40 Hu 08

40th International Chemistry Olympiad

Theoretical Problems

17 July 2008

Budapest, Hungary

Instructions

- Write your name and code number 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 will receive no marks.
- 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 27 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}	$\Delta_r G^\circ = -RT \ln K = -nFE^\circ_{cell}$	
Planck constant:	$h = 6.626 \cdot 10^{-34}$ J s	Nernst equation:	$E = E^\circ + \frac{RT}{zF} \ln \frac{c_{ox}}{c_{red}}$
Speed of light:	$c = 3.000 \cdot 10^{8}$ m s^{-1}	Energy of a photon:	$E = \frac{hc}{\lambda}$
Zero of the Celsius scale:	273.15 K	Lambert-Beer law:	$A = \log \frac{I_0}{I} = \varepsilon c l$

In equilibrium constant calculations all concentrations are referenced to a standard concentration of 1 mol L^{-1}. Consider all gases ideal throughout the exam.

Periodic table with relative atomic masses

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H 1.008																	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											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 -

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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.

b) Could the dilute solution have 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 working.

pH:

c) Could the solution have 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 working.

pH:

d) Could the solution have 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.

c_{EDTA}:

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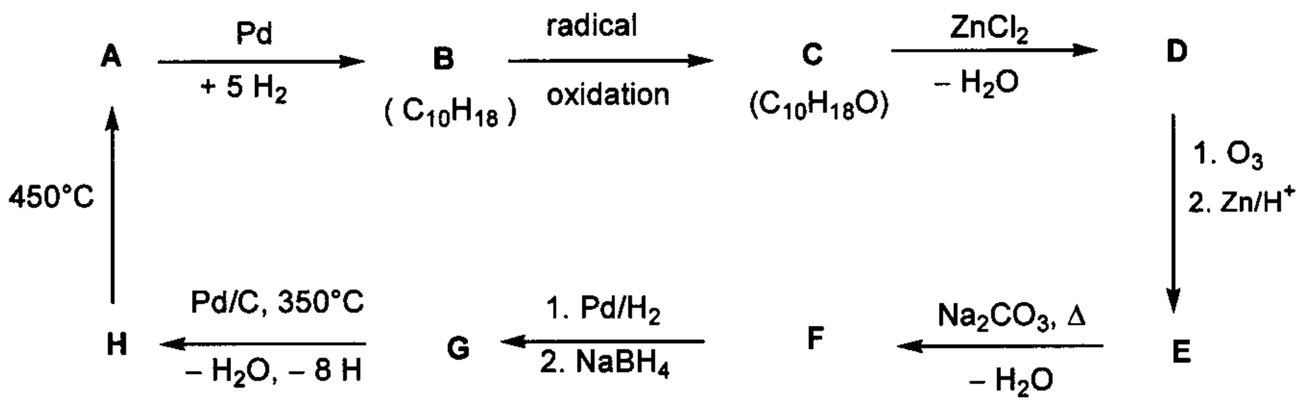
Problem 2 7% of the total

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. This gives **F** on dehydration.

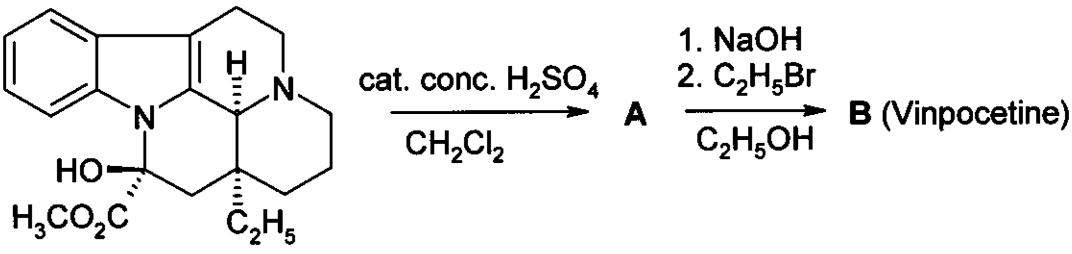
A	**B**	**C**	**D**
H	**G**	**F**	**E**

Name: Code: NZL -

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.

- 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 intermediate **A** and vinpocetine (**B**).

A **B**

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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.

E and **F** are oxidation products.

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

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.
  D and **F** each have 7 other stereoisomers.
- **F** is a pentacyclic zwitterion and it has the same elemental 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.

C	**D**
E	**F**

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

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Problem 4 — 6% of the total

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

Oxiranes (epoxides) react by ring opening. This may be accomplished in various ways.

Acid catalysed reactions proceed through cation-like (carbenium ion-like) species. For substituted oxiranes (epoxides), 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.

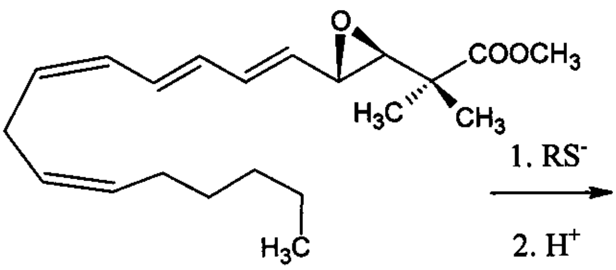
In base catalysed reactions, the sterically less hindered C–O bond is cleaved predominantly.

Keep stereochemistry in mind throughout the entire 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) $NaOCH_3$

2,2-dimethyloxirane

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 and 4).

c) Draw the structure(s) of the most probable 1,4-dioxane derivative(s) formed by reaction of (*S*)-2-methyloxirane ((*S*)-1,2-epoxypropane).
Give the structure of the reactant as well.

(*S*)-2-methyloxirane product

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

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

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

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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 acidified KI solution.

When boiled, the filtrate evaporates without the appearance of any residue.

The white solid **D** can be prepared by heating **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 85.8% of **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 heating above 1400 °C is required.

The reaction of **B** and **D** in water gives a precipitate, **C**, and is accompanied by a characteristic odour.

a) <u>Give the formulae of</u> the substances **A** - **F**

A	**B**	**C**
D	**E**	**F**

b) Write balanced equations for **all reactions occurring** except for the thermal decomposition of **B**.

Equations:

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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 the 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. The resulting substances are referred to as clathrates.

The crystals of chlorine and methane clathrates have the same structure. The main characteristics are dodecahedra formed from 20 water molecules. The unit cell of the crystal can be thought as a body-centered cubic arrangement of 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 unit cell. 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?

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

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

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

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?

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 covalently bonded (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 estimate lower and upper bounds for the average radii of the cavities where possible. Show your reasoning.

< r (**A**) < < r(**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) What are the signs of the following molar quantities referring to these reactions in the given direction at 4 °C?
Mark with a –, 0 or +.

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

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 continuously into ice-cooled water to which manganese dioxide is added in small increments. Both dithionate and sulphate ions are formed under these conditions.

a) Write balanced chemical equations for the two reactions.

After 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) Write the balanced equation for the reaction occurring upon addition of Na_2CO_3.

Sodium dithionate is then crystallized by evaporating some of the solvent. The resulting 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 also does not give a precipitate with $BaCl_2$ solution.

When another sample of the original crystals is heated 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) Give the composition of the crystals prepared above.
Write balanced equations for the two processes that occur during heating.

Formula:

Equation (130 °C):

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 solution. A series of kinetic experiments were carried out with bromine as the 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.

$[Br_2]_0$ (mmol L^{-1})	$[Na_2S_2O_6]_0$ (mol L^{-1})	$[H^+]_0$ (mol L^{-1})	v_0 (nmol L^{-1} 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 $S_2O_6^{2-}$, the experimental rate equation, and the value of and units for the rate constant.

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

Experimental rate equation:

k:

In similar experiments, chlorine, bromate ion, hydrogen peroxide and chromate ion have been used as oxidants (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 in the absence of an oxidant (oxidizing agent). When following the processes by UV spectrophotometry, the slow appearance of a new absorption band around 275 nm was observed. Hydrogen sulphate ion is a detectable product of the reaction, but this species does not absorb light above 200 nm.

f) Give the formula of the major species causing the new absorption band.
Write the balanced equation for the reaction occurring in the absence of an oxidant.

Species:
Reaction:

An experiment was carried out to follow the absorbance at 275 nm. The initial concentrations were $[Na_2S_2O_6] = 0.0022$ mol L^{-1}, $[HClO_4] = 0.70$ mol L^{-1}, 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.

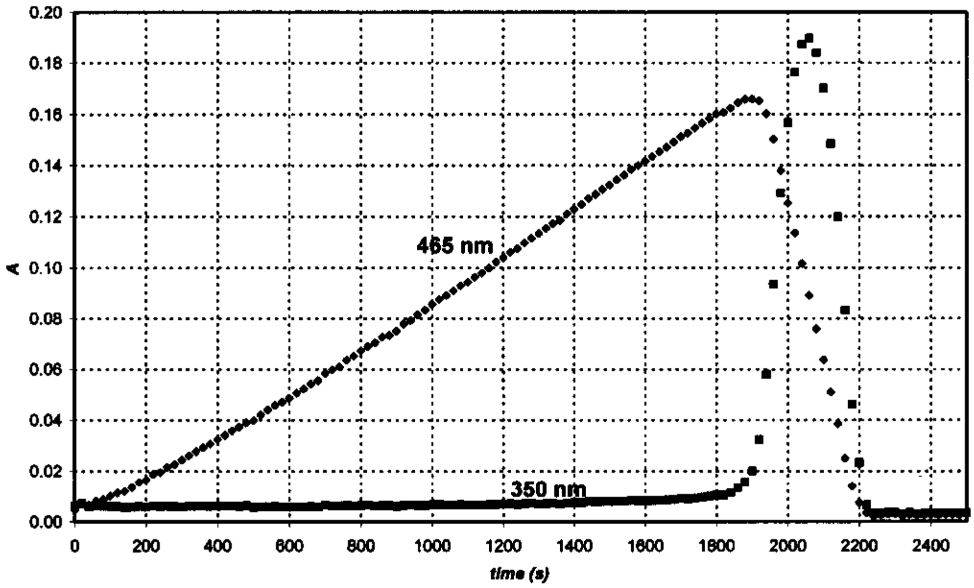
k:

Suggest a balanced chemical equation for the rate determining step of the reactions that occurred in the presence of an oxidant (oxidizing agent).

Rate determining step:

When periodate ion (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 two different wavelengths in the same experiment at 75 °C. The initial concentrations were $[H_4IO_6^-]$ = $5.3\cdot10^{-4}$ mol L^{-1}, $[Na_2S_2O_6]$ = 0.0519 mol L^{-1}, $[HClO_4]$ = 0.728 mol L^{-1}

At 465 nm, only I_2 absorbs and its molar absorption coefficient is 715 L mol^{-1}cm^{-1}.
At 350 nm, only I_3^- absorbs and its molar absorption coefficient is 11000 L mol^{-1}cm^{-1}.
The optical path length was 0.874 cm.



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}:

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

Slope ratio:

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Problem 8 7 % of the total

8a	8b	8c	8d	8e	8f	8g	8h	8i	Task 8
3	3	4	3	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 was not necessary to see the bubble formation, and she continued her experiments with an acidified $CeCl_3$ solution. Bubble formation never occurred when she kept the solution in the spectrophotometer without turning on the instrument.

Next, Ms Z used a small quartz flask, into 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 results shown at the right.

c_{NaCl} (mol L^{-1})	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).

$[Cl^-]$ =

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

b) Give a formula to calculate the Ce^{3+} concentration from an absorbance (A) reading at 295 nm measured in a solution containing $CeCl_3$ (cell path length: 1.000 cm).

$[Ce^{3+}]$ =

Ms Z prepared a solution which contained 0.0100 mol L^{-1} $CeCl_3$ and 0.1050 mol L^{-1} 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}=

E =

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.

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^+.

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

$d[Cl^-]/dt$ =

$d[H^+]/dt$ =

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+} (ε = 2400 L $mol^{-1}cm^{-1}$) at 254 nm.

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

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 having a volume of 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) Estimate the amount of substance of the gas collected in the chamber.

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.
Give the balanced equation for the chemical reaction that occurs when the sample is illuminated.

Gas(es):

Reaction:

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

p =

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

Quantum yield:

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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:

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

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

Assume that the temperature is 25 °C throughout this problem.

a) Calculate the reduction potential for the following reactions:

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

$E°_4$ =

$I_3^-(aq) + 2e^- \rightarrow 3I^-(aq)$ $E°_5$

$E°_5$ =

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

Which empirical formula could belong to two different compounds?

Based on the standard reduction potentials,
Which of the two compounds mentioned above is the stable one at standard conditions?
Write the chemical reaction for the inter-conversion of the two thallium iodide compounds.

More stable:

Inter-conversion:

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

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

Reaction:

K_2:

If the solution of the more stable compound is treated with a strongly 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 formation of this compound.

Formula:

Equation: