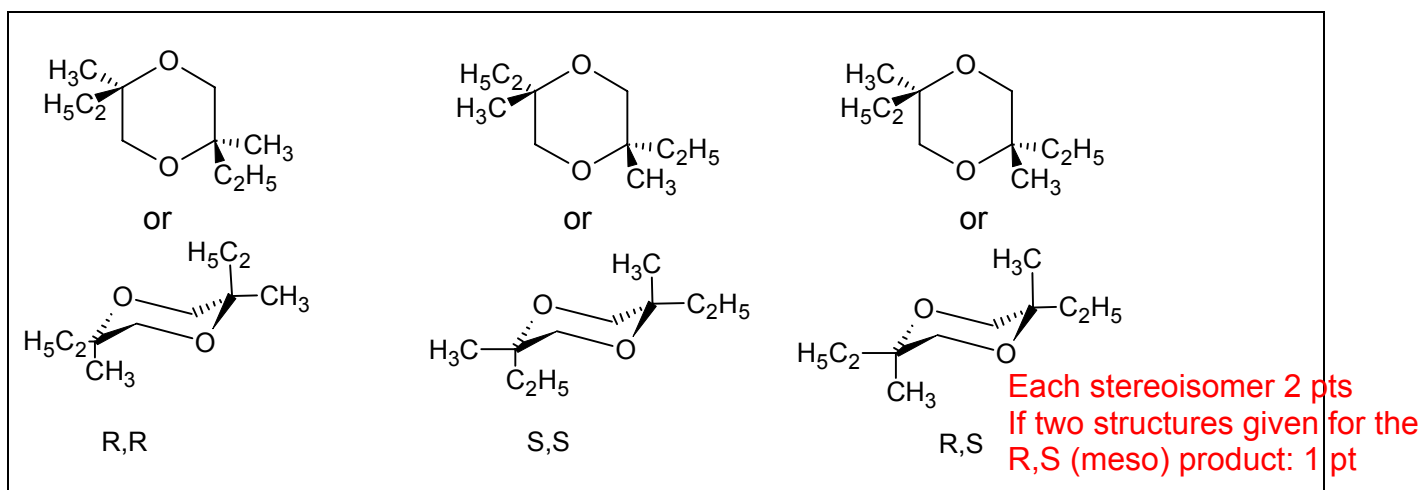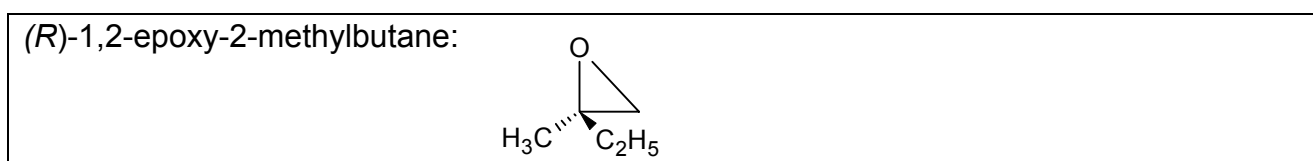
e) <u>Give</u> the structure(s) of the substituted 1,4-dioxane(s) when this reaction is carried out with racemic 1,2-epoxy-2-methylbutane (2-ethyl-2-methyloxirane).

R,R   S,S   R,S

Each stereoisomer 2 pts
If two structures given for the R,S (meso) product: 1 pt
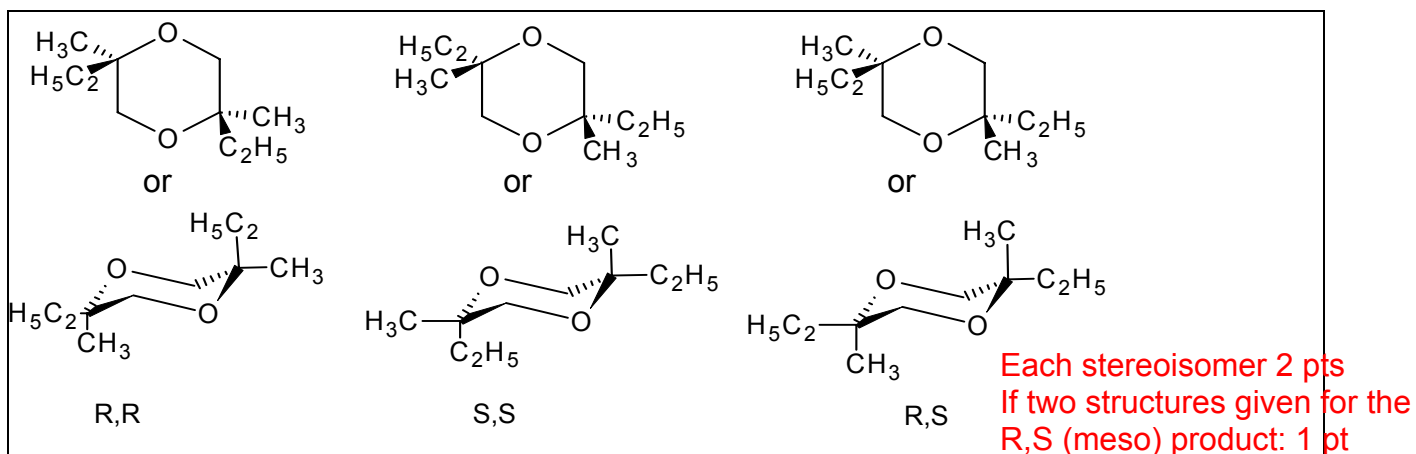
Problem 5   7% of the total

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** $(NH_4)_2SO_4$ 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 HPO_4^{2-} 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).

$Ba(NO_2)_2 = BaO + NO + NO_2$	6 pts
$(NH_4)_2SO_4 = NH_4HSO_4 + NH_3$	0 pts

(*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.)

$Ba^{2+} + SO_4^{2-} = BaSO_4$	2 pts
$2\ NO_2^- + 2\ I^- + 4\ H^+ = 2\ NO + I_2 + 2\ H_2O$	4 pts
$NH_4^+ + NO_2^- = N_2 + 2\ H_2O$	8 pts
$BaO + H_2O = Ba^{2+} + 2\ OH^-$	1 pt
$Ba^{2+} + 2\ OH^- + CO_2 = BaCO_3 + H_2O$	1 pt
$BaO + CO_2 = BaCO_3$	1 pt
$2\ BaO + O_2 = 2\ BaO_2$	4 pts
$BaO_2 + 2\ I^- + 4\ H^+ = Ba^{2+} + I_2 + 2\ H_2O$	4 pts
$BaCO_3 = BaO + CO_2$	1 pt
$NH_4^+ + OH^- = NH_3 + H_2O$	1 pt

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 $Ca(OH)_2$ 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 $M_{Ca} + 45.8$, or $M_{Sr} + 39.05$, or $M_{Ba} + 32$. 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 $Ba(OH)_2$ 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, $(NH_4)_2HPO_4$ would not give the same $BaHPO_4$ precipitate with $Ba(OH)_2$ as with $Ba(NO_2)_2$. If we accept that **B** is $(NH_4)_2SO_4$, 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 = 20x2 (dodecahedra) + 6x2 /2 (faces)

c)   If all cavities contain a guest molecule, <u>what</u> 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. <u>What</u> is the density of the clathrate?

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

Density:

e) The density of chlorine hydrate is 1.26 g/cm^3. <u>What</u> 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 nm^3·1.26 g/cm^3 = 2.081·10^{-21} g, meaning 1253 g/mol for the contents.

Substracting 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:

<u>Which</u> 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).

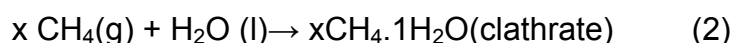| Atom	Covalent radius (pm)	Nonbonded radius (pm)
H	37	120
C	77	185
O	73	140
Cl	99	180

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

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

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

Let us consider the following processes

    $H_2O(l) \rightarrow H_2O(s)$ (1)

    $x\ CH_4(g) + H_2O\ (l) \rightarrow xCH_4.1H_2O(clathrate)$ (2)

g)   <u>What</u> are the signs of the following molar quantities referring to these reactions in the given direction at 4 °C? <u>Mark</u> 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:
$\Delta G_m(1) > \Delta G_m(2)$
$\Delta H_m(1) - T\,\Delta S_m(1)\ > \Delta H_m(2) - T\,\Delta S_m(2)$
$T\,(\Delta S_m(2) - \Delta S_m(1)\,) > \Delta H_m(2) - \Delta H_m(1)$
a negative quantity $> \Delta H_m(2) - \Delta H_m(1)$

1 pt each, the last 3 pts.

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 ($S_2O_6^{2-}$) is a rather inert inorganic ion. It can be prepared by bubbling sulphur-dioxide continously into ice-cooled water to which manganese dioxide is added in small increments. Dithionate and sulphate ions are formed under these circumstances.

a) <u>Write</u> the balanced chemical equations for the two reactions.

$$MnO_2 + 2SO_2 \rightarrow Mn^{2+} + S_2O_6^{2-}$$

$$MnO_2 + SO_2 \rightarrow Mn^{2+} + SO_4^{2-} \qquad \text{1 pt each}$$
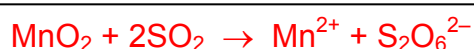
After the reaction is complete, $Ba(OH)_2$ is added to the mixture until the sulphate ions are fully precipitated. This is followed by the addition of Na_2CO_3.

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

$$MnS_2O_6 + Na_2CO_3 \rightarrow Na_2S_2O_6 + \underline{MnCO_3} \qquad \text{1 pt}$$

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 °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 °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) <u>Give</u> the composition of the prepared crystals and <u>write</u> balanced equations for the two processes that occur during heating.

Formula:

    $Na_2S_2O_6 \cdot 2H_2O$ (2 pts only for the correct formula)

Equation (130 °C):

    $Na_2S_2O_6 \cdot 2H_2O \rightarrow Na_2S_2O_6 + 2H_2O$ (1 pt)

    $Na_2S_2O_6 \rightarrow Na_2SO_4 + SO_2$ or with H_2O (1 pt)

Equation (300 °C):

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) <u>Write</u> the balanced chemical equation for the reaction between bromine and dithionate ion.

> $S_2O_6^{2-} + Br_2 + 2H_2O \rightarrow 2SO_4^{2-} + 2Br^- + 4H^+$ 2 pts

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

$[Br_2]_0$ (mmol/dm^3)	$[Na_2S_2O_6]_0$ (mol/dm^3)	$[H^+]_0$ (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) <u>Determine</u> the order of the reaction with respect to Br_2, H^+ and $S_2O_6^{2-}$, the experimental rate equation, and the value and unit of the rate constant.

Reaction order for Br_2:   for H^+:   for $S_2O_6^{2-}$:

> 0   1   1
>
> (2 pts each)

Experimental rate equation:

> $v = k[S_2O_6^{2-}][H^+]$ (1 pt)

> $k = 2.56 \cdot 10^{-5}$ dm^{3}mol^{-1}s^{-1} (1 pt: no point if unit is incorrect; unorthodox but correct unit acceptable)

k:

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 $2.54 \cdot 10^{-5}$ ($Cr_2O_7^{2-}$).

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:	$S_2O_6^{2-} + H^+ \rightarrow HSO_4^- + SO_2$ 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: $[Na_2S_2O_6] = 0.0022$ mol/dm^3, $[HClO_4] = 0.70$ 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.

| |
|---|
| $t_{1/2}$ = 10 h 45 min = $3.87 \cdot 10^4$ s
k_{obs} = ln2 / $t_{1/2}$ = $1.79 \cdot 10^{-5}$ s^{-1} 2 pts
$k = k_{obs}/[H^+] = 2.56 \cdot 10^{-5}$ dm^{3}mol^{-1}s^{-1} 2 pts (other consistent units also acceptable) |

k:

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

Rate determining step:	$S_2O_6^{2-} + H^+ \rightarrow HSO_4^- + SO_2$ 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 $[H_4IO_6^-] = 5.3 \cdot 10^{-4}$ mol/dm^3, $[Na_2S_2O_6] = 0.0519$ mol/dm^3, $[HClO_4] = 0.728$ mol/dm^3 At 465 nm, only I_2 absorbs and its molar absorption coefficient is 715 dm^{3}mol^{-1}cm^{-1}. At 350 nm, only I_3^- absorbs and its molar absorption coefficient is 11000 dm^{3}mol^{-1}cm^{-1}. The optical path length was 0.874 cm.
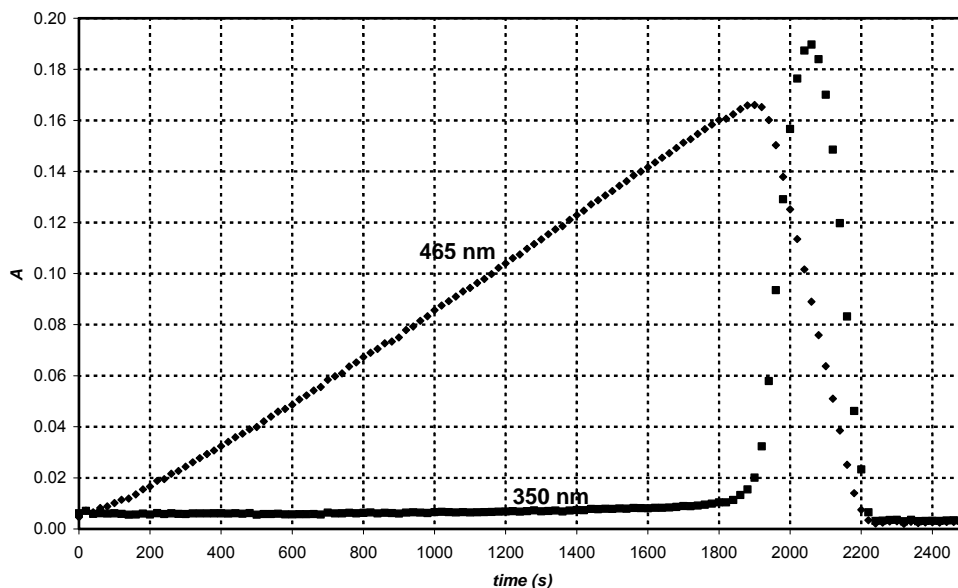
h) <u>Write</u> balanced chemical equations for the reactions that occur in the region where the absorbance increases at 465 nm, and in the region where the absorbance decreases at 465 nm.

Increase:	$2\ H_4IO_6^- + 7\ S_2O_6^{2-} + 2\ H_2O + 2\ H^+ \rightarrow\ 14\ HSO_4^- + I_2$ 2 pts
Decrease:	$I_2 + S_2O_6^{2-} + 2\ H_2O \rightarrow\ 2\ HSO_4^- + 2\ I^- + 2\ H^+$ 2 pts

<u>Calculate</u> the expected time for the maximum absorbance of the kinetic curve measured at 465 nm.

$$t_{max} = \frac{7}{2} \frac{[H_4IO_6^-]_0}{k[S_2O_6^{2-}]_0[H^+]_0} = \frac{7 \times 5.3 \times 10^{-4}\ M}{2 \times 2.56 \times 10^{-5}\ M^{-1}s^{-1} \times 0.0519\ M \times 0.728\ M} = 1900$$

5 pts

t_{max}:

<u>Estimate</u> 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:

Name: _____   Code: XXX-_____

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).

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

Ms. Z also determined the molar absorption coefficient for Ce^{3+} (ε = 35.2 dm^{3}mol^{-1}cm^{-1}) at 295 nm, and, as a precaution, also for Ce^{4+} (ε = 3967 dm^{3}mol^{-1}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).

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

Ms. Z prepared a solution which contained 0.0100 mol/dm^3 $CeCl_3$ and 0.1050 mol/dm^3 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_{295nm}= $[Ce^{3+}]$ = 0.0100 mol/dm^3 $\Rightarrow$ A_{295nm}= 0.352

E = $[Cl^-]$ = 3·0.0100 mol/dm^3 + 0.1050 mol/dm^3 = 0.1350 mol/dm^3 $\Rightarrow$ E = 19.2 mV

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) <u>Give</u> the formula of two gases, comprised of elements in the illuminated sample, which could not be present given the results of this experiment.

> HCl, Cl_2, (O_3, ClO_2) (no oxidation of indicator)

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

time (min)	0	120	240	360	480
$A_{295\ nm}$	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 Ce^{3+}, Cl^-, and H^+.

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

> No significant change in either Cl^- or Ce^{3+} concentrations.
> $[H^+] = [Cl^-] - 3\ [Ce^{3+}]$,   no significant change.
> All three values zero. 1 pt each.

$d[Cl^-]/dt =$

$d[H^+]/dt =$

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 $CeCl_3$ solution she had used before. She measured the molar absorption coefficient for Ce^{3+} ($\varepsilon = 2400\ dm^3mol^{-1}cm^{-1}$) at 254 nm.

f) <u>What</u> percentage of the light is absorbed in this experimental setup?

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

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 cm^3. 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.

g) <u>Estimate</u> the amount of substance of the gas collected in the chamber.

$p_{partial}$ = p_{final} − $p_{initial}$ = 114075 Pa − 102165 Pa = 11910 Pa

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

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

Gas(es):

identity of gases: H_2, O_2 4 pts

reaction: $2H_2O \xrightarrow{h\nu} 2H_2 + O_2$ 1pt
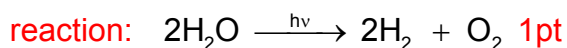
Reaction:

h) <u>What</u> 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) <u>Estimate</u> the quantum yield of product formation in the Ce(III) solution.

Quantum yield:
3.3·10^{-4} mol gas formed altogether: 2.2·10^{-4} mol H_2 and 1.1·10^{-4} mol O_2.
Light beam intensity 0.0500 Js^{-1} $\Rightarrow$ $\dfrac{0.0500 \text{ J/s } \lambda}{hcN_A}$ = 1.06·10^{-7} mols^{-1} photon

Total time 18.00 h = 64800 s
Total number of absorbed photons: 64800 s·1.06·10^{-7} mols^{-1} = 6.87·10^{-3} mol

Quantum yield for H_2 production: Φ = 2.2·10^{-4} mol / 6.87·10^{-3} mol = 0.032
Quantum yield for O_2 production: Φ = 1.1·10^{-4} mol / 6.87·10^{-3} mol = 0.016

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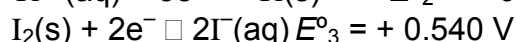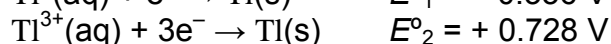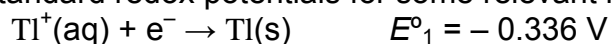
Quantum yield:

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 aquous solutions,
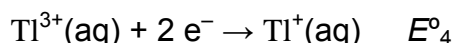The standard redox potentials for some relevant reactions are:

$\qquad Tl^+(aq) + e^- \rightarrow Tl(s) \qquad E°_1 = -0.336$ V
$\qquad Tl^{3+}(aq) + 3e^- \rightarrow Tl(s) \qquad E°_2 = +0.728$ V
$\qquad I_2(s) + 2e^- \square 2I^-(aq)\, E°_3 = +0.540$ V

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

Use T=25 °C throughout this problem.

a) Calculate the redox potential for the following reactions:

$\qquad Tl^{3+}(aq) + 2\,e^- \rightarrow Tl^+(aq) \qquad E°_4$

$$E_4^\circ = \frac{3E_2^\circ - E_1^\circ}{2} = 1.26 \text{ V} \qquad \text{6 pts}$$
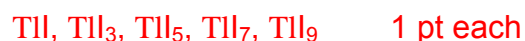
$E°_4 =$
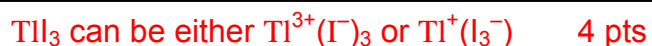
$\qquad I_3^-(aq) + 2\,e^- \rightarrow 3\,I^-(aq) \qquad E°_5$
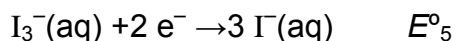
$$E°_5 = E°_3 + 0.059/2 \lg(1/K_1) = 0.550 \text{ V} \qquad \text{6 pts}$$

$E°_5 =$

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).

$TlI, TlI_3, TlI_5, TlI_7, TlI_9 \qquad$ 1 pt each

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

TlI_3 can be either $Tl^{3+}(I^-)_3$ or $Tl^+(I_3^-)$ $\qquad$ 4 pts

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

More stable:	$Tl^+(I_3^-)$ as $E^o_4 > E^o_5$ or E^o_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) <u>Write</u> the reaction that takes place when a solution of the more stable isomer of thallium iodide is treated with an excess of KI. <u>Calculate</u> the equilibrium constant for this reaction.

Reaction:

$Tl^+ + I_3^- + I^- \rightarrow TlI_4^-$ 3 pts

This reaction could be regarded as sum of three reactions:
$Tl^+(aq) \rightarrow Tl^{3+}(aq) + 2e^-$ $-E^o_4 = -1.26$ V, thus $\Delta_r G_4^o = nFE_4^o = 243.1$ kJ/mol
$I_3^-(aq) + 2e^- \rightarrow 3I^-(aq)$ $E^o_5 = 0.550$ V, thus $\Delta_r G_5^o = -nFE_5^o = -106.1$ kJ/mol
$Tl^{3+} + 4I^- \rightarrow TlI_4^-$ $\beta_4 = 10^{35.7}$ thus $\Delta_r G_6^o = -RT \ln\beta_4 = -203.8$ kJ/mol
The net free enthalpy change is $\Delta_r G_7^o = \Delta_r G_4^o + \Delta_r G_5^o + \Delta_r G_6^o = -66.8$ kJ/mol

Thus $K_2 = \exp\left(-\dfrac{\Delta_r G_7}{RT}\right) = 4.96 \cdot 10^{11}$

3 pts each for $\Delta_r G^o_{(4-6)}$ and for K_2.

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) <u>What</u> is the empirical formula of this compound? Show your calculations. <u>Write</u> a balanced equation for its formation.

Supposing that the substance contains Tl and an anion, the formula of the compound is Tl_aX_b and the following equation holds:

$$\frac{a \cdot 204.4}{a \cdot 204.4 + bM_X} = 0.895$$

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

Formula:

Tl_2O_3. 2 pts

Equation:

$2\ TlI_3 + 6\ OH^- \rightarrow Tl_2O_3 + 6\ I^- + 3\ H_2O$ 3 pts
2 pts if H^+ or H_3O^+ ions are written at the right side of the equation.