48th International Chemistry Olympiad

Practical Tasks
Part I.

26 July 2016

Tbilisi, Georgia

Instructions

- Begin only when the START command is given. The exam contains two parts. You have 100 minutes to work on Part I (Task 1). After this you will have to leave the lab for 30 minutes.

- Part I of the exam (Task 1) contains 5 pages, its answer sheets have 3 pages.

- Follow the safety rules announced in the preparatory tasks. You get one warning for violations. On the second warning you will get disqualified.

- Wear your lab coat and safety goggles while in the lab. Ask your lab assistant for the gloves of your size when you need them.

- Use only the pen, marker pen and calculator provided. Do not write with the marker on paper; use it only to label glass or plastic labware.

- Make sure that your student code is on every answer sheet.

- All answers must be written in the appropriate boxes on the answer sheet. Anything written elsewhere will not be graded. Use the reverse of the exam sheets if you need scratch paper.

- You have no access to sinks in the lab. You are provided with a sufficient quantity of labware. Only a few items need to be used again. Wash these carefully with an appropriate solvent into the waste container. Use the brush if needed. Distilled water and paper tissues are freely available.

- Liquid waste is to be put into the container labeled "LIQUID WASTE". Do not put rubbish (tissues, plastic, etc.) in this container, but into the waste baskets in the lab.

- Chemicals and labware are not supposed to be refilled or replaced. Each such incident (other than the first in the entire exam, which you will be allowed) will result in the loss of 1 point from your 40 practical points.

- Raise your hand if you have a safety question or you need a restroom break or drinking water.

- When you have finished this part of the examination, put your answer sheet into the envelope provided and leave it on the table. Do not seal the envelope. You will not have further access to the answer sheets from this part.

- You must stop your work immediately when the STOP command is given. A delay in doing this may lead to cancellation of your exam. Do not leave your place until permitted by the lab assistants. You can keep the task text.

- The official English version of this examination is available on request only for clarification.

Labware

Item	Quantity
All tasks, on the table of common use	
Latex gloves of different sizes, choose your size	-
General equipment for all tasks, for each student, on the table	
Test tube rack (60 holes)	1
Paper tissue (can ask for extra)	5
Permanent marker	1
Glass stirring rod, 20 cm	1
Polypropylene funnel, diam. 3.5 cm	1
Soft plastic cup	3
Strong plastic cup	1
All tasks, for each student in the soft plastic cup	
Caps for polystyrene test tubes	22
Task 1, for each student, on the table	
Rack for centrifuge tubes (21 holes)	1
Container with a screw cap for waste,1 dm^3, labeled "Liquid Waste, Test 1"	1
Paper filters in zip-bag	5
Task 1, for each student, in the strong plastic cup	
Pasteur pipettes	20
Task 1, for each student, in the 60-hole rack	
Polystyrene test tubes, 10 cm^3	35

Chemicals

Name	State	Conc.	Q-ty	Placed in	Labeled
All tasks, for each student, on the table					
Distilled water	Liquid	-	1 dm³	Wash bottle, 1 dm³	H₂O dist.
Task 1, for each student, on the table					
Hexane	Liquid	-	25 cm³	Glass bottle with screw cap, 50 cm³	Hexane
Sodium hydroxide	Aqueous solution	1 M	80 cm³	Amber plastic bottle with screw cap, 125 cm³	NaOH
Nitric acid*	Aqueous solution	2 M	150 cm³	Glass bottle with dropper cap, 250 cm³	HNO₃
Task 1, for each student, in the 21-hole rack					
5 unknowns	Aqueous solution	-	45 cm³	Centrifuge tubes, 50 cm³	Unknown No __
Silver nitrate	Aqueous solution	0.1 M	25 cm³	Centrifuge tube, 50 cm³	AgNO₃
Aluminium sulfate	Aqueous solution	0.3 M	25 cm³	Centrifuge tube, 50 cm³	Al₂(SO₄)₃
Barium nitrate	Aqueous solution	0.25 M	25 cm³	Centrifuge tube, 50 cm³	Ba(NO₃)₂
Iron(III) nitrate	Aqueous acidic (HNO₃) solution	0.2 M	25 cm³	Centrifuge tube, 50 cm³	Fe(NO₃)₃
Potassium iodide	Aqueous solution	0.1 M	25 cm³	Centrifuge tube, 50 cm³	KI
Potassium iodate	Aqueous solution	0.1 M	25 cm³	Centrifuge tube, 50 cm³	KIO₃
Magnesium chloride	Aqueous solution	0.2 M	25 cm³	Centrifuge tube, 50 cm³	MgCl₂
Sodium carbonate	Aqueous solution	0.2 M	25 cm³	Centrifuge tube, 50 cm³	Na₂CO₃
Sodium sulfite	Aqueous solution	0.2 M	25 cm³	Centrifuge tube, 50 cm³	Na₂SO₃
Ammonia*	Aqueous solution	1 M	25 cm³	Centrifuge tube, 50 cm³	NH₃(aq)

* Nitric acid and ammonia solutions are needed in a subsequent task.

Task 1

You have 10 different compounds dissolved in water in 5 unknown solutions. Each numbered container contains two of the following compounds in aqueous solution (every compound is used, and each compound is used only once):

$AgNO_3$, $Al_2(SO_4)_3$, $Ba(NO_3)_2$, $Fe(NO_3)_3$, KI, KIO_3, Na_2CO_3, Na_2SO_3, $MgCl_2$, NH_3

You are given HNO_3 solution, NaOH solution, hexane and the aqueous solutions of the 10 pure compounds listed above.

You can use empty test tubes and any of the liquids provided (including the unknowns) to identify the unknown samples. A funnel and filter paper can be used for separation.

Identify the compounds in the solutions **1-5**. Give the number of the solution that contains the individual compounds on the answer sheet. Indicate two observations caused by a chemical reaction for each compound in your unknown mixtures by giving the letter code of the appropriate observation (choose one or more from the list), and write appropriate balanced ionic equation(s) that explain the observation. At least one of the reactions has to be specific for clearly identifying the compound from this selection of unknowns.

Note: After the STOP signal close all the centrifuge test tubes containing the unknown mixtures with the blue caps labeled with the student code and leave these in the rack.

48th International Chemistry Olympiad

Practical Tasks Part I.

Answer Sheets

26 July 2016

Tbilisi, Georgia

Task 1   13% of the total

7	7	7	7	7	7	7	7	7	7	Sum: 70

Only fill out this table when you are ready with all your assignments. Use the following observation codes:

A - Formation of white precipitate

B - Formation of colored precipitate (red, brown, yellow, black etc.)

C - Dissolution of precipitate

D - Color change in the solution

E - Formation of colored solution

F - Brown color in the organic phase

G - Purple color in the organic phase

H - Formation of colored gas

I - Formation of colorless and odorless gas

J - Formation of colorless and odorous gas

K – Change in the color of precipitate

Compound	No. of unknown	Formula of reaction partner(s)	Observation code(s)	Balanced net ionic equation(s)
NH_3				
$Fe(NO_3)_3$				
$Al_2(SO_4)_3$				
$AgNO_3$				
KIO_3				

Compound	No. of unknown	Formula of reaction partner(s)	Observation code(s)	Balanced net ionic equation(s)
Na_2CO_3				
$MgCl_2$				
Na_2SO_3				
$Ba(NO_3)_2$				
KI				

Replacements:

Item	Quantity	Lab assistant's signature	Student's signature

5p for locating each compound, 1 p for each relevant equation. Altogether 10x7p.

Subpoints for 1p: 0.4p for correct observation with appropriate reagent(s); 0.6p for the relevant balanced ionic equation (-0.1p for minor typos; maximum of -0.3p for poor balancing; maximum of 0.3p for an equation in other than ionic form)

The unknowns are identical mixtures for every student in different order. Most are mixed in 1:1 ratio by volume.

Characteristic reactions are marked with bold letters. One of these or equivalent has to be shown on the answer sheet.

NH$_3$

AgNO$_3$, B)	$2\ Ag^+ + 2\ OH^- = Ag_2O + H_2O$ *(if Ag^+ is not mixed with Fe^{3+})*
C)	$Ag_2O + H_2O + 4\ NH_3 = 2\ [Ag(NH_3)_2]^+ + 2\ OH^-$ *(if Ag^+ is not with Fe^{3+})*
Fe(NO$_3$)$_3$, B)	**$Fe^{3+} + 3\ OH^- = Fe(OH)_3$**
Al$_2$(SO$_4$)$_3$, A)	**$Al^{3+} + 3OH^- = Al(OH)_3$ (or $[Al(H_2O)_6]^{3+} + 3\ OH^- = Al(OH)_3 + 6\ H_2O$)**
MgCl$_2$, A)	**$Mg^{2+} + 2\ OH^- = Mg(OH)_2$**
NaOH, J)	**$NH_4^+ + OH^- = NH_3 + H_2O$**
(KIO$_3$) + AgNO$_3$, C)	**$AgIO_3 + 2\ NH_3 = [Ag(NH_3)_2]^+ + IO_3^-$**

Fe(NO$_3$)$_3$

NaOH, B)	**$Fe^{3+} + 3\ OH^- = Fe(OH)_3$**
NH$_3$, B)	**$Fe^{3+} + 3\ OH^- = Fe(OH)_3$**
KI, D) or E)	**$2\ Fe^{3+} + 2\ I^- = 2\ Fe^{2+} + I_2$**
MgCl$_2$, E)	**$Fe^{3+} + Cl^- = [FeCl]^{2+}$ (or $Fe^{3+} + 3\ Cl^- = FeCl_3$ etc.)**

Al$_2$(SO$_4$)$_3$

NaOH, A)	$Al^{3+} + 3\ OH^- = Al(OH)_3$ (or $[Al(H_2O)_6]^{3+} + 3\ OH^- = Al(OH)_3 + 6\ H_2O$)
C)	**$Al(OH)_3 + OH^- = [Al(OH)_4]^-$**
(NaOH +) HNO$_3$ A)	**$[Al(OH)_4]^- + H^+ = Al(OH)_3 + H_2O$**
Ba(NO$_3$)$_2$, A)	**$Ba^{2+} + SO_4^{2-} = BaSO_4$**
Na$_2$CO$_3$, A)	$Al^{3+} + 3\ OH^- = Al(OH)_3$ (or $[Al(H_2O)_6]^{3+} + 3\ OH^- = Al(OH)_3 + 6\ H_2O$)

AgNO$_3$

NaOH, B)	**2 Ag$^+$ + 2 OH$^-$ = Ag$_2$O + H$_2$O**
KI, B)	**Ag$^+$ + I$^-$ = AgI**
NH$_3$, B)	2 Ag$^+$ + 2 OH$^-$ = Ag$_2$O + H$_2$O *(if* Ag$^+$ *is not mixed with* Fe^{3+}*)*
C)	Ag$_2$O + H$_2$O + 4 NH$_3$ = 2 [Ag(NH$_3$)$_2$]$^+$ + 2 OH$^-$ *(if* Ag$^+$ *is not with* Fe^{3+}*)*
MgCl$_2$, A)	**Ag$^+$ + Cl$^-$ = AgCl**
Na$_2$CO$_3$, A) or B)	2 Ag$^+$ + CO$_3^{2-}$ = Ag$_2$CO$_3$
Na$_2$SO$_3$, A)	2 Ag$^+$ + SO$_3^{2-}$ = Ag$_2$SO$_3$
C)	**Ag$_2$SO$_3$ + 3 SO$_3^{2-}$ = 2 [Ag(SO$_3$)$_2$]$^{3-}$**
KIO$_3$, A)	Ag$^+$ + IO$_3^-$ = AgIO$_3$

KIO$_3$

Na$_2$SO$_3$ + HNO$_3$, B) or E) (+ hexane, G)	**5 SO$_3^{2-}$ + 2 IO$_3^-$ + 2 H$^+$ = I$_2$ + 5 SO$_4^{2-}$ + H$_2$O**
KI + HNO$_3$, B) or E) (+ hexane, G)	**5 I$^-$ + IO$_3^-$ + 6 H$^+$ = 3 I$_2$ + 3 H$_2$O**
AgNO$_3$, A)	Ag$^+$ + IO$_3^-$ = AgIO$_3$
Ba(NO$_3$)$_2$, A)	Ba^{2+} + 2 IO$_3^-$ = Ba(IO$_3$)$_2$

Na$_2$CO$_3$

HNO$_3$, I)	**CO$_3^{2-}$ + 2 H$^+$ = H$_2$O + CO$_2$**
Ba(NO$_3$)$_2$, A)	Ba^{2+} + CO$_3^{2-}$ = BaCO$_3$
+ HNO$_3$, C), I)	**BaCO$_3$ + 2 H$^+$ = Ba^{2+} + H$_2$O + CO$_2$**
AgNO$_3$, A) or B)	2 Ag$^+$ + CO$_3^{2-}$ = Ag$_2$CO$_3$
+ HNO$_3$, C), I)	**Ag$_2$CO$_3$ + 2 H$^+$ = 2 Ag$^+$ + H$_2$O + CO$_2$**
MgCl$_2$, A)	Mg^{2+} + CO$_3^{2-}$ = MgCO$_3$
+ HNO$_3$, C), I)	**MgCO$_3$ + 2 H$^+$ = Mg^{2+} + H$_2$O + CO$_2$**

MgCl$_2$

NaOH, A)	**Mg^{2+} + 2 OH$^-$ = Mg(OH)$_2$**
NH$_3$, A)	**Mg^{2+} + 2 OH$^-$ = Mg(OH)$_2$**
AgNO$_3$, A)	**Ag$^+$ + Cl$^-$ = AgCl**
Na$_2$CO$_3$, A)	Mg^{2+} + CO$_3^{2-}$ = MgCO$_3$
Fe(NO$_3$)$_3$, E)	**Fe^{3+} + Cl$^-$ = [FeCl]$^{2+}$ (or Fe^{3+} + 3 Cl$^-$ = FeCl$_3$ etc.)**

Na$_2$SO$_3$

HNO$_3$, J	**SO$_3^{2-}$ + 2 H$^+$ = H$_2$O + SO$_2$**
KIO$_3$ + HNO$_3$, B) or E) (+hexane, G)	**5 SO$_3^{2-}$ + 2 IO$_3^-$ + 2 H$^+$ = I$_2$ + 5 SO$_4^{2-}$ + H$_2$O**
Ba(NO$_3$)$_2$, A)	Ba^{2+} + SO$_3^{2-}$ = BaSO$_3$
+ HNO$_3$, C)	**BaSO$_3$ + 2 H$^+$ = Ba^{2+} + SO$_2$ + H$_2$O**
AgNO$_3$, A)	**2 Ag$^+$ + SO$_3^{2-}$ = Ag$_2$SO$_3$**
C)	**Ag$_2$SO$_3$ + 3 SO$_3^{2-}$ = 2 [Ag(SO$_3$)$_2$]$^{3-}$**
KI + KIO$_3$, D)	**I$_2$ + SO$_3^{2-}$ + H$_2$O = 2 I$^-$ + SO$_4^{2-}$ + 2 H$^+$**

Ba(NO$_3$)$_2$

Al$_2$(SO$_4$)$_3$, A)	**Ba^{2+} + SO$_4{}^{2-}$ = BaSO$_4$**
KIO$_3$, A)	Ba^{2+} + 2 IO$_3{}^-$ = Ba(IO$_3$)$_2$
Na$_2$CO$_3$, A)	Ba^{2+} + CO$_3{}^{2-}$ = BaCO$_3$
Na$_2$SO$_3$, A)	Ba^{2+} + SO$_3{}^{2-}$ = BaSO$_3$
+ HNO$_3$, C)	**BaSO$_3$ + 2 H$^+$ = Ba^{2+} + SO$_2$ + H$_2$O**

KI

Fe(NO$_3$)$_3$, E) or D)	**2 Fe^{3+} + 2 I$^-$ = 2 Fe^{2+} + I$_2$**
AgNO$_3$, B)	**Ag$^+$ + I$^-$ = AgI**
KIO$_3$, + HNO$_3$, B) or E) (+hexane, G)	**5 I$^-$ + IO$_3{}^-$ + 6 H$^+$ = 3 I$_2$ + 3 H$_2$O**

48th International Chemistry Olympiad

Practical Tasks
Part II.

26 July 2016

Tbilisi, Georgia

Instructions

- You have a 15 minute reading time before you start work. Begin reading only when the START command is given.

- Follow the safety rules announced in the preparatory tasks. You get one warning for violations. On the second warning you will get disqualified.

- Wear your lab coat and safety goggles while in the lab. Ask your lab assistant for the gloves of your size when you need them.

- Use only the pen, marker pen and calculator provided. Do not write with the marker on paper; use it only to label glass or plastic labware.

- Make sure that your student code is on every answer sheet.

- All answers must be written in the appropriate boxes on the answer sheet. Anything written elsewhere will not be graded. Use the reverse of the exam sheets if you need scratch paper.

- You have no access to sinks in the lab. You are provided with a sufficient quantity of labware. Only a few items need to be used again. Wash these carefully with appropriate solvent into the waste container. Use the brush if needed. Distilled water and paper tissues are freely available.

- Liquid waste is to be put into the container labeled "LIQUID WASTE". Do not put rubbish (tissues, plastic, etc.) in this container, but into the waste baskets in the lab.

- Chemicals and labware are not supposed to be refilled or replaced. Each such incident (other than the first in the entire exam, which you will be allowed) will result in the loss of 1 point from your 40 practical points.

- Raise your hand if you have a safety question or you need a restroom break or drinking water.

- When you have finished the examination, put your answer sheet into the envelope provided and leave it on the table. Do not seal the envelope.

- You must stop your work immediately when the STOP command is given. A delay in doing this may lead to cancellation of your exam. Do not leave your place until permitted by the lab assistants. You can keep the task text.

- The official English version of this examination is available on request only for clarification.

Instructions specific for Part II

- The working time for Part II (Task 2 and 3) is 200 minutes.

- Start Part II with Task 2. When you are ready to start with Task 3, tell the lab assistant, and you will receive the chemicals and labware for Task 3. Reagents for Task 2 will be taken away from you at this point.

- Part II of the exam (Task 2-3) contains 10 pages, its answer sheets have 7 pages.

- Ask the lab assistants when you need your alcohol lamp lighted. Heat only glass test tubes. Close the alcohol lamp with the cap when finished.

Labware

Item	Quantity
General equipment for all tasks, for each student, on the table	
Test tube rack (60 holes)	1
Paper tissue	5
Permanent marker	1
Glass stirring rod, 20 cm	1
Polypropylene funnel, diam. 3.5 cm	1
Soft plastic cups	3
Strong plastic cup	1
Caps for polystyrene test tubes	22
Tasks 2 and 3, for each student, on the table	
Container with a screw cap for waste, 3 dm³, labeled "Liquid Waste, Tests 2&3"	1
Task 2, for each student, on the table	
Storage box labeled "Task 2"	1
Laboratory stand with double burette clamp	1
Burette, 25.00 cm³	2
Graduated pipette, 10.0 cm³	1
Graduated pipette, 1.00 cm³	1
Bulb (Mohr) pipette, 10.00 cm³	1
Erlenmeyer flask, 100 cm³	2
Graduated cylinder, 10.0 cm³	2
Brush	1
Polypropylene funnel, 5.5 cm	1
Task 2, for each student, in the storage box "Task 2"	
Polystyrene test tubes, 10 cm³	8
Pipette filler	1
Pasteur pipettes for indicators	2
Task 3, for each student, get from the lab assistants	
Storage box labeled "Task 3"	1
Task 3, for each student, in the storage box "Task 3"	
Polystyrene test tubes, 10 cm³	20
Alcohol lamp	1
Test tube holders, wooden	1
Glass test tubes	10
Pasteur pipettes	10
Strong plastic cup	1

Chemicals

Name	State	Conc.	Q-ty	Placed in	Labeled
Task 2, for each student, on the table					
Nitric acid	Aqueous solution	2 M	-*	Glass bottle with dropper cap, 250 cm^3	HNO$_3$
Task 2, for each student, in the storage box "Task 2"					
Water sample solution	Aqueous solution	To be determined	100 cm^3	Glass bottle with screw cap, 100 cm^3	Water sample
Sodium fluoride	Aqueous solution	9 mg/dm^3 in fluoride	50 cm^3	Glass bottle with screw cap, 50 cm^3	F$^-$, 9 mg/dm^3
Zirconyl Alizarin indicator	Acidic aqueous solutions	0.055% ZrOCl$_2$, 0.028% Alizarin Red S	10 cm^3	Glass bottle with screw cap, 25 cm^3	Zirconyl Alizarin
Sodium chloride	Aqueous solution	0.0500 M	50 cm^3	Glass bottle with screw cap, 50 cm^3	NaCl, 0.0500 M
Ammonium iron(III) sulfate dodecahydrate	Aqueous acidic solution	20 g/dm^3	10 cm^3	Glass bottle, 15 cm^3	Fe^{3+} ind.
Silver nitrate	Aqueous solution	To be determined	200 cm^3	Amber glass bottle, 250 cm^3	AgNO$_3$
Ammonium thiocyanate	Aqueous solution	See exact concentration on the label	100 cm^3	Glass bottle with screw cap, 100 cm^3	NH$_4$SCN, X.XXXX M
Potassium chromate	Aqueous solution	10%	5 cm^3	Glass bottle, 15 cm^3	K$_2$CrO$_4$
Task 3, for each student, on the table					
Ethanol	Liquid	95 %	150 cm^3	Glass bottle with dropper cup, 250 cm^3	C$_2$H$_5$OH
Task 3, for each student, in the storage box "Task 3"					
Organic unknowns 1 to 8	Liquid	-	0.5 cm^3	Syringes, 2 cm^3	1 to 8
Potassium permanganate	Aqueous solution	0.13 %	5 cm^3	Amber glass bottle, 50 cm^3	KMnO$_4$
Ammonium cerium(IV) nitrate reagent	2.0 M HNO$_3$ aqueous solution	28.6 %	5 cm^3	HDPE bottle, 30 cm^3	Ce(IV)
Acetonitrile	Liquid	-	45 cm^3	Glass bottle, 50 cm^3	CH$_3$CN

Name	State	Conc.	Q-ty	Placed in	Labeled
2,4-Dinitrophe-nylhydrazine reagent	Sulfuric acid solution in aqueous ethanol	3 %	20 cm³	HDPE bottle, 30 cm³	DNPH
Iron(III) chloride	0.5 M HCl aqueous solution	2.5 %	1 cm³	HDPE bottle, 30 cm³	FeCl₃
Hydroxylamine hydrochloride	Ethanolic solution	0.5 M	10 cm³	HDPE bottle, 30 cm³	NH₂OH× HCl
Sodium hydroxide	Aqueous solution	6 M	5 cm³	HDPE bottle, 30 cm³	NaOH
Hydrochloric acid	Aqueous solution	1 M	25 cm³	HDPE bottle, 30 cm³	HCl

*In the quantity left after doing Task 1.

Periodic table with relative atomic masses

Task 2

Determination of fluoride and chloride content in mineral water

Georgia is world famous for its splendid mineral waters. Many of these are used to cure various diseases. Manufacturers have to carefully control the ionic composition of waters, fluoride and chloride being among the most important ions.

Visual colorimetric detection of fluoride

The method of fluoride determination is based on the decrease in the color intensity of zirconium(IV)-Alizarin Red S complex in the presence of fluoride ions due to formation of a more stable colorless complex. The equilibrium is achieved in about 20 minutes after the reagent addition. The fluoride concentration is determined visually by comparing the color developed in the sample with those in the calibration solutions.

Transfer 9.0 cm^3 of mineral water from the sample into the plastic test tube labeled "X".

Calculate how much of the 9.0 mg/dm^3 standard fluoride solution you will need to prepare a set of calibration solutions with the following fluoride ion content: 0.0; 1.0; 2.0; 3.5; 5.0; 6.5; 8.0 mg/dm^3 (calculate for 9.0 cm^3 of each solution).

Using the 1.0 cm^3 and 10.0 cm^3 graduated pipettes, add the calculated amounts of the standard fluoride solution to the test-tubes, then add 1.0 cm^3 of Zirconyl Alizarin indicator into each test tube, and bring the volume in each calibration test tube to the 10.0 cm^3 mark with distilled water (the mark is shown in the figure with the arrow).

2.1.1. Report the fluoride volumes used in your dilutions.

Mix the obtained solutions in the test tubes. Set the tube rack aside for at least 20 minutes.

2.1.2. Compare the color of the sample and the calibration solutions looking on them from the top down and from the front. Select the concentration of the standard that is closest to the fluoride concentration of the water sample.

Note: the rack with the test tubes will be photographed by the lab staff after the whole exam is finished.

Standardization of silver nitrate solution by the Mohr method

Transfer 10.0 cm^3 of the standard 0.0500 mol/dm^3 NaCl solution into an Erlenmeyer flask using the bulb (Mohr) pipette. Add approximately 20 cm^3 of distilled water and 10 drops of 10% aqueous K_2CrO_4 solution.

Fill a burette with the silver nitrate solution. Titrate the contents of the flask with the silver nitrate solution while vigorously mixing the solution containing the precipitate formed. The final titrant drops are added slowly with vigorous swirling of the flask. The titration is complete when the faint color change visible on titrant addition does not disappear in the pure yellow suspension. Take the final burette reading. Repeat the titration as necessary.

2.2.1. Report your volumes on the answer sheet.

2.2.2. Write balanced chemical equations for the titration of NaCl with $AgNO_3$ and for the end-point indication reaction.

2.2.3. Calculate the concentration of the $AgNO_3$ solution from your measurement.

2.2.4. The Mohr titration method requires a neutral medium. Write down equations for the interfering reactions that take place at lower and at higher pH.

Chloride determination by the Volhard method

Wash the bulb (Mohr) pipette with distilled water. Wash the Erlenmeyer flasks first with a small portion of the ammonia solution left over from Task 1 to help removing the silver salt precipitate and then with distilled water. (In case you used up all the ammonia solution in the first task, you can get a refill without penalty.)

Transfer a 10.0 cm^3 aliquot of the mineral water from the sample into an Erlenmeyer flask using the bulb (Mohr) pipette. Add 5 cm^3 of 2 mol/dm^3 nitric acid using a graduated cylinder. Add 20.00 cm^3 of the silver nitrate solution from the burette and mix well the suspension. Add appr. 2 cm^3 of the indicator (Fe^{3+}) solution with the Pasteur pipette.

Fill the second burette with the standard ammonium thiocyanate solution (see the exact concentration on the label). Titrate the suspension with this solution while vigorously swirling. At the end point one drop produces a faint brown color that is stable even after intense mixing. Take the final burette reading. Repeat the titration as necessary.

Note. The AgCl precipitate exchanges Cl^- ions with SCN^- ions from the solution. If you titrate too slowly or with breaks, the brown color disappears with time, and too much titrant is spent for the titration. Therefore when approaching the endpoint you should add the titrant at a *constant* slow rate swirling the flask *constantly* so that the suspension would stay white. The appearance of faint brown color will mean reaching the endpoint.

2.3.1. Report your volumes on the answer sheet.

2.3.2. Write down balanced chemical equations for the back titration with NH_4SCN and that for the end-point indication reaction.

2.3.3. Calculate the chloride concentration (in mg/dm^3) in the water sample from your measurements.

2.3.4. If Br^-, I^-, and F^- ions are present in the sample in addition to chloride, the concentration of which ion(s) will contribute to the result of the Volhard titration?

2.3.5. When trying to determine the concentration of Cl⁻ in the presence of other halides, an analyst added some potassium iodate and sulfuric acid to the sample and boiled the solution. Afterwards he reduced the excess of iodate to iodine by boiling the sample with phosphorous acid H_3PO_3. <u>What</u> interfering anions were removed by this operation? <u>Write</u> the chemical equations for the reactions of these ions with iodate.

Task 3

Identifying flavors and fragrances

Tourists coming to Georgia admire many specialties, local cuisine occupying one of the top positions in the list of adventures. Excellent meat, fresh vegetables and greens, ripe fruits, home-made jams… What else is needed to satisfy true gourmets? Of course, unique flavors and fragrances!

You are given 8 samples of unknown organic compounds (labeled 1 to 8), which are industrially used as flavors and fragrances. All samples are pure individual compounds. Their possible structures are found among **A**-**M** given here.
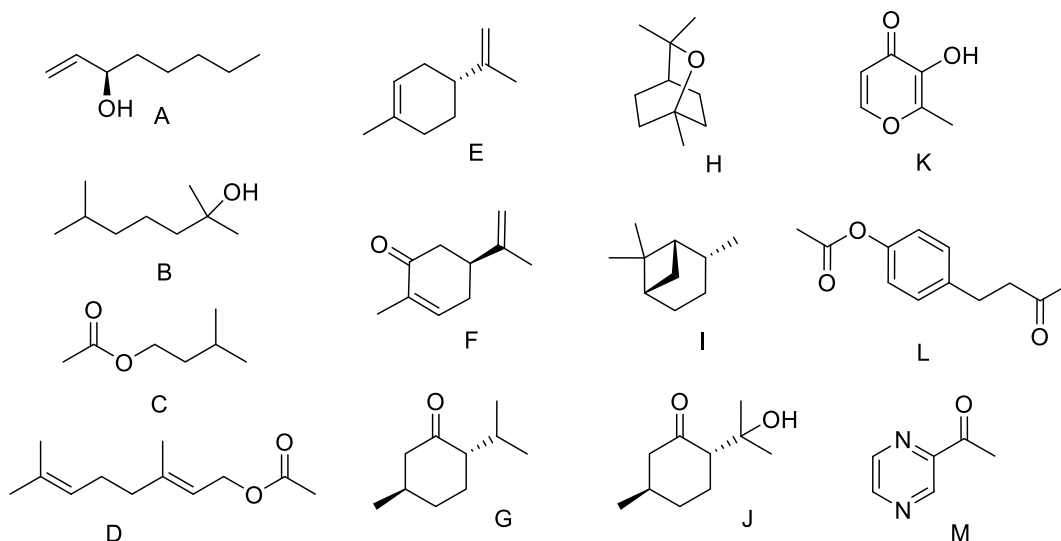
The organic compounds in your unknown samples are readily soluble in ether, and insoluble in dilute aqueous NaOH and HCl. These compounds, but the unknown No. 6. are insoluble in water, the latter being slightly soluble (3.5 g/dm^3).

3.1. <u>Perform</u> test reactions described below to identify the samples **1-8**. <u>Indicate</u> the results of the tests by giving the Roman numeral of the appropriate observation (choose one or more from the list). <u>Fill</u> in all cells of the table. <u>Use</u> **+** and **–** to indicate positive and negative tests.

3.2. Identify the unknowns based on the test results and the information given above. <u>Write</u> the structure codes (of **A** to **M**) of the identified samples in the appropriate box.

Test procedures

KMnO$_4$ test (Baeyer test)

Place appr. 1 cm^3 of 95% ethanol in a <u>plastic</u> test tube and add 1 drop of an unknown. Add 1 drop of KMnO$_4$ solution and shake the mixture. Treat the test as positive if the permanganate color disappears immediately after shaking.

3.3.   <u>Write</u> the reaction scheme for a positive Baeyer test with one of the compounds **A**-**M**.

Cerium(IV) nitrate test

Place 2 drops of the **Ce(IV) reagent** into a <u>glass</u> test tube, add 2 drops of acetonitrile and then 2 drops of an unknown (the sequence is important!). Shake the mixture. In the case of positive test the mixture color promptly changes from yellow to orange-red.

Note 1. Use only glass test tubes to perform the test. In case you need to wash the glass test tubes, carefully choose the appropriate solvent. Use caps to prevent the strong odor.

Note 2. Comparison with blank (no unknown) and reference (with ethanol) tests is recommended for adequate interpretation.

Note 3. Ce(IV) ions initially form brightly colored coordination compounds with alcohols. Complexes formed from primary or secondary alcohols react further (within 15 seconds to 1 hour) with the disappearance of the color.

2,4-dinitrophenylhydrazine (2,4-DNPH) test

Add <u>only</u> 1 drop of an unknown to 1 cm^3 of 95% ethanol in a <u>plastic</u> test tube. Add 1 cm^3 of the DNPH reagent to the prepared solution. Shake the mixture and let it stand for 1-2 min. Observe formation of yellow to orange-red precipitate if the test is positive.

3.4.   <u>Write</u> the reaction scheme for a positive 2,4-DNPH test with one of the compounds **A**-**M**.

Ferric hydroxamate test

Ask a lab assistant to light up your alcohol lamp. Mix 1 cm^3 of 0.5 mol/dm^3 ethanolic hydroxylamine hydrochloride solution with 5 drops of 6 mol/dm^3 sodium hydroxide aqueous solution in a <u>glass</u> test tube. Add 1 drop of an unknown and use the alcohol lamp to heat the mixture to boiling while gently swirling the test tube to avoid splashes of the reaction mixture. Allow it to cool down slightly and add 2 cm^3 of 1 mol/dm^3 HCl solution. Add 1 drop of 2.5% iron(III) chloride solution. Observe appearance of magenta color if the test is positive. Close the alcohol lamp with the cap when finished.

Note 1. Use <u>glass</u> test tubes only to perform the test; use the test tube holder when heating. In case you need to wash the glass test tubes, use an appropriate solvent. Stopper the test tubes with a green cap after completing the test to prevent a strong odor.

Note 2. Fe(III) ions form a colored 1:1 complex with hydroxamic acids (R-CO-NHOH).

3.5.   <u>Write</u> the reaction scheme for a positive ferric hydroxamate test with one of the compounds **A**-**M**.

Note: After the STOP signal reattach the corresponding needles on the syringes with the unknown compounds, and place them into the plastic cup and leave them on the table.

48th International Chemistry Olympiad

Practical Part II.

Answer Sheets

26 July 2016

Tbilisi, Georgia

Task 2   # 14% of the total

2.1.1	2.1.2	2.2.1	2.2.2	2.2.3	2.2.4	2.3.1	2.3.2	2.3.3	2.3.4	2.3.5	Sum
2	15	30	2	2	2	30	2	4	2	4	95

2.1.1. Report the fluoride volumes used in your dilutions.

F^- content (mg/dm^3)	0.0	1.0	2.0	3.5	5.0	6.5	8.0
Calculated volume of F^- solution (cm^3)							

2p

2.1.2. Circle the concentration of the standard that is closest to the fluoride concentration of the water sample.   15p, 5p for adjacent values.

F^- content (mg/dm^3)	0.0	1.0	2.0	3.5	5.0	6.5	8.0

2.2.1. Report your titration volumes.

Titration no.	1	2				
Initial burette reading, cm^3						
Final burette reading, cm^3						
Volume spent, cm^3						

Your accepted volume, V_1:   cm^3 30p on a sliding scale

2.2.2. Write a balanced chemical equation for the titration of NaCl with AgNO$_3$ and that for the end-point indication reaction.

Titration reaction:

$Cl^- + Ag^+ \longrightarrow AgCl\downarrow$

$CrO_4^{2-} + 2\ Ag^+ \longrightarrow Ag_2CrO_4\downarrow$

Indicatio
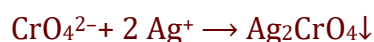
2p

2.2.3. Calculate the concentration of the AgNO$_3$ solution from your measurement.

Your work:

$c(Ag^+) = c(Cl^-)10.0\ cm^3 / V_1$

2 p

$c(Ag^+)$:

2.2.4. The Mohr titration method requires a neutral medium. <u>Write</u> equations for the interfering reactions that take place at lower and at higher pH.

Low pH: $2\ CrO_4^{2-} + 2\ H^+ \longrightarrow Cr_2O_7^{2-} + H_2O$ (dichromic or chromic acids also accepted),

or $Ag_2CrO_4 + H^+ \longrightarrow 2Ag^+ + HCrO_4^-$

High pH: $2\ Ag^+ + 2\ OH^- \longrightarrow Ag_2O + H_2O$

2p

2.3.1. <u>Report</u> your volumes on the answer sheet.

Titration no.	1	2				
Initial burette reading, cm^3						
Final burette reading, cm^3						
Volume spent, cm^3						

Your accepted volume, V_2:	cm^3	30p on a sliding scale

2.3.2. <u>Write</u> a balanced chemical equation for the back titration with NH_4SCN and that for the end-point indication reaction.

Titration reaction:

$Ag^+ + SCN^- \longrightarrow AgSCN\downarrow$

$SCN^- + Fe^{3+} \longrightarrow Fe(SCN)^{2+}$ or analogous reaction

Indication

2p

2.3.3. <u>Calculate</u> the chloride concentration (in <u>mg/dm³</u>) in the water sample from your measurements.

Your work:

$c(Cl^-) = [20.00\ cm^3\ c(Ag^+) - V_2\ c(SCN^-)]\ M(Cl)/\ 10.00\ cm^3$

4p, 3p if in different unit

$c(Cl^-)$: mg/dm^3

2.3.4. If Br^-, I^-, and F^- ions are present in the sample in addition to chloride, the concentration of which ion(s) will contribute to the result of the Volhard titration? Tick the appropriate box(es).

☐ Br^- ☐ I^- ☐ F^- ☐ none

Br⁻, I⁻   2p, 1p if 1 mistake committed

2.3.5. When trying to determine the concentration of Cl^- in the presence of other halogens, an analyst added some potassium iodate and sulfuric acid to the sample and boiled the solution. Afterwards he reduced the excess of iodate to iodine by boiling the sample with phosphorous acid H_3PO_3. <u>What</u> interfering anions were removed by this operation?

☐ Br^- ☐ I^- ☐ F^- ☐ none

Br⁻, I⁻   2p

<u>Write</u> the reaction equations of these ions with iodate.

$$5I^- + IO_3^- + 6H^+ \rightarrow 3I_2 + 3H_2O$$

$$10Br^- + 2IO_3^- + 12H^+ \rightarrow 5Br_2 + I_2 + 6H_2O \quad \text{(IBr also accepted)}$$

2p

Replacements:

Item	Quantity	Lab assistant's signature	Student's signature

Grading scheme for the titration results
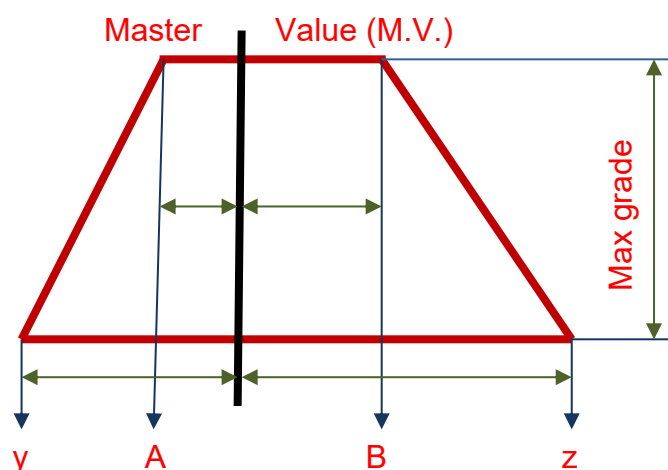
If A< Value < B, then Grade = Max grade
If Value < y, then Grade = 0, If Value > z, then Grade = 0
If y < Value < A, then Grade = Max grade × (Value – y)/(A – y)
If B < Value < z, then Grade = Max grade × (z – Value)/(z – B)

Question	M.V., mL	A, mL	B, mL	y, mL	z, mL	Max grade
2.2.1.	10.0	9.9	10.15	9.8	10.4	30p
2.3.1.	Theoretical values	−0.1	+0.3	−0.3	+0.8	30p

Task 3   13% of the total

3.1.	3.2.	3.3.	3.4.	3.5.	Sum
32	16	4	4	4	60

3.1. Indicate the results and observations of tests by giving the Roman numerals of the appropriate observations in the table. Fill in all cells of the table. Use **+** and **–** to indicate positive and negative tests. Choose one or more codes from the list below.

I – Immediate disappearance of purple color

II – Slow disappearance of purple color

III - Disappearance of yellow color

IV – Formation of a brown or black precipitate

V - Formation of a white precipitate

VI - Formation of a yellow or orange-red precipitate

VII - Appearance of orange or red color in solution

VIII - Appearance of magenta color

IX - The unknown compound is insoluble in ethanol

X – no visible changes

Sample No.	1	2	3	4	5	6	7	8
Baeyer test result (**+/–**)	+	–	+	–	–	–	–	+
Baeyer test observations (**I-X**)	I, IV	X	I, IV	II, IV	X	II, IV	X	I, IV
Ce(IV) nitrate test result (**+/–**)	+	+	–	–	–	–	–	–
Ce(IV) nitrate test observations (**I-X**)	VII	VII	III, V	III	X	X or III	X	III
2,4-DNPH test result (**+/–**)	–	–	–	+	–	–	–	–
2,4-DNPH test observations (**I-X**)	X	X	X	VI	X	X	X	X
Fe(III) hydroxamate test result (**+/–**)	–	–	–	–	+	–	–	+
Fe(III) hydroxamate test observations (**I-X**)	X	X	X	X	VIII	X	X or IX	VIII

3.2. Write the structure codes (of **A** to **M**) of the identified samples in the appropriate boxes when you are certain in your assignments.

Sample No.	1	2	3	4	5	6	7	8
Structure code	**A**	**B**	**E**	**G**	**C**	**H**	**I**	**D**

3.3. Write the reaction scheme for a positive Baeyer test with one of the compounds **A-M**.
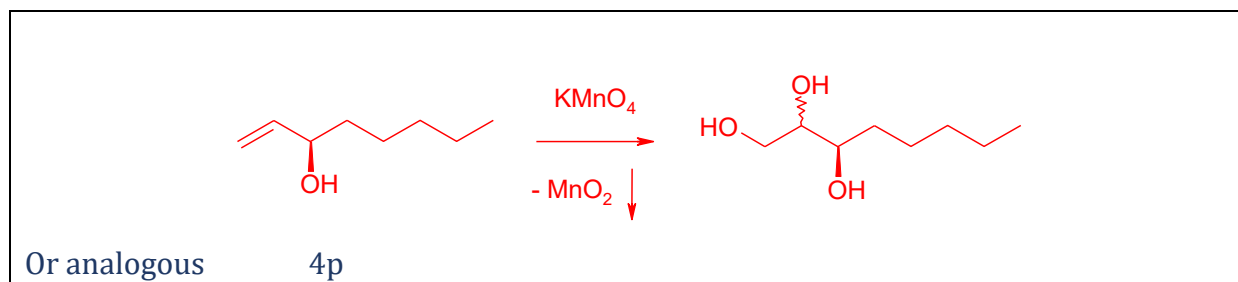
Or analogous   4p

3.4. Write the reaction scheme for a positive 2,4-DNPH test with one of the compounds **A-M**.

4p

3.5. Write the reaction scheme for a positive ferric hydroxamate test with one of the compounds **A-M**.

Or analogous   4p (any 1:1 hydroxamate – Fe(III) complex is acceptable)
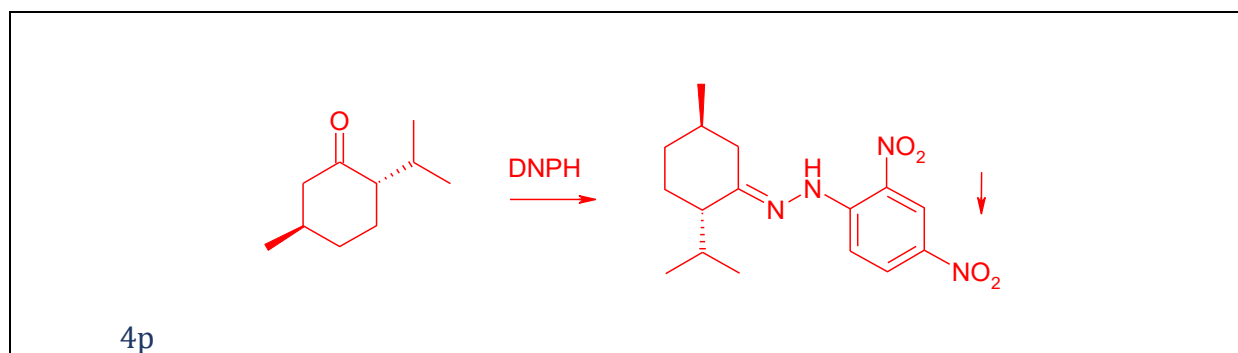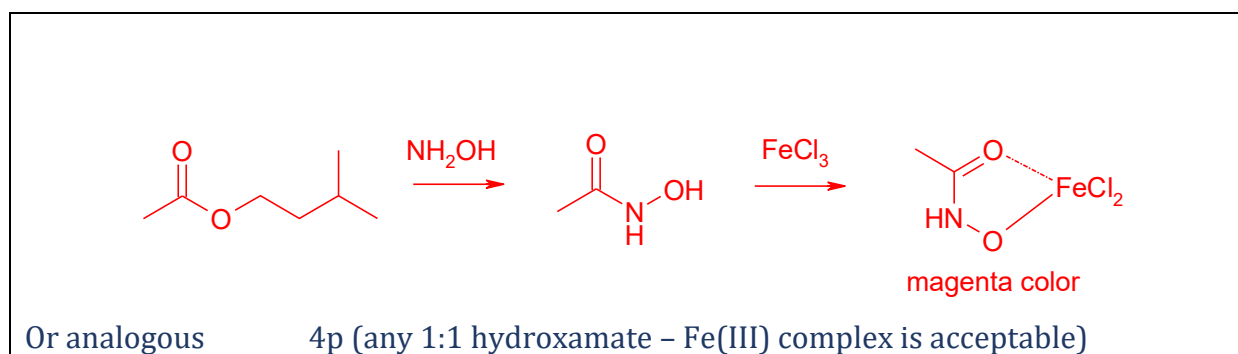
The problem can be approached in many ways. A systematic solution for one variant of the unknown compounds encoding is given below (other variants are processed similarly).
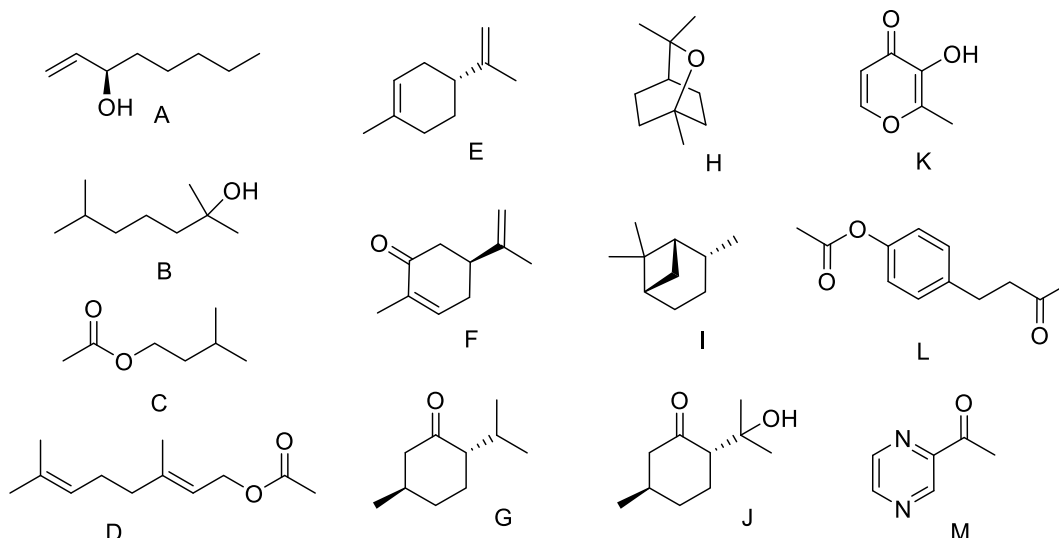
Step 1. Solubility data analysis.

The data given allow excluding compounds K (presence of phenol-like moiety) and M (presence of azine nitrogen) soluble in aqueous NaOH and aqueous HCl, respectively.

Step 2. Tests for the functional groups.

2.1 Unsatured compounds excluding those aromatic give positive Baeyer test, and those with keto- or aldehyde group give positive 2,4-DNPH test

2.2 For avoiding mistakes in true-positive / false-positive interpretation the precise description of true-positive tests is given in the test procedures.
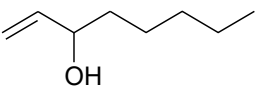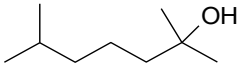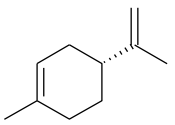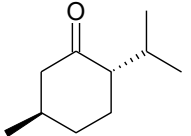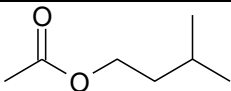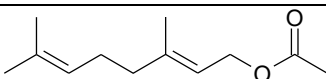
2.3 The information given in the Notes after the test procedures CLEARLY indicates the following prompts:

Note	Prompt
Comparison with blank (no unknown) and reference (with ethanol) tests is recommended for adequate interpretation of the test.	The cerium(IV) nitrate test is one for alcohols
Brightly colored Ce(IV) coordination compounds bearing C_{sp3}-O→Ce(IV) moiety have the formation constant in the range of 0.51 (MeOH, kinetically unstable) to 2.76 (t-BuOH, kinetically stable).	Red color appearing as a result of a positive cerium(IV) nitrate test can disappear due to further oxidation of alcohols by Ce(IV) in the case of primary and secondary alcohols
Brightly colored Fe(III)-hydroxamic acids coordination compounds have the formation constants $K_1 \sim 42$; $K_2 \sim 2.5$; $K_3 \sim 1.2 \cdot 10^{-2}$ (for acetohydroxamate in ethanol–water 1:1 mixture).	The ferric hydroxamate test is the one for the compounds capable of forming the hydroxamic acids in the reaction with NH_2OH. ONLY ESTERS are appropriate candidates for the positive test. Amides (J) do not afford hydroxamic acid under NH_2OH treatment, thus giving negative test.

The results of the experimental work can be summed up in the hereunder table.

# of sample	KMnO$_4$	Ce(NH$_4$)$_2$(NO$_3$)$_6$	2,4-DNPH	Ferric Hydroxamate Test
1	+	+	–	–
2	–	+	–	–
3	+	–	–	–
4	–	–	+	–
5	–	–	–	+
6	–	–	–	–
7	–	–	–	–
8	+	–	–	+

Analysis of the table allows unanimously identifying **A**, **B**, **E**, C, and **G**. **L** (Ferric hydroxamate and 2,4-DNPH), **J** (2,4-DNPH and Cerium(IV) nitrate test), and **F** (KMnO$_4$ and 2,4-DNPH tests) can be excluded from further consideration, since these provide for two positive tests each.

#	Structure	KMnO$_4$	Ce(NH$_4$)$_2$(NO$_3$)$_6$	2,4-DNPH	Ferric Hydroxamate Test
1		+	+	–	–
2		–	+	–	–
3		+	–	–	–
4		–	–	+	–
5		–	–	–	+
6	?	–	–	–	–
7	?	–	–	–	–
8		+	–	–	+

Step 3. Choosing of right structures of the samples 6 and 7 based on additional data given.

Among all compounds in the list, only H and I cannot give any positive test, the attribution requiring consideration of the solubility data. Sample 7 in the above table is soluble in ether only (attributed as I), whereas Sample 6 is partially soluble in water (attributed as H).

The final assignment is given below.

Sample No	1	2	3	4	5	6	7	8
Structure code	A	B	E	G	C	H	I	D

1 points for each test (1p × 4 tests × 8 unknowns=32p)

2 points for each correct assignment (2p× 8 unknowns=16p)

Appendix A

Hazard codes, provided by Globally Harmonized System of Classification and Labeling of Chemicals (not to be printed for students)

Substance	Name	GHS Hazard Statement
C_6H_{14}	Hexane	225, 304, 315, 336, 361f, 373, 411
NaOH	Sodium hydroxide	290, 314
HNO_3	Nitric acid	272, 290, 314
$AgNO_3$	Silver nitrate	272, 290, 314, 400, 410
$Al_2(SO_4)_3$	Aluminium sulfate	290, 318
$Ba(NO_3)_2$	Barium nitrate	272, 302+332, 319
$Fe(NO_3)_3$	Iron(III) nitrate	314
KI	Potassium iodide	302, 315, 319
KIO_3	Potassium iodate	272, 315, 319, 335
$MgCl_2$	Manganese chloride	-
Na_2CO_3	Sodium carbonate	-
Na_2SO_3	Sodium sulfite	-
NH_3	Ammonia	221, 280, 314, 331, 400, 410
NaF	Sodium fluoride	301, 315, 319
$ZrOCl_2 + C_{14}H_7NaO_7S$	Zirconyl Alizarin indicator	314
NaCl	Sodium chloride	-
$NH_4Fe(SO_4)_2 \times 12H_2O$	Ammonium iron(III) sulfate dodecahydrate	315, 319
NH_4SCN	Ammonium thiocyanate	302, 312, 332, 412
K_2CrO_4	Potassium chromate	301, 315, 317, 319, 335, 400, 410
$C_8H_{16}O$	1-Octen-3-ol, Matsutake alcohol	302, 315, 319
$C_9H_{20}O$	2,6-Dimethyl-2-heptanol, Dimetol, Freesiol	302, 318
$C_7H_{14}O_2$	Isoamyl Acetate	226
$C_{12}H_{20}O_2$	Geranyl acetate	315, 319, 335
$C_{10}H_{16}$	Limonene	226, 315, 317, 410
$C_{10}H_{14}O$	(+)-Carvone	-
$C_{10}H_{18}O$	(−)-Menthone	315, 317
$C_{10}H_{18}O$	1,8-Cineole	226
$C_{10}H_{18}$	Pinane	226
$C_{10}H_{18}O_2$	8-Hydroxy-p-menthan-3-one	315, 317
$C_6H_6O_3$	Maltol	302, 315, 319, 335
$C_{12}H_{14}O_3$	Raspberry ketone acetate	-
$C_6H_6N_2O$	2-Acetylpyrazine	315, 319, 335
$KMnO_4$	Potassium permanganate	400, 410
$Ce(NH_4)_2(NO_3)_6$	Ammonium cerium(IV) nitrate	272, 290, 302, 314, 317, 400, 410

CH_3CN	Acetonitrile	225, 302, 312, 319, 332
$C_6H_6N_4O_4$	2,4-Dinitrophe-nylhydrazine	228, 302
$FeCl_3$	Iron(III) chloride	290, 302, 315, 318
$NH_2OH \cdot HCl$	Hydroxylamine hydrochloride	290, 302, 312, 315, 317, 319, 373, 400, 410
HCl	Hydrochloric acid	290, 315, 319, 335

Appendix B

Hazard Statement Descriptions

Statement	Description
H221	Flammable gases
H225	Highly flammable liquid and vapour
H272	May intensify fire; oxidizer
H226	Flammable liquid and vapour
H228	Flammable solid
H280	Gases under pressure
H290	May be corrosive to metals
H301	Acute toxicity, oral
H302	Acute toxicity, oral
H302+332	Harmful if swallowed or if inhaled
H304	May be fatal if swallowed and enters airways
H312	Acute toxicity, dermal
H314	Causes severe skin burns and eye damage
H315	Causes skin irritation
H317	Skin sensitisation
H318	Causes serious eye damage
H319	Causes serious eye irritation.
H331	Acute toxicity, inhalation
H332	Acute toxicity, inhalation
H335	May cause respiratory irritation
H336	May cause drowsiness or dizziness
H361f	Suspected of damaging fertility
H373	May cause damage to organs through prolonged or repeated exposure
H400	Acute aquatic toxicity
H410	Chronic aquatic toxicity
H411	Toxic to aquatic life with long lasting effects
H412	Chronic aquatic toxicity

48th International
Chemistry Olympiad

Theoretical Problems

28 July 2016

Tbilisi, Georgia

Instructions

- Begin only when the START command is given. You have 5 hours to work on the problems.

- Use only the pen and calculator provided.

- The problem booklet has 23 pages, the answer sheet is 28 pages.

- Make sure that your code is on every page of the answer sheet.

- Questions are identical in the problem text and on the answer sheets.

- All results must be written in the appropriate boxes on the answer sheets. Anything written elsewhere will not be graded. Use the reverse of the problem pages if you need scratch paper.

- Write relevant calculations in the appropriate boxes when necessary. If you provide only correct end results for complicated questions, you will receive no score.

- Raise your hand if you need a restroom break.

- When you have finished the examination, put your answer sheets into the envelope provided. Do not seal the envelope.

- You can keep the problem booklet.

- You must stop your work immediately when the STOP command is given. A delay in doing this may lead to cancellation of your exam.

- Do not leave your seat until permitted by the supervisors.

- 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	Zero of the Celsius scale:	273.15 K
Gas constant:	$R = 8.314$ J K⁻¹ mol⁻¹	Faraday constant:	$F = 96485$ C mol⁻¹
Ideal gas equation:	$pV = nRT$	Gibbs energy:	$G = H - TS$
$\Delta_r G^o = -RT \ln K = -nF E^o_{cell}$		Ionic product of water at 298.15K :	$K_w = 10^{-14}$
Nernst equation:	$E = E^o + \dfrac{RT}{nF} \ln \dfrac{c_{ox}}{c_{red}} = E^o + \dfrac{0.059 \text{ V}}{n} \log \dfrac{c_{ox}}{c_{red}}$ $\text{or } E = E^o - \dfrac{RT}{nF} \ln Q = E^o - \dfrac{0.059 \text{ V}}{n} \log Q$		
Beer-Lambert law:	$A = \log \dfrac{I_0}{I} = \varepsilon c l$		

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 72.63	33 As 74.92	34 Se 78.97	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 95.95	43 Tc -	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
55 Cs 132.9	56 Ba 137.3	57-71	72 Hf 178.5	73 Ta 180.9	74 W 183.8	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	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 -	112 Cn -	113 Nh -	114 Fl -	115 Mc -	116 Lv -	117 Ts -	118 Og -

57 La 138.9	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm -	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0
89 Ac -	90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np -	94 Pu -	95 Am -	96 Cm -	97 Bk -	98 Cf -	99 Es -	100 Fm -	101 Md -	102 No -	103 Lr -

Problem 1   5% of the total

Nitrogen trifluoride is a surprisingly stable compound that was first prepared in the melt electrolysis of a mixture of ammonium fluoride and hydrogen fluoride.

1.1.   <u>On which electrode</u> does nitrogen trifluoride form? <u>Write</u> a balanced chemical equation for the electrode half reaction for the formation of NF_3.

Interestingly the related fluoroamine (NH_2F) and difluoroamine (NHF_2) are very unstable materials; decomposition of either pure substance can even be explosive. This is dangerous as they are formed in the electrolysis as side products.

1.2.   <u>Which of NF_3, NHF_2 or NH_2F compound is</u> expected to condense at the lowest temperature?

The N-F bond lengths in these molecules were determined to be 136, 140 and 142 pm. The change in the bond lengths can be explained with a simple electrostatic model taking into account the partial charges on the atoms.

1.3.   <u>Assign</u> the N-F bond lengths (136, 140, 142 pm) to the molecules.

When NHF_2 is bubbled through a solution of KF in HF, a binary nitrogen – fluorine compound can be obtained as a mixture of two geometric isomers.

1.4.   <u>Write</u> a balanced chemical equation for the formation of the binary nitrogen-fluorine compound.

Tetrafluoroammonium ion (NF_4^+) and its corresponding salt can form from NF_3 with elementary fluorine in the presence of an appropriate reagent.

1.5.   <u>Propose</u> a suitable reagent and <u>write</u> a balanced chemical equation for the reaction.

NF_4^+ ions form stable salts with a number of anions. These are very sensitive to humidity, because NF_4^+ ion hydrolyzes forming NF_3 and O_2. Interestingly nitrogen trifluoride always forms quantitatively, while the quantity of oxygen is often less than expected due to side reactions.

1.6.   <u>Write</u> a balanced chemical equation for the hydrolysis of NF_4^+. <u>Write</u> a balanced chemical equation for a possible side reaction that can decrease the theoretically expected O_2:NF_3 mole ratio.

Tetrafluoroammonium salts were investigated for use as solid rocket fuels, because NF_3 and F_2 are released from them on heating. One of them has a fluorine content of 65.6 $m/m\%$, all of which is converted into NF_3 and F_2 upon decomposition. During the decomposition 2.5 times as many moles of F_2 are formed as of NF_3.

1.7.   <u>Determine</u> the formula of the salt in question.

Problem 2   8% of the total

One of the first materials used in solid state electronics was red copper(I) oxide. Interest is renewed nowadays because it could be a non-toxic and cheap component of solar cells.
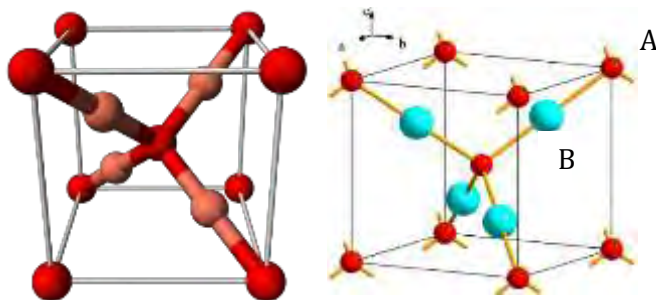
The two figures above depict the cubic unit cell of the Cu_2O crystal. The lattice constant of the structure is 427.0 pm.

2.1.1. <u>Which</u> of the atoms (A or B) is copper?
<u>Which basic structure</u> (primitive cubic, face centered cubic, body centered cubic, diamond) is formed by the A atoms and <u>which structure</u> is formed by the B atoms?
<u>What</u> are the coordination numbers of the atoms?

2.1.2. <u>Calculate</u> the smallest O-O, Cu-O and Cu-Cu distances in the structure.

2.1.3. <u>What</u> is the density of pure copper(I) oxide?

A common defect in this crystal is some copper atoms missing with the oxygen lattice unchanged. The composition of one such crystal sample was studied, and 0.2% of all copper atoms were found to be in oxidation state +2.

2.2. <u>What</u> percentage of normal copper sites are empty in the crystal sample? <u>What</u> is x in the empirical formula $Cu_{2-x}O$ of the crystal?

Copper(I) oxide is insoluble in water. It is stable in dry air, but humidity in the air catalyzes a transformation (Reaction 1).

When copper(I) oxide is dissolved in dilute sulfuric acid, a blue solution containing a precipitate is formed without evolution of a gas (Reaction 2). When hot, concentrated sulfuric acid is used, no precipitate remains, but an odorous gas forms (Reaction 3). The same gas forms when the precipitate from reaction 2 is dissolved in hot concentrated sulfuric acid.

2.3. <u>Write</u> balanced chemical equations for reactions (1-3).

Copper(I) oxide can be produced in a number of ways. Heating copper in air is a common method in the synthesis of semiconductor Cu_2O. In a pure oxygen atmosphere, the three species containing copper (Cu(s), Cu_2O(s) or CuO(s)) can potentially interconvert.

Suppose that the $\Delta_f H^o$ and S^o data given for 10^5 Pa are independent of temperature:

	$\Delta_f H^o$ / kJ mol^{-1}	S^o/ J mol^{-1} K^{-1}
Cu(s)	0	65
O_2(g)	0	244
CuO(s)	−156	103
Cu_2O(s)	−170	180

2.4. <u>Determine</u> the temperature ranges, if any, of thermodynamic stability of copper and its oxides between 500 and 1500 K in a 10^5 Pa oxygen atmosphere.

Important data are given for 298 K. Use this temperature in the following calculations:

$K_{sp}(Cu(OH)_2)=2 \cdot 10^{-19}$

Cu_2O(s) + H_2O(l) + 2e$^-$ $\longrightarrow$ 2Cu(s) + 2OH$^-$(aq) E^o= −0.360 V

Cu^{2+}(aq) + e$^-$ $\longrightarrow$ Cu^+(aq) E^o= +0.159 V

Cu^{2+}(aq) + 2e$^-$ $\longrightarrow$ Cu(s) E^o= +0.337 V
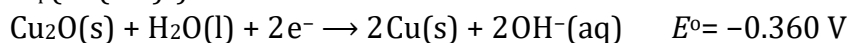
One possibility for producing Cu_2O is the anodic oxidation of copper. Electrolysis of an aqueous basic solution (e.g. NaOH) with a copper anode and platinum cathode can lead to formation of copper(I) oxide on the anode.

2.5. <u>Write</u> the half reaction equations for the electrode processes during the anodic production of Cu_2O in NaOH solution with a platinum cathode and copper anode.

Electrolytic reduction of copper(II) ions in solution is another possibility.

2.6.1. <u>Write</u> the half reaction equation of the cathode process giving Cu_2O in acidic medium.

Let us use 0.100 mol dm^{-3} Cu^{2+} solution and carry out electrolysis with platinum electrodes.

2.6.2. <u>What</u> is the maximum pH at which the concentration of copper(II) can be maintained at 0.100 mol dm^{-3}?

If the pH is too low, reduction to metallic copper is preferred to the formation of copper(I) oxide.

2.6.3. <u>What</u> is the minimum pH at which the cathodic production of Cu_2O in a 0.100 mol dm^{-3} Cu^{2+} solution is still possible?

Problem 3   9% of the total

Iodine deficiency is of special concern in Georgia because it occupies a region where iodine is scarce in soil and water. Iodine deficiency can be effectively and inexpensively prevented if salt for human consumption is fortified with small amounts of iodine. Methods for analyzing salt for iodine content are thus important. Current regulations in Georgia are that iodized salt must contain between 25-55 ppm iodine (1 ppm = 1 mg iodine/kg salt).

Most salt is iodized by fortification with potassium iodate (KIO_3). Iodate content can be determined in salt samples using iodometric titration. In a typical procedure, 10.000 g of an iodized salt sample is dissolved in 100 cm³ of 1.0 mol/dm³ aqueous HCl to which 1.0 g KI has been added. The solution is then titrated with 0.00235 mol/dm³ aqueous sodium thiosulfate solution to a starch endpoint; this requires 7.50 cm³ of titrant.

3.1.1. <u>Write</u> a balanced net ionic equation for the reaction when iodate reacts with excess iodide in acidic solution.

3.1.2. <u>Write</u> a balanced net ionic equation for the reaction taking place during the titration with thiosulfate.

3.1.3. <u>Calculate</u> the iodization level, in ppm, of this salt sample.

A less common agent for iodizing salt is potassium iodide, which cannot be easily measured by iodometric titration.

One possible method for analyzing iodide in the presence of chloride is potentiometric titration. However, this method is not very precise in the presence of large amounts of chloride.

In this method, a silver wire is immersed in the solution (containing iodide and chloride) to be analyzed and silver ion is gradually added to the solution. The potential of the silver wire is measured relative to a reference electrode consisting of a silver wire in a 1.000 mol/dm³ solution of $AgNO_3$. The measured potentials are negative and the absolute values of these potentials are reported. The solution to be analyzed has a volume of 1.000 dm³ (which you may assume does not change as silver ion is added), and T = 25.0°C.

The results of this experiment are governed by three equilibria: the solubility of AgI(s) [K_{spI}] and AgCl(s) [K_{spCl}] and the formation of $AgCl_2^-$(aq) [K_f]. (Iodide also forms complex ions with silver but this may be neglected at the very low concentrations of iodide present in this experiment).

$$AgI(s) \rightleftharpoons Ag^+(aq) + I^-(aq) \qquad K_{spI}$$

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq) \qquad K_{spCl}$$

$$Ag^+(aq) + 2\,Cl^-(aq) \rightleftharpoons AgCl_2^-(aq) \qquad K_f$$
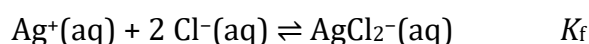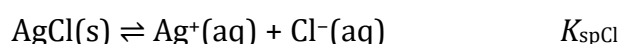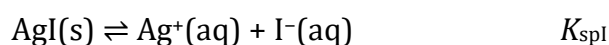
Below are shown the results of two experiments measuring the observed potential as a function of added number of moles of silver ion. Experiment **A** (solid circles) was carried out with 1.000 dm³ of solution containing $1.00 \cdot 10^{-5}$ mol/dm³ iodide and no chloride ion. Experiment **B** (open circles) was done using 1.000 dm³ of solution containing $1.00 \cdot 10^{-5}$ mol/dm³ iodide and $1.00 \cdot 10^{-1}$ mol/dm³ chloride.
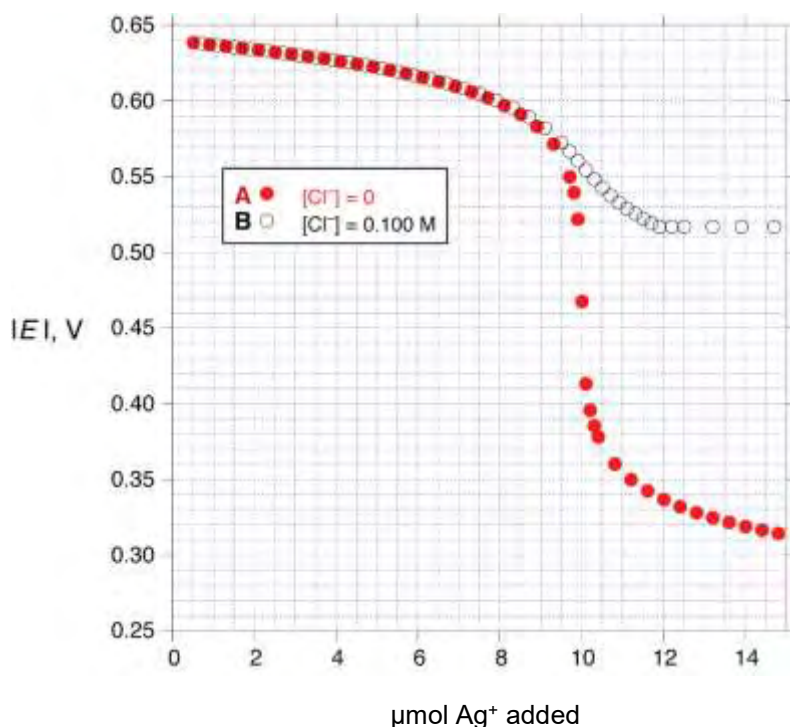
μmol Ag⁺ added	$|E|$, V exp. **A**	$|E|$, V exp. **B**
1.00	0.637	0.637
3.00	0.631	0.631
5.00	0.622	0.622
7.00	0.609	0.610
9.00	0.581	0.584
10.0	0.468	0.558
11.0	0.355	0.531
12.0	0.337	0.517
13.0	0.327	0.517
15.0	0.313	0.517

μmol Ag⁺ added

3.2.1. Select an appropriate data point from the experiments and use it to <u>calculate</u> the solubility product of AgI (K_{spI}).

3.2.2. Select an appropriate data point from the experiments and use it to <u>calculate</u> the solubility product of AgCl (K_{spCl}).

3.2.3. Select an appropriate data point from the experiments and use it to <u>calculate</u> K_f. You may need to use values of K_{spI} or K_{spCl} to do this calculation. If you were unable to carry out the calculations in **3.2.1.** or **3.2.2.**, you may use the arbitrary values of $K_{spI} = 1.00 \cdot 10^{-15}$ and $K_{spCl} = 1.00 \cdot 10^{-9}$ without penalty.

An analytical method that is more practical, because it is not sensitive to the presence of chloride, uses the Sandell-Kolthoff reaction. This is the reaction of H_3AsO_3 with Ce(IV) to give Ce(III) in acidic solution, which is strongly catalyzed by iodide ion.

3.3.1. Write balanced net ionic equations for the reaction of cerium(IV) with H_3AsO_3 in acidic solution, as well as reactions of cerium(IV) with a species containing the element iodine and H_3AsO_3 with a species containing the element iodine, that could reasonably account for the catalysis of the net reaction by iodide.

The reaction of Ce(IV) with H_3AsO_3 can be monitored by measuring the absorbance at 405 nm, as Ce(IV) is orange and absorbs significantly at 405 nm, while the other reactants and products are colorless and do not absorb appreciably. Three runs were carried out, all in 0.50 mol/dm³ H_2SO_4 at 25.0°C using the following initial concentrations:

Run	$[H_3AsO_3]_0$, mol dm⁻³	$[Ce(IV)]_0$, mol dm⁻³	$[I^-]_0$, mol dm⁻³
1	0.01250	0.00120	$1.43 \cdot 10^{-6}$
2	0.00625	0.00060	$1.43 \cdot 10^{-6}$
3	0.01250	0.00120	$7.16 \cdot 10^{-7}$

An analyst initiated the reactions by mixing the reagents in a cuvette. After a short variable delay absorbance measurements were started, with the first measurement recorded at $t=0$ s. The data obtained are shown below:
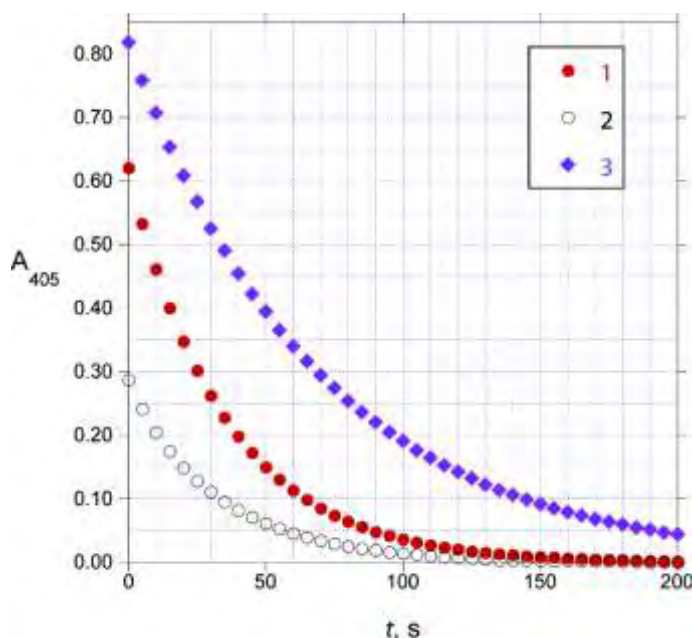
t, s	A_{405} Run **1**	A_{405} Run **2**	A_{405} Run **3**
0	0.621	0.287	0.818
20	0.348	0.149	0.608
40	0.198	0.083	0.455
60	0.113	0.046	0.340
80	0.064	0.025	0.254
100	0.037	0.014	0.191

Under these conditions (0.5 mol/dm³ H_2SO_4, 25.0°C), the rate law for the reaction can be written as

Rate = $k[H_3AsO_3]^m[Ce(IV)]^n[I^-]^p$ where m, n, and p are integers.

3.3.2. Determine the values of m, n, and p and calculate the value of k (be sure to specify its units).

A 1.000 g sample of iodized salt is dissolved in water to give 10.00 cm³ of solution. A 0.0500 cm³ aliquot of this solution is added to a mixture of 1.000 cm³ 0.025 mol/dm³ H_3AsO_3 in 0.5 mol/dm³ H_2SO_4 and 0.800 cm³ 0.5 mol/dm³ H_2SO_4. To this mixture is added 0.200 cm³ 0.0120 mol/dm³ $Ce(NH_4)_2(NO_3)_6$ in 0.5 mol/dm³ H_2SO_4 and the absorbance at 405 nm is measured as a function of time at 25.0°C:

t, s	A_{405}
0	0.756
20	0.531
40	0.373
60	0.262
80	0.185
100	0.129
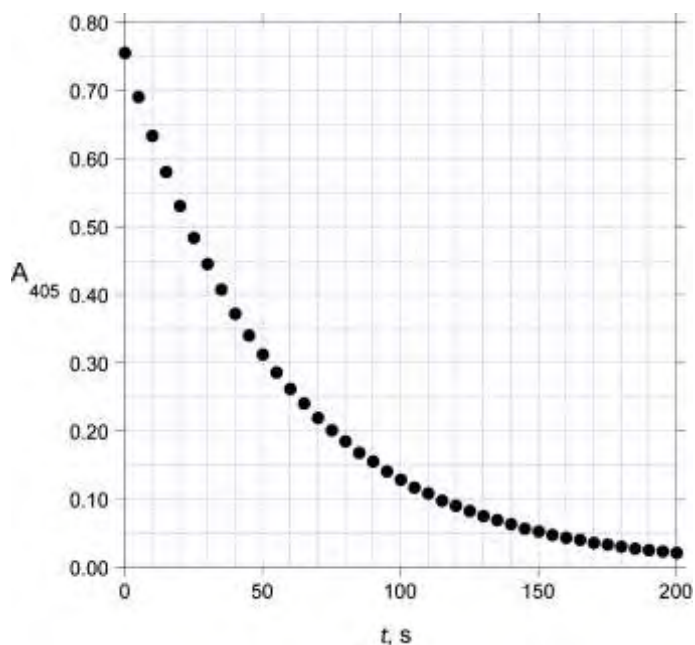
3.3.3. <u>Calculate</u> the iodization level, in ppm, of this salt sample.

Problem 4   8% of the total

Application of kinetic studies in water treatment

Industrial waste is a major cause of water pollution and kinetic studies are carried out in a laboratory to design effluent treatment. 1,4-dioxane, more commonly known as dioxane ($C_4H_8O_2$), an industrial solvent and by-product, is a significant water contaminant. It can be oxidised to hazard free chemicals using oxidants such as peroxodisulfate, ozone or hydrogen peroxide.

The data obtained in the kinetic study of oxidation of dioxane with potassium peroxodisulfate ($K_2S_2O_8$) as oxidant and $AgNO_3$ as catalyst at $T = 303.15$ K are given below. The reaction was monitored by the estimation of unreacted peroxodisulfate. The concentration of $AgNO_3$ used in this study was $1.00 \cdot 10^{-3}$ mmol·dm^{-3}.

Trial	Dioxane mmol·dm^{-3}	$K_2S_2O_8$ mmol·dm^{-3}	Initial rate mmol·dm^{-3}·min^{-1}
1	0.0100	2.50	$1.661 \cdot 10^{-2}$
2	0.0100	5.10	$3.380 \cdot 10^{-2}$
3	0.00500	13.8	$9.200 \cdot 10^{-2}$
4	0.0110	13.8	$9.201 \cdot 10^{-2}$

In many countries the accepted maximum level of dioxane in drinking water is specified as 0.35 µg dm^{-3}.

A water sample contains an initial dioxane concentration of 40.00 µg dm^{-3}. Assume that 1 mol dioxane requires 1 mol of peroxodisulfate for oxidation. The concentration of $AgNO_3$ used in this study was $1.00 \cdot 10^{-3}$ mmol·dm^{-3}.

4.1.1. <u>Calculate</u> the time in minutes the oxidation process has to continue in order to reach the accepted level of dioxane at 303.15 K if the initial concentration of $K_2S_2O_8$ is $5.0 \cdot 10^{-6}$ mol dm^{-3}. Assume that the rate law obtained from the data above is valid under these conditions.

Various mechanisms have been proposed for the peroxodisulfate oxidation of dioxane. Misra and Ghosh (1963) proposed the following mechanism:
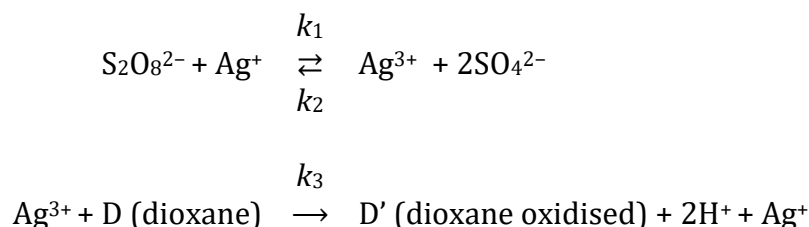
$$S_2O_8^{2-} + Ag^+ \underset{k_2}{\overset{k_1}{\rightleftarrows}} Ag^{3+} + 2SO_4^{2-}$$

$$Ag^{3+} + D \text{ (dioxane)} \overset{k_3}{\longrightarrow} D' \text{ (dioxane oxidised)} + 2H^+ + Ag^+$$

4.1.2. Assuming Ag(III) to be in steady state, <u>deduce</u> the rate equation for the oxidation of dioxane.

4.1.3. Which of the following is/are correct?

A) The rate equation based on the mechanism given in **4.1.2**, at very high concentrations of dioxane, is consistent with the experimental data in **4.1.1.**
B) The rate equation based on the mechanism given in **4.1.2**, at very low concentrations of dioxane, is consistent with the experimental data in **4.1.1.**
C) The units of the observed rate constant are $dm^3 \cdot mol^{-1} \cdot s^{-1}$ at very high concentrations of dioxane.
D) The units of the observed rate constant are $dm^3 \cdot mol^{-1} \cdot s^{-1}$ at very low concentrations of dioxane.

Degradation of pharmaceutical products – a kinetic overview

Kinetic studies are important in deciding the shelf life of a pharmaceutical product. Several chemical reactions can affect the shelf life of pharmaceutical products and the rates of these reactions depend on conditions such as pH, temperature, humidity.

Lysine acetylsalicylate (LAS) is prescribed as a pain killer and anti-inflammatory drug under the brand name Aspegic. LAS on hydrolysis forms lysine salicylate and acetic acid.
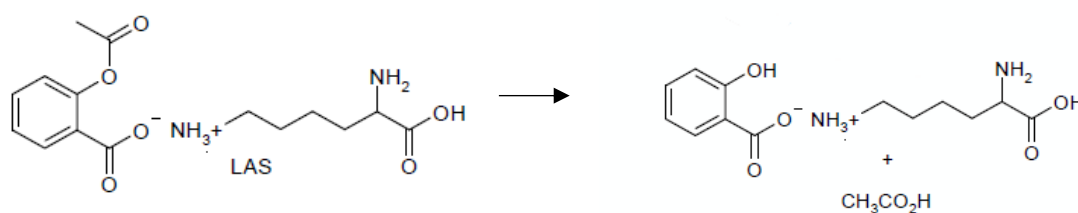
Hydrolysis of LAS can proceed via three different pathways (a) acid catalysed, (b) uncatalysed and (c) base catalysed.

If [LAS] denotes the concentration of LAS at time 't', the overall rate of the hydrolysis reaction can be written as

$$-\frac{d[LAS]}{dt} = k_H[LAS][H^+] + k_0[LAS] + k_{OH}[LAS][OH^-]$$

where k_H, k_0 and k_{OH} are the rate constants of the acid catalysed, uncatalysed and base catalysed pathways of hydrolysis, respectively. The observed rate constant is defined by:

$$-\frac{d[LAS]}{dt} = k_{obs}[LAS]$$

4.2.1. Write an expression for k_{obs} in terms of k_H, k_0, k_{OH} and $[H^+]$.

Hydrolysis of LAS was carried out at 298.15 K at various pH values (0.50 to 13.0). A very low initial concentration of LAS ensured that the pH did not change during the course of the reaction.

The following graph shows the pH dependence of the hydrolysis of LAS.
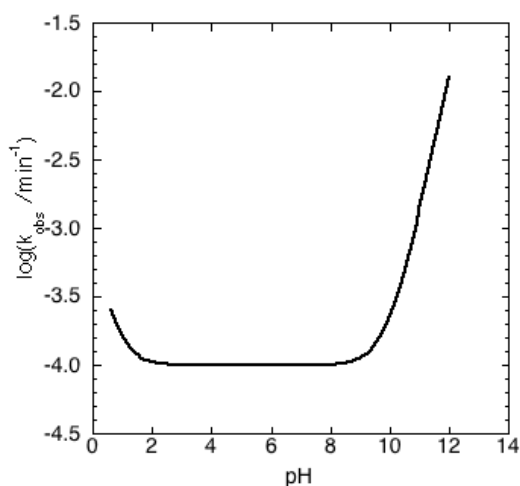
4.2.2. Which of the following is/are correct?
A) $k_{obs} \cong k_0$ at pH = 12
B) $k_{obs} \cong k_0$ at pH = 5.0
C) The rate of the reaction increases when the pH is changed from 0.50 to 1.0.
D) The rate of the reaction increases when the pH is changed from 10 to 12.

4.2.3. Using the diagram and the data given below, <u>calculate</u> k_H, k_0 and k_{OH}. Make sure to specify the units.

pH	1.300	5.300	12.180
log (k_{obs}/min^{-1})	−3.886	−4.000	−1.726

Acetylsalicylic acid, more commonly known as aspirin, is a medicine often used for reducing fever, pain and inflammation. Like LAS, the hydrolysis of aspirin can also take different pathways depending on the pH. The pH rate profile of aspirin hydrolysis at **333.15 K** is given below:
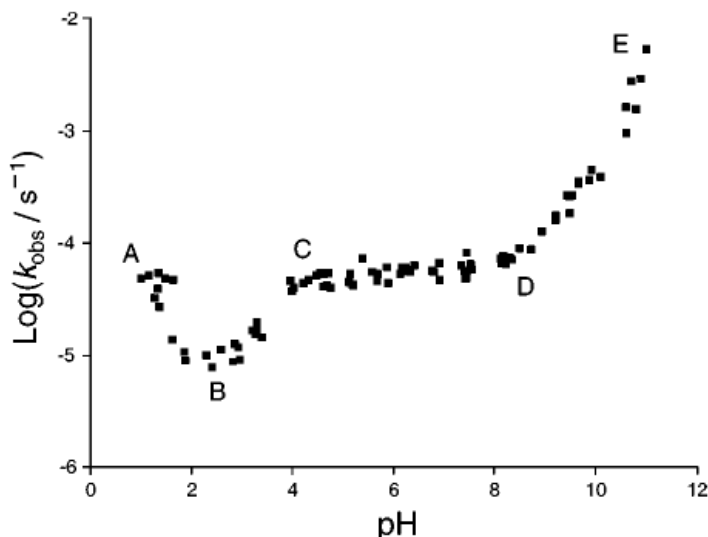
The following are possible reactions for the hydrolysis of aspirin. Depending on the pH, one or more of these reactions will predominate.

I. $CH_3COOC_6H_4COOH + H_3O^+ \longrightarrow HOC_6H_4COOH + CH_3COOH + H^+$
II. $CH_3COOC_6H_4COOH + H_2O \longrightarrow HOC_6H_4COOH + CH_3COOH$
III. $CH_3COOC_6H_4COOH + OH^- \longrightarrow HOC_6H_4COO^- + CH_3COOH$
IV. $CH_3COOC_6H_4COO^- + H_3O^+ \longrightarrow HOC_6H_4COOH + CH_3COOH$
V. $CH_3COOC_6H_4COO^- + H_2O \longrightarrow HOC_6H_4COO^- + CH_3COOH$
VI. $CH_3COOC_6H_4COO^- + OH^- \longrightarrow HOC_6H_4COO^- + CH_3COO^-$

4.3.1. Using the pH-rate profile diagram and the reactions given above, <u>state</u> which of the following statements is/are correct. (pK_a of aspirin = 3.57 at 333.15 K)

a) In the region C-D, reaction IV is predominant
b) In the region C-D, reaction V is predominant
c) In the region D-E reaction VI is predominant
d) In the region A-B, reaction II is predominant

A separate plot of k_{obs} vs pH for the hydrolysis of aspirin has been confirmed to show a minimum at a particular pH. At **290.15 K** the following rate constants for reactions I, II and III were determined:

k_H (reaction I)	k_0 (reaction II)	k_{OH} (reaction III)
1.99 dm^3·mol^{-1}·day^{-1}	2.29·10^{-4} day^{-1}	3.18·10^9 dm^3·mol^{-1}·day^{-1}

The ionic product of water at 290.15 K can be taken as 1.0·10^{-14}.

4.3.2. Assuming that only reactions I, II and III occur, <u>calculate</u> the value of the pH at the minimum of k_{obs}.

Problem 5   8% of the total

5500 years ago in ancient Egypt people learned for the first time how to synthesize a blue pigment. Now we know this pigment as Egyptian blue. About 2000 years later in ancient China another pigment was widely used, which is now referred to as Chinese blue. The two pigments are similar in structure, but have different elemental compositions.

Ushabti figurines from Egyptian pharaoh tomb covered with Egyptian blue and a Chinese blue soap dispenser sold at Alibaba

The ancient method of preparation for these pigments can be easily reproduced in a modern laboratory.

When considering the amounts, assume that all of the compounds in this task are pure, and the yields are quantitative.

To make **Egyptian blue**, one should heat 10.0 g of mineral **A** with 21.7 g of SiO_2 and 9.05 g of mineral **B** at 800–900°C for a prolonged time. 16.7 dm^3 of a mixture of two gaseous products are released (the volume is measured at 850°C and $1.013 \cdot 10^5$ Pa (1.013 bar) pressure. In result, 34.0 g of the pigment was obtained. No other products are formed. As the gas mixture is cooled, one component of the mixture condenses. As the remaining gas is further cooled to 0°C, the gaseous volume reduces to 3.04 dm^3.

5.1.1. <u>Find</u> the mass of the gaseous mixture formed upon heating of **A** with **B** and SiO_2.

5.1.2. <u>Determine</u> the quantitative composition of this gas mixture.

When 10.0 g of mineral **A** is heated with 21.7 g of SiO_2 in the absence of **B**, it forms 8.34 dm^3 of gaseous products (measured at 850°C and $1.013 \cdot 10^5$ Pa = 1.013 bar pressure). Mineral **A** contains only one metal.

5.1.3. <u>Calculate</u> the molar mass and determine the formula of mineral **B**. Hint: it is an ionic solid insoluble in water and containing no water of crystallization.

In order to obtain **Chinese blue**, one should take 17.8 g of mineral **C** instead of mineral **B** (keeping the amounts of mineral **A** and SiO_2 same as for Egyptian blue), and run the reaction at higher temperatures. Besides the pigment, the same gaseous products in the same quantities are formed as in the preparation of Egyptian blue.

5.1.4.   Determine the formula of mineral **C**.

5.1.5.   Determine the formulae of Egyptian blue and Chinese blue.

5.1.6.   Determine the formula of mineral **A**.

Elemental analysis of some samples of Chinese blue shows traces of sulfur. This led to a conclusion that those were synthesized using another common mineral instead of **C**.

5.2.1.   Suggest a formula for the mineral used in place of **C**.

5.2.2.   Could the temperature of synthesis of Chinese blue be decreased if this mineral is used instead of **C**?

If during the synthesis of Chinese blue we take a smaller amount of silica than in the process above, we will obtain a purple pigment: Chinese violet. It was used, in particular, for coloring the famous Terracotta army soldiers.

Terracotta army from Xian, China and reconstruction of its original coloring

5.3.   Write down the formula of a binary compound that forms under the conditions required for Chinese violet and is responsible for the change of the color.

Problem 6   7% of the total

Although there is currently no known cure for Alzheimer's disease, there are medications available to manage the neurodegenerative disorder. Among these are acetylcholinesterase inhibitors, of which galantamine **1** is an example. This molecule can be isolated from the Caucasian snowdrop, a plant native to Georgia; however, the large amounts needed for therapy require a synthetic route. Shown below is the route used to prepare galantamine industrially.
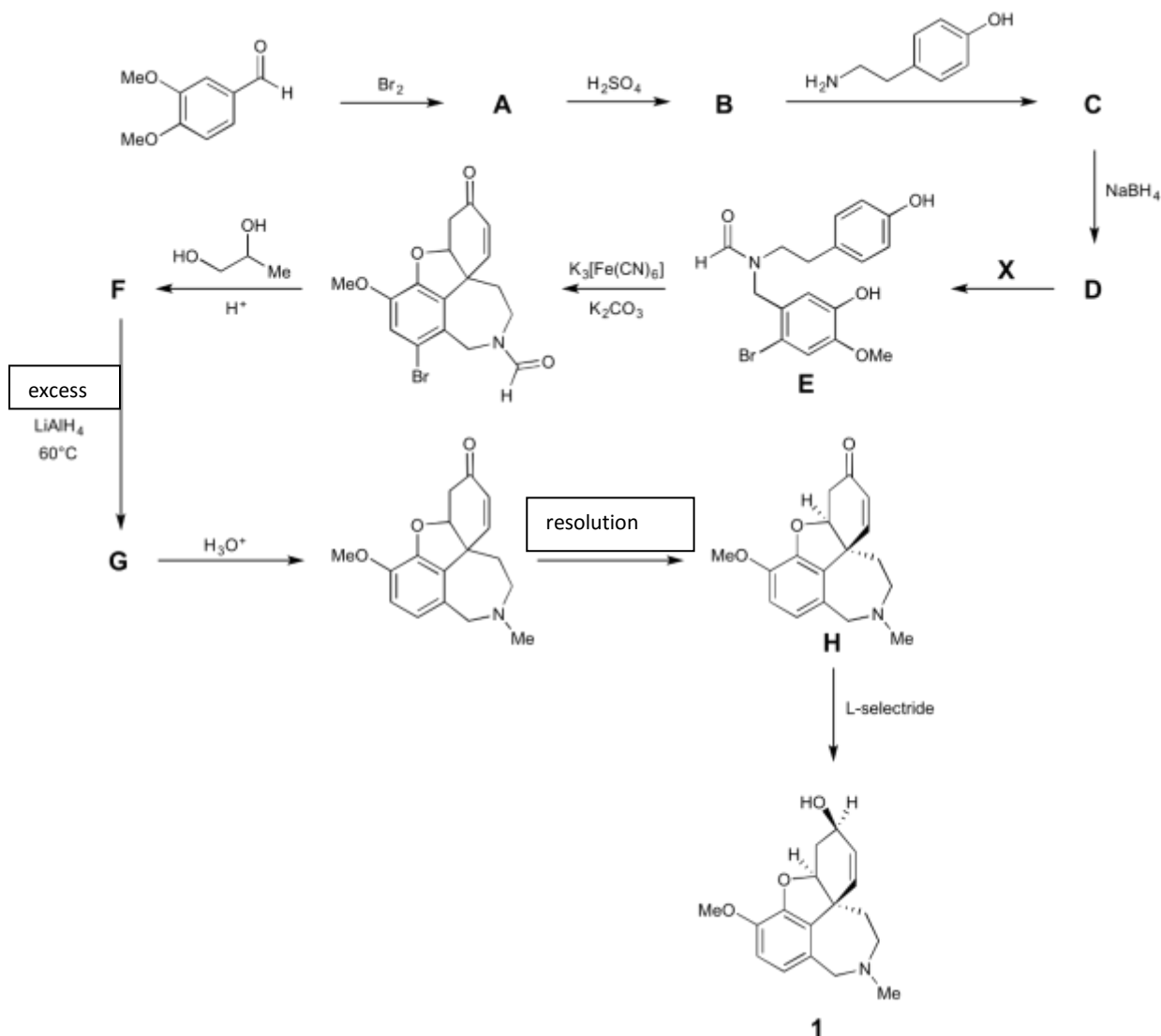
Notes about the synthesis:

- ^{1}H NMR of **A** indicates 2 aromatic protons in a *para* arrangement.

- **C** is labile in aqueous conditions, so it is not isolated, but rather reacted immediately with NaBH$_4$ to convert it to **D**.

6.1.1. Suggest structures for **A**, **B**, **C**, **D**, **F**, and **G**. None of the reactions except for the final transformation with L-selectride are stereoselective. Therefore, stereochemistry does not need to be indicated in your answers.

6.1.2. <u>Give</u> the formula for a possible reagent, **X**, to convert compound **D** to **E**.

The optical rotation of the material obtained by resolution was $-400°$ cm^2 g^{-1}, while that of the enantiomerically pure compound is $-415°$ cm^2 g^{-1} when measured under the same conditions. You may assume that the only optical impurity is the other enantiomer.

One way of describing optical purity is enantiomeric excess (*ee*). It is defined as the difference in the percentages of the enantiomers in a mixture. For example in a mixture of 70% *R* and 30% *S*, the *ee* is 40%.

6.2.1. <u>What</u> is the enantiomeric excess of the resolved compound as prepared by the industrial route?

L-selectride is a commercial reagent that performs the final reaction stereoselectively.

6.2.2. <u>Assign</u> the labelled stereocentres (α, β, γ) in (–)-**1** as *R* or *S*.

6.2.3. <u>Give</u> the formula for a reagent that carries out the same reaction as L-selectride, converting **H** to **1**. You need not worry about stereoselectivity.
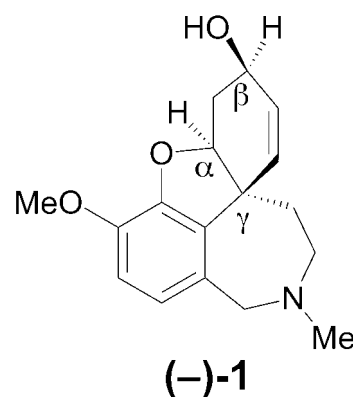
An alternative route to galantamine occurs with the seven-membered ring being the last ring to form.

(–)-**1**

$C_{17}H_{18}N_2O_3$

DIBAL-H

(4 equivalents)

J

$C_{17}H_{22}N_2O_3$

H_3O^+

K

$C_{17}H_{21}NO_4$

NaCNBH$_3$

pH = 5

1

$C_{17}H_{21}NO_3$
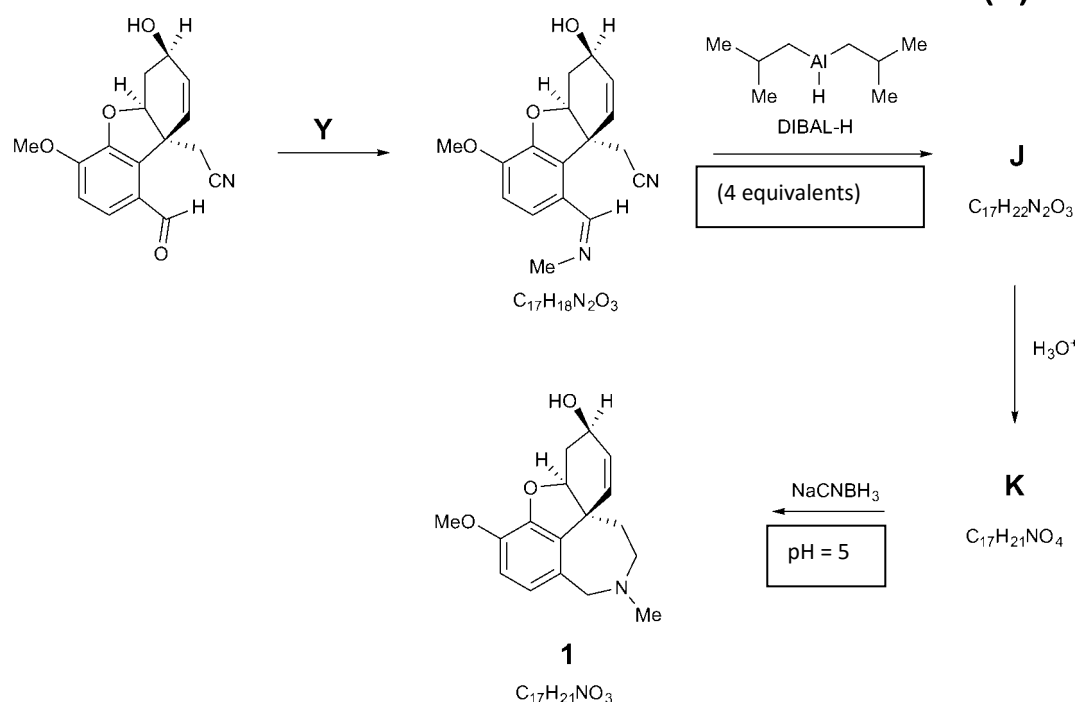
6.3.1. <u>Give</u> the formula for compound **Y** to carry out the first step of the route.

6.3.2. <u>Suggest</u> structures for **J** and **K**.

Problem 7   **8% of the total**

This question looks at the synthesis of *dolasetron mesylate*, **Z** (shown right), a drug sold under the tradename *Anzemet* and used to treat post-operative nausea and vomiting.
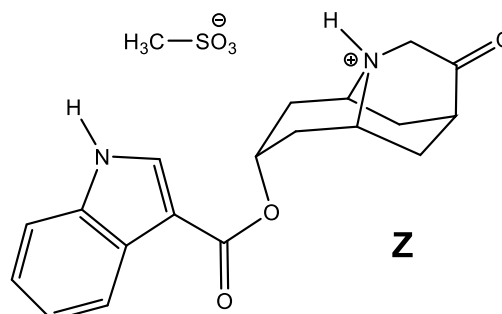
The synthesis begins as shown below.
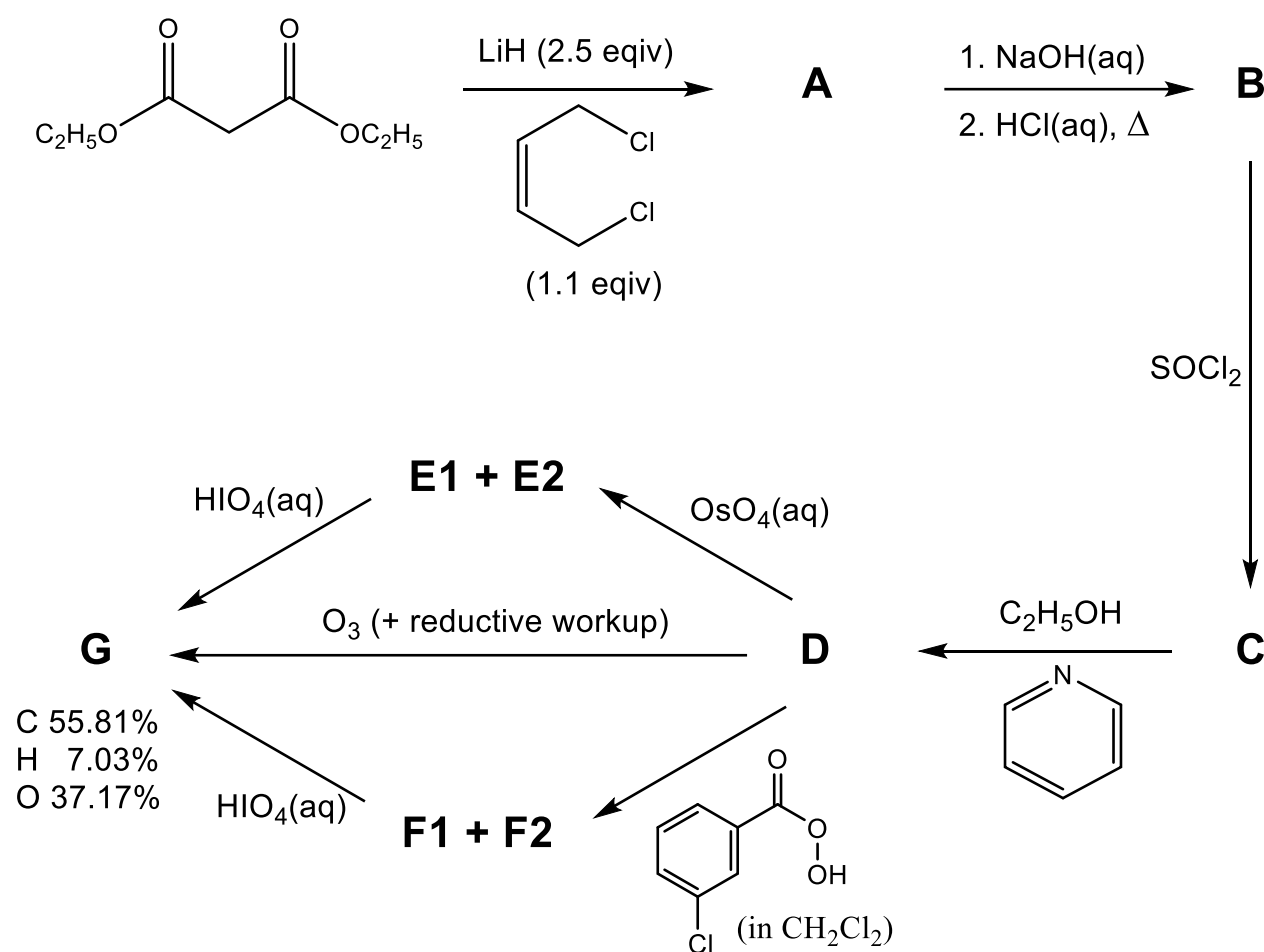
First cyclic compound **A** is made, which contains C, H, and O only. Compound **G** is achiral and can be prepared directly from **D** using ozone under reductive conditions, or via stereoisomers **E1** and **E2** using OsO_4, or via stereoisomers **F1** and **F2** using the peracid shown.

7.1.   <u>Determine</u> the empirical formula of **G** from the percentage masses given.

7.2.   <u>Give</u> the structures of **A**, **B**, **C**, **D**, **E1**, **E2**, **F1**, **F2** and **G**.

Compound **G** is used in the next stage of the synthesis, under buffered conditions, to form **H** (as a mixture of two achiral diastereoisomers). Reduction of **H** with NaBH₄ gives alcohol **I** (as a mixture of four achiral diastereoisomers). **I** reacts with acidified dihydropyran to form **J** (as a mixture of even more diastereoisomers). **J** is then treated first with *t*-butoxide base, then refluxed with acid before finally extracting under weakly basic conditions to form **K** as a mix of two diastereomers, **K1** (major product) and **K2** (minor product). These could be separated, and **K1** was used in the final stages of the synthesis.
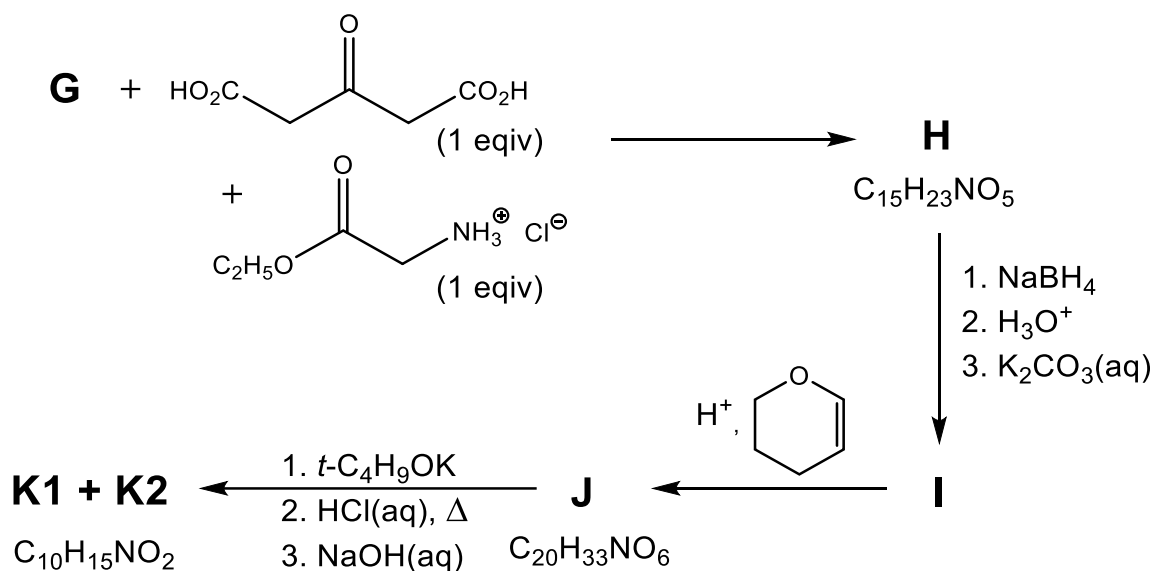
G + HO₂C⎯⎯(O)⎯⎯CO₂H (1 eqiv)

+ C₂H₅O⎯⎯(O)⎯⎯NH₃⊕ Cl⊖ (1 eqiv)

⟶ **H** $C_{15}H_{23}NO_5$

1. NaBH₄
2. H₃O⁺
3. K₂CO₃(aq)

I

H⁺, (dihydropyran)

J $C_{20}H_{33}NO_6$

1. *t*-C₄H₉OK
2. HCl(aq), Δ
3. NaOH(aq)

K1 + K2 $C_{10}H_{15}NO_2$

7.3.1. <u>Give</u> the structures of **H**, **I**, and **J**. There is no need to show the different diastereoisomers formed.

7.3.2. Give the structures of diastereoisomers **K1**, and **K2**.

In the final stage of the synthesis, **L** and **M** react to form intermediate **N**. **N** then reacts with **K1** to form, after extraction, the neutral amine which gives the target compound upon protonation with CH₃SO₃H.

L (indole-3-carboxylic acid)

+ **M** F₃C⎯(O)⎯O⎯(O)⎯CF₃

⟶ **N**

K1 —1. **N**→ **Z**
2. CH₃SO₃H
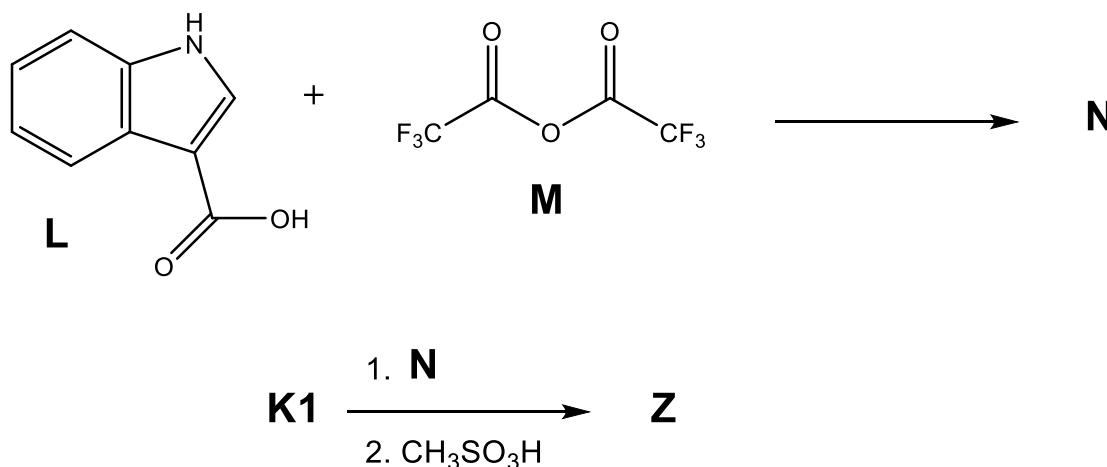
7.4. <u>Give</u> the structure of **N**.

Problem 8   7% of the total

An exotic, but biologically relevant sugar analogue can be prepared from D-glucose in the following manner. Heating a mixture of D-glucose and acetone with a few drops of concentrated acid results in the formation of a diacetonide **A**. Then **A** can be hydrolyzed selectively to **B**.
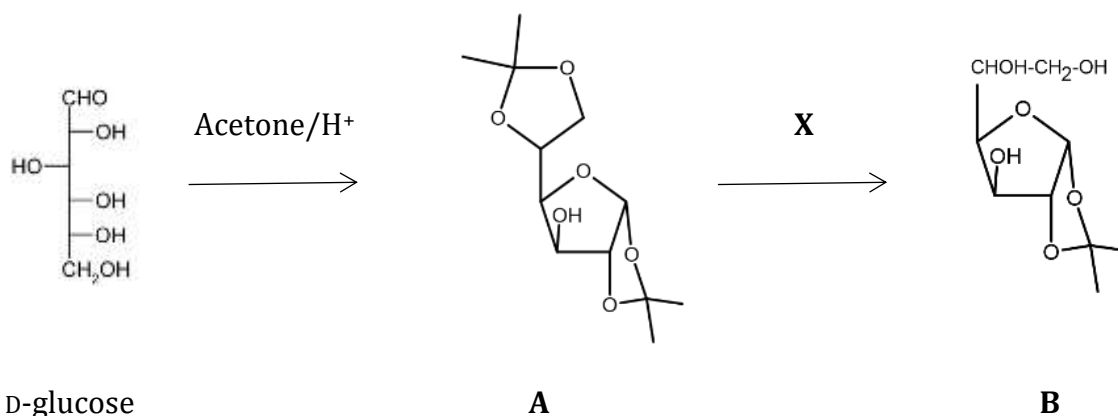
D-glucose   **A**   **B**

8.1.1. Which of the following sentences is true?

     A is an α isomer.   **A** is neither α nor β.
     A is a β isomer.   **A** is a mixture of α and β isomers.

8.1.2. Which of the following sentences is true?

     We can get product **A** only if we use α-D glucose as starting material.
     We can get product **A** only if we use β-D glucose as starting material.
     We can get product **A** either from α- or from β-D glucose as starting material.

8.1.3. Which one of these reagents can be utilized as **X** for the selective hydrolysis of **A**?

     50% acetic acid   concentrated H_2SO_4
     6 M HCl in water   1 M NaOH in water
     6 M HCl in acetic acid

8.1.4. Which is the stereochemically correct structure for compound **B**?
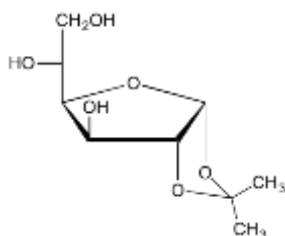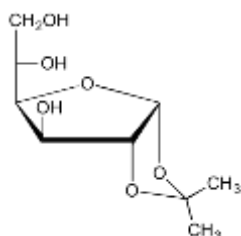
Neither of these

B is treated with sodium metaperiodate to get **C**. **C** is then reacted with an aqueous solution of NaCN, then heated with 10% NaOH solution to get a mixture of two diastereomeric compounds **D₁** and **D₂**. These compounds can be separated by column chromatography.

$$\text{B} \xrightarrow{\text{IO}_4^-} \underset{\text{188.2 g/mol}}{\text{C}} \xrightarrow[\text{2. NaOH/H}_2\text{O}]{\text{1. NaCN}} \text{D}_1 + \text{D}_2$$
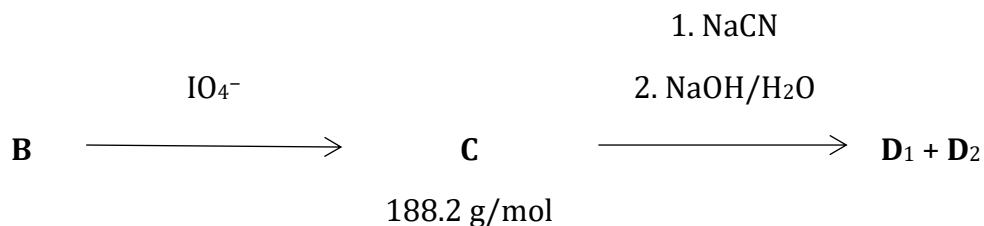
Reaction of **D₁** with LiAlH₄ followed by heating with 1M HCl solution gives sugar **F** that is the hydrolysis product of the most abundant natural polysaccharide.
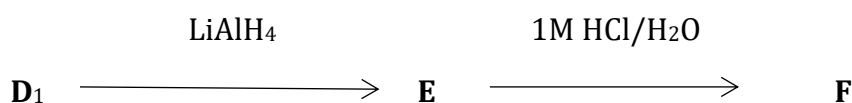
$$\text{D}_1 \xrightarrow{\text{LiAlH}_4} \text{E} \xrightarrow{\text{1M HCl/H}_2\text{O}} \text{F}$$

8.2.1. <u>Draw</u> the structures of **C**, **D₁**, **D₂**, **E** and **F** including stereochemical information. <u>Show</u> **F** as the more stable 6-membered ring containing isomer using the ring skeleton. <u>Indicate</u> with a wavy line if absolute chirality around a carbon is not known.

8.2.2. The reaction sequence from glucose to **F** does not seem to be useful. In some cases, however, this is the most economical way to produce **F**. <u>In which case</u>?

   ${}^{13}\text{C}$ labelling at carbon 6 of **F**
   ${}^{13}\text{C}$ labelling at carbon 5 of **F**
   ${}^{13}\text{C}$ labelling at carbon 1 of **F**
   ${}^{15}\text{O}$ labelling at glycosidic OH of **F**
   synthesis of an uncommon isomer of **F**

Neutralization of **D₂** with HCl followed by heating in toluene results in dehydration and formation of **G**, which has a tricyclic structure in water-free solvents. Boiling **G** in 1M HCl solution gives **H** ($C_6H_{10}O_7$), which is a natural sugar derivative containing a 6 membered ring. **H** is a building block of heparin, an anticoagulant polysaccharide produced by our bodies.

$$\text{D}_2 \xrightarrow[-\text{H}_2\text{O}]{\substack{\text{1. Equimolar HCl} \\ \text{2. Heat, toluene}}} \text{G} \xrightarrow{\text{1M HCl/H}_2\text{O}} \text{H}$$
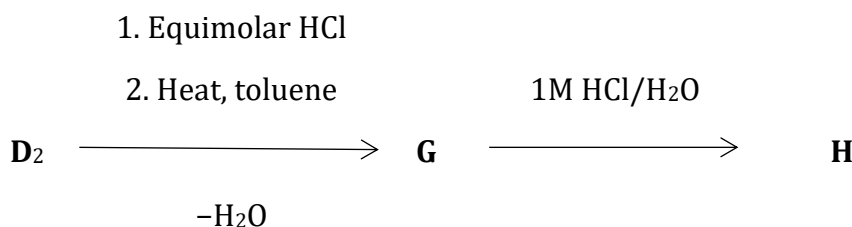
8.3.1. <u>Draw</u> the structure of **G** including the stereochemistry.
   <u>Draw</u> **H** as the more stable 6-membered ring containing isomer using the ring skeleton. <u>Indicate</u> with a wavy line if absolute chirality around a carbon is not known.

8.3.2. How are the rings of **G** fused together?

both junctions cis
one cis and one trans junction
both junctions trans

8.3.3. Which of the following is true for **H**? (You can choose more than one option.)

H is a reducing sugar (reacts with Fehling's reagent)
H is an aldaric acid (dicarboxylic derivative of an aldose)
H is an aldonic acid (C1 is a carboxyl group)
H is a uronic acid (C5 or C6 is a carboxyl group)
H is a ketose
H is a lactone
H is a D sugar
H is achiral
H is a meso compound

48th International Chemistry Olympiad

Theoretical Problems

Answer sheets

28 July 2016

Tbilisi, Georgia

Problem 1   5% of the total

1.1.	1.2.	1.3.	1.4.	1.5.	1.6.	1.7.	Sum
3	1	2	2	2	4	3	17

1.1. <u>On which electrode</u> does nitrogen trifluoride form?

☐ Cathode ☐ Anode

<u>Write a balanced chemical equation for</u> the electrode half reaction for the formation of NF_3.

$NH_4^+ + 3\ F^- \longrightarrow NF_3 + 4\ H^+ + 6\ e^-$ or $NH_4F + 2\ HF \longrightarrow NF_3 +\ 6\ H^+ + 6\ e^-$ or equ.

3p (1p choosing anode, 1p species, 1p coefficients)

1.2. <u>Which of NF_3, NHF_2 or NH_2F compound is</u> expected to condense at the lowest temperature?

☐ NF_3 ☐ NHF_2 ☐ NH_2F | NF_3 |

1.3. <u>Assign</u> the N-F bond lengths (136, 140, 142 pm) to the molecules.

Molecule	NH_2F	NHF_2	NF_3
N-F bond length, pm			

The partial positive charge on N increases in this order, so the attraction also increases between the N and F.

1.4. <u>Write</u> a balanced chemical equation for the formation of the binary nitrogen – fluorine compound.

$2\ NHF_2 + 2\ KF \longrightarrow N_2F_2 + 2\ KHF_2$ or $2\ NHF_2 \longrightarrow N_2F_2 + 2\ HF$

2p (1p N_2F_2, 1p equation)

1.5. <u>Propose</u> a suitable reagent for the formation of NF_4^+ and <u>write</u> a balanced chemical equation for the reaction.

$NF_3 + F_2 + SbF_5 \longrightarrow NF_4^+ + SbF_6^-$ any strong fluoride acceptor (AsF_5, BF_3)

2p (1p species, 1p coefficients)

1.6. <u>Write</u> a balanced chemical equation for the hydrolysis of NF_4^+.

$2\ NF_4^+ + 2\ H_2O \longrightarrow 2\ NF_3 + O_2 + 2\ HF + 2\ H^+ \Rightarrow n(O_2){:}n(NF_3) = 1{:}2$

2p (1p species, 1p coefficients)

<u>Write</u> a balanced chemical equation for a possible side reaction that can decrease the theoretically expected $O_2{:}NF_3$ mole ratio.

e.g.: $NF_4^+ + 2\ H_2O \longrightarrow NF_3 + H_2O_2 + HF + H^+$ HOF, O_3, OF_2 also accepted.

2p (1p species, 1p coefficients)

1.7. <u>Determine</u> the formula of the salt in question.

Your work:

From the $NF_3{:}F_2$ ratio it is clear that the anion also contains fluorine. Moreover, the starting NF_4^+: liberated F_2 ratio is 1:2, and all fluorine content is released. With a $(NF_4)_x AF_y$ composition, $x{:}y = 1{:}4$.

$$\frac{8xM(F)}{8xM(F)+xM(N)+M(A)} = 0.656 \Rightarrow \frac{M(A)}{x} = 65.7 \text{ g/mol}$$

With $x=1$, the atomic mass of **A** is close to zinc, but not all fluorine would be released with Zn. If $x=2$, then the element is xenon, and the formula is $(NF_4)_2 XeF_8$

3p (1.5p for Zn)

Formula:

Problem 2   8% of the total

2.1.1	2.1.2	2.1.3	2.2	2.3	2.4	2.5	2.6.1	2.6.2	2.6.3	Sum
5	3	2	2	3	6	2	1	3	6	33

2.1.1. <u>Which</u> of the atoms (A or B) is copper?

Cu:	There are 2 A atoms and 4 B atoms in the cell. Cu: B

<u>Which basic structure</u> (primitive cubic, face centered cubic, body centered cubic, diamond) is formed by the A atoms and <u>which structure</u> is formed by the B atoms?

	pr. cubic	fcc	bcc	diamond
A				
B				

B: fcc   A: bcc

<u>What</u> are the coordination numbers of the atoms?

A: B:	B: 2 A: 4

2.1.2. <u>Calculate</u> the smallest O-O, Cu-O and Cu-Cu distances in the structure.

Your work:

O-O:

O-O: half of the cell body diagonal $1/2 \cdot 427.0$ pm$\cdot\sqrt{3}$ = 369.8 pm. Cu-O: $1/4^{\text{th}}$ of the cell body diagonal $1/4 \cdot 427.0$ pm$\cdot\sqrt{3}$ = 184.9 pm. Cu-Cu: half of the face diagonal: $1/2 \cdot 427.0$ pm$\cdot\sqrt{2}$ = 301.9 pm. 1p each, no penalty for Cu and O switched.

Cu-O:

Cu-Cu:

2.1.3. <u>What</u> is the density of pure copper(I) oxide?

Your work:

The volume of the unit cell is $(427.0 \text{ pm})^3$. The mass of a unit cell is $(4M_{\text{Cu}} + 2\,M_{\text{O}})/\,N_{\text{A}}$. The density is 6.106 g/cm^3. 2p

density:

2.2. <u>What percentage</u> of normal copper sites are empty in the crystal sample?

Your work:

> From 1000 coppers 998 atoms are Cu(I) and 2 are Cu(II). To balance the charge of the anions, there has to be 2 vacant Cu sites.
> The percentage of empty sites is: $2/1002 \approx 0.2\%$
>
> 1 p

percentage:

<u>What</u> is x in the empirical formula $Cu_{2-x}O$ of the crystal?

Your work:

> 0.2% of 2 coppers is missing. That is 0.004.
>
> 1 p

x:

2.3. <u>Write</u> balanced chemical equations for reactions (1-3).

Reaction 1:

> (1) $2\ Cu_2O + O_2 \longrightarrow 4\ CuO$ (copper(II)-hydroxides and carbonates accepted)
>
> (2) $Cu_2O + 2\ H^+ \longrightarrow Cu + Cu^{2+} + H_2O$
>
> (3) $Cu_2O + H_2SO_4 + 4\ H^+ \longrightarrow 2\ Cu^{2+} + SO_2 + 3\ H_2O$
>
> 3p (non-ionic equations also accepted)

Reaction

Reaction

2.4. <u>Determine</u> the temperature ranges, if any, of thermodynamic stability of copper and its oxides between 500 and 1500 K in a 10^5 Pa oxygen atmosphere.

Your work:

> $\Delta_fG(CuO) = -156000$ J mol^{-1} + 84 J mol^{-1} K^{-1} T
> $\Delta_fG(Cu_2O) = -170000$ J mol^{-1} + 72 J mol^{-1} K^{-1} T
>
> Both Gibbs energies of formation are negative in the range 500-1500 K, so the oxides are more stable than the elements. Cu is not stable.
>
> Looking at the conversion process: $2\ CuO = Cu_2O + 0.5\ O_2$
> $\Delta_rG = 142000$ J mol^{-1} -96 J mol^{-1} K^{-1} T
> The Gibbs energy of the reaction is negative above 1480 K.
> CuO is stable below 1480 K, Cu$_2$O above 1480 K.
>
> 6 p (1 for each ΔG or equivalent calculation, 1 for each conclusion)

Temperature range between 500-1500K	The most stable form (Cu, Cu$_2$O or CuO)

2.5. Write the half reaction equations for the electrode processes during the anodic production of Cu$_2$O in NaOH solution with a platinum cathode and copper anode.

Cathode

Anode:

> C: 2 H$_2$O +2 e$^-$ $\longrightarrow$ H$_2$ + 2 OH$^-$
>
> A: 2 Cu + 2 OH$^-$ $\longrightarrow$ Cu$_2$O + H$_2$O + 2e$^-$
>
> 2p

2.6.1. Write the half reaction equation of the cathode process giving Cu$_2$O in acidic medium.

> 2 Cu^{2+} + H$_2$O + 2 e$^-$ $\longrightarrow$ Cu$_2$O + 2 H$^+$
>
> 1p

2.6.2. What is the maximum pH at which the concentration of copper(II) can be maintained at 0.100 mol dm^{-3}?

Your work:

> If the pH is too high, Cu(OH)$_2$ precipitates.
>
> K$_{sp}$ $\geq$ 0.1[OH$^-$]^2 $\Rightarrow$ pH $\leq$ 5.15
>
> 3 p (1p realizing that precipitation occurs, 1p equation, 1p result)

maximum pH:

2.6.3. <u>What</u> is the minimum pH at which the cathodic production of Cu_2O in a 0.100 mol dm^{-3} Cu^{2+} solution is still possible?

Your work:

The potential of the cathodic process (2 Cu^{2+} + H_2O + 2 e$^-$ = Cu_2O + 2 H$^+$) depends on the pH.

The standard potential of the cathodic process can be calculated from:

$Cu_2O(s) + H_2O(l) + 2e^- \longrightarrow 2\ Cu(s) + 2\ OH^-$ (aq)	$\Delta G^o_1 = -2F(-0.36\ V)$
$Cu^{2+}(aq) + 2\ e^- \longrightarrow Cu(s)$	$\Delta G^o_2 = -2F(+0.337\ V)$
$H_2O(l) \longrightarrow H^+(aq) + OH^-$ (aq)	$\Delta G^o_3 = -RT \ln K_w$
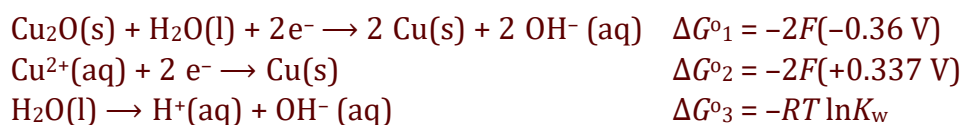
For 2 Cu^{2+}(aq) + H_2O(l) + 2 e$^- \longrightarrow Cu_2O$(s) + 2 H$^+$(aq):

$\Delta G^o = -\Delta G^o_1 + 2\Delta G^o_2 + 2\Delta G^o_3$

$E^o = -\Delta G^o /2F = 0.36\ V + 2 \cdot 0.337\ V - (RT/F) \cdot \ln K_w = 0.208\ V$

The concentration dependence of the cathodic Cu_2O production potential:

$E = 0.208\ V + 0.059/2 \log ([Cu^{2+}]^2/[H^+]^2)$

This potential has to be higher than the potential of the reduction of Cu^{2+}.

$0.337 + 0.059/2 \log [Cu^{2+}] = 0.208 + 0.059/2 \log ([Cu^{2+}]^2/[H^+]^2)$

$[H^+]^2 = [Cu^{2+}]/23600$

pH = 2.69

6 p (3p for standard potential, 3p for calculation)

Many other routes possible – all correct ones accepted.

minimum pH:

Problem 3 9% of the total

3.1.1.	3.1.2.	3.1.3.	3.2.1.	3.2.2.	3.2.3.	3.3.1.	3.3.2.	3.3.3.	Sum
2	2	6	5	4	7	6	11	5	48

3.1.1. Write a balanced net ionic equation for the reaction when iodate reacts with excess iodide in acidic solution.

> $IO_3^- + 8\ I^- + 6\ H^+ \rightarrow 3\ I_3^- + 3\ H_2O$ or $IO_3^- + 5\ I^- + 6\ H^+ \rightarrow 3\ I_2 + 3\ H_2O$
>
> 2p (1p species, 1p coefficients, 0.5p penalty if spectator ions are included.)

3.1.2. Write a balanced net ionic equation for the reaction taking place during the titration with thiosulfate.

> $I_3^- + 2\ S_2O_3^{2-} \rightarrow 3\ I^- + S_4O_6^{2-}$ or $I_2 + 2\ S_2O_3^{2-} \rightarrow 2\ I^- + S_4O_6^{2-}$
>
> 2p (1p species, 1p coefficients, 0.5p penalty if spectator ions are included.)

3.1.3. Calculate the iodization level, in ppm, of this salt sample.

Your work:

> $(0.00750\ dm^3\ titrant) \cdot (0.00235\ mol\ dm^{-3}\ S_2O_3^{2-}) = 1.76 \cdot 10^{-5}\ mol\ S_2O_3^{2-}$
>
> $(1.76 \cdot 10^{-5}\ mol\ S_2O_3^{2-}) \cdot (1\ mol\ IO_3^-/6\ mol\ S_2O_3^{2-}) = 2.94 \cdot 10^{-6}\ mol\ IO_3^-$
>
> $(2.94 \cdot 10^{-6}\ mol\ IO_3^-) \cdot (126.90\ g/mol) = 3.73 \cdot 10^{-4}\ g\ iodine$
>
> $\{(3.73 \cdot 10^{-4}\ g\ iodine)/(10.00\ g\ salt)\} \cdot 10^6\ ppm = 37.3\ ppm\ iodine$
>
> 2p for calculating mol thiosulfate
>
> 2p for calculating mol iodate
>
> 2p for converting to ppm

ppm iodine =

3.2.1. <u>Select</u> an appropriate data point from the experiments and <u>use it to calculate</u> the solubility product of AgI (K_{spI}).

Your work:

> In the experiments, $|E| = -(RT/nF)\ln([Ag^+]_{cell}/[Ag^+]_{ref}) = -0.0591 \cdot \log[Ag^+]$
>
> There is a sharp endpoint at n(added Ag^+) = n (I^- initially present) in experiment **A** ($[Cl^-]$ = 0), so precipitation of AgI(s) must be essentially complete at any point in the titration curve. If one considers, for example, 5.0 μmol added Ag^+, then
>
> $[I^-] = [I^-]_0 - 5.0 \cdot 10^{-6}$ mol/dm^3 = $5.0 \cdot 10^{-6}$ mol/dm^3
>
> $|E|$ = 0.622 V = $-0.0591 \cdot \log[Ag^+] \Rightarrow [Ag^+] = 3.2 \cdot 10^{-11}$ mol/dm^3
>
> $K_{spI} = [Ag^+][I^-] = 1.6 \cdot 10^{-16}$
>
> 2p for relationship between E and $[Ag^+]$ (full credit if used even if not stated explicitly)
>
> 1p for selecting a data point with $n(Ag^+) \leq 10.0$ μmol
>
> 2p for calculation of K_{spI}
>
> Full marks are awarded here and later for correct answers with numerical differences stemming from using different data points or minor rounding

K_{spI}:

3.2.2. <u>Select</u> an appropriate data point from the experiments and <u>use it to calculate</u> the solubility product of AgCl (K_{spCl}).

Your work:

> In the titration with $[Cl^-]$ = 0.100 mol/dm^3 (experiment **B**), the fact that the potential stops changing at n(added Ag^+) $\geq$ 11.8 μmol must be due to the precipitation of AgCl(s) (the high concentration of chloride therefore effectively fixes the $[Ag^+]$ in the solution). So in this regime:
>
> $|E|$ = 0.517 V = $-0.0591 \cdot \log[Ag^+] \Rightarrow [Ag^+] = 1.6 \cdot 10^{-9}$ mol/dm^3
>
> $K_{spCl} = [Ag^+][Cl^-] = 1.6 \cdot 10^{-10}$
>
> 1p for selecting a data point with $n(Ag^+) > 11.8$ μmol
>
> 3p for calculation of K_{spCl}

K_{spCl}:

3.2.3. <u>Select</u> an appropriate data point from the experiments and <u>use it to calculate</u> K_f. You may need to use values of K_{spI} or K_{spCl} to do this calculation. If you were unable to carry out the calculations in **3.2.1.** or **3.2.2.**, you may use the arbitrary values of $K_{spI} = 1.00 \cdot 10^{-15}$ and $K_{spCl} = 1.00 \cdot 10^{-9}$ without penalty.

Your work:

> There are a number of good approaches to this problem.
>
> One can use the point at which AgCl(s) first precipitates (estimated at 11.8 μmol Ag^+ added) to calculate K_f. At this point, $[Ag^+] = 1.6 \cdot 10^{-9}$ mol/dm³, $[Cl^-] = 0.100$ mol/dm³ (see above).
> Almost all of the originally present $1.0 \cdot 10^{-5}$ mol/dm³ iodide has been precipitated out as 9.9 μmol AgI, since $[I^-] = K_{spI}/[Ag^+] = 1.0 \cdot 10^{-7}$ mol/dm³
>
> Total Ag in solution = 11.8 μmol – 9.9 μmol = 1.9 μmol
>
> $[AgCl_2^-] = 1.9 \cdot 10^{-6}$ mol/dm³ (since free $[Ag^+]$ is only $1.6 \cdot 10^{-9}$ mol/dm³)
>
> $$K_f = \frac{[AgCl_2^-]}{[Ag^+][Cl^-]^2} = \frac{1.9 \cdot 10^{-6}}{1.6 \cdot 10^{-9} \cdot 0.100^2} = 1.2 \cdot 10^5 \quad [1.9 \cdot 10^4 \text{ given const.}]$$
>
> Same approach works for 11 μmol Ag^+ added.
>
> 2p for selecting a data point between 10-12.0 μmol
>
> 3p for reasonable method of calculating K_f
>
> 2p for value of K_f

> An alternative approach is to look at the equivalence point, where
>
> $|E| = 0.558$ V $= -0.0591 \cdot \log[Ag^+] \Rightarrow [Ag^+] = 3.62 \cdot 10^{-10}$ mol/dm³
>
> Since AgI(s) is present, $[I^-] = K_{spI}/[Ag^+] = 4.42 \cdot 10^{-7}$ mol/dm³
>
> The amount of dissolved iodine and silver is equivalent:
>
> $[I^-] = [Ag^+] + [AgCl_2^-] \Rightarrow [AgCl_2^-] = 4.42 \cdot 10^{-7}$ mol/dm³
>
> $$K_f = \frac{[AgCl_2^-]}{[Ag^+][Cl^-]^2} = \frac{4.42 \cdot 10^{-7}}{3.62 \cdot 10^{-10} \cdot 0.100^2} = 1.2 \cdot 10^5 \quad [7.6 \cdot 10^5 \text{ given const.}]$$

K_f:

3.3.1. <u>Write</u> balanced net ionic equations for the reaction of cerium(IV) with H_3AsO_3 in acidic solution, as well as reactions of cerium(IV) with a species containing the element iodine and H_3AsO_3 with a species containing the element iodine, that could reasonably account for the catalysis of the net reaction by iodide.

Net reaction of cerium(IV) with H_3AsO_3 in acidic solution:

> $2\ Ce^{4+} + H_3AsO_3 + H_2O \rightarrow 2\ Ce^{3+} + H_3AsO_4 + 2\ H^+$
>
> 2p (1p for H_3AsO_3/H_3AsO_4 couple, 1p balanced)

Reaction of cerium(IV) with an iodine-containing species:

> $2\ Ce^{4+} + 2\ I^- \rightarrow 2\ Ce^{3+} + I_2$
>
> 2p (1p species, 1p balanced). Full marks for I_3^- or $I\cdot$ as products

Reaction of H_3AsO_3 with an iodine-containing species:

> $H_3AsO_3 + I_2 + H_2O \rightarrow H_3AsO_4 + 2\ I^- + 2\ H^+$
>
> 2p (1p species, 1p balanced). Full marks for I_3^- or $I\cdot$ as products
>
> Two iodine-containing reactions must add up to the net reaction, otherwise −2p for the iodine-containing reactions

---

3.3.2. <u>Determine</u> the integer values of m, n, and p and <u>calculate</u> the value of k (be sure to <u>specify</u> its units).

Your work:

> The limiting reactant is Ce(IV) which is < 10% of the concentration of H_3AsO_3, so only the concentration of Ce(IV) changes appreciably over the course of the reaction. (I^- is a catalyst and is not consumed.) So the order in Ce(IV) can be judged by the time course of the reaction. By eye, it appears to be first order.

This can be verified by calculating $-\ln(A/A_0)\cdot(1/t)$, which should be a constant (k_{obs}) if the reaction is first-order:

t, s	k_{obs}, s^{-1}, Run **1**	k_{obs}, s^{-1}, Run **2**	k_{obs}, s^{-1}, Run **3**
20	0.0290	0.0328	0.0148
40	0.0286	0.0310	0.0147
60	0.0284	0.0305	0.0146
80	0.0284	0.0305	0.0146
100	0.0282	0.0302	0.0145
avg.	0.0285	0.0310	0.0146

So n = 1.

Since k_{obs} is unchanged (within 10%) from run **1** to run **2** despite decreasing [H_3AsO_3] by a factor of two, m = 0.

In contrast, decreasing [I$^-$] by a factor of two from run **1** to run **3** results in a decrease in observed rate constant of a factor of two, so p = 1.

k = k_{obs}/[I$^-$], giving values of $1.99\cdot10^4$, $2.17\cdot10^4$, and $2.04\cdot10^4$ dm^3 mol^{-1} s^{-1} for runs **1-3**; average k = $2.07\cdot10^4$ dm^3 mol^{-1} s^{-1}.

4p for documenting 1st-order in Ce(IV), 2p each for m and p,

2p for value of k, 1p for unit of k consistent with given rate law

m = n = p = k =

3.3.3. <u>Calculate</u> the iodization level, in ppm, of the salt sample.

Your work:

t, s	$-\ln(A/A_0)\cdot(1/t)$, s^{-1}
20	0.0177
40	0.0177
60	0.0177
80	0.0176
100	0.0177

So k_{obs} = 0.0177 s^{-1} = k[I$^-$] = ($2.07\cdot10^4$ dm^3 mol^{-1} s^{-1})[I$^-$]

[I$^-$] = $8.55\cdot10^{-7}$ mol/dm^3

Since the salt solution was diluted by a factor of (2.05 cm^3)/(0.050 cm^3) = 41, the concentration in the original salt solution was $41\cdot(8.55\cdot10^{-7}$ mol/dm^3) = $3.51\cdot10^{-5}$ mol/dm^3.

($3.51\cdot10^{-5}$ mol dm^{-3})(0.01000 dm^3) = $3.51\cdot10^{-7}$ mol I in the salt sample
($3.51\cdot10^{-7}$ mol iodine)(126.90 g/mol) = $4.45\cdot10^{-5}$ g iodine
{($4.45\cdot10^{-5}$ g iodine)/(1.000 g salt)}$\cdot10^6$ ppm = 44.5 ppm I

2p for calculating k_{obs}, 1p for [I$^-$] from k_{obs}, 2p for converting to ppm

ppm I =

Problem 4 8% of the total

4.1.1	4.1.2	4.1.3	4.2.1	4.2.2	4.2.3	4.3.1	4.3.2	Sum
5	3	2	1	2	6	2	4	25

4.1.1. Calculate the time in minutes the oxidation process has to continue in order to reach the accepted level of dioxane at 303.15 K if the initial concentration of $K_2S_2O_8$ is $5.0 \cdot 10^{-6}$ mol/dm³. Assume that the rate law obtained from the data above is valid under these conditions.

Your work:

> Trial1 and 2 ⇒ the rate doubles when concentration of $K_2S_2O_8$ is doubled. Order w.r.t. $K_2S_2O_8$ =1.
>
> Trial3 and 4 ⇒ the rate does not change with concentration of dioxane. Order w.r.t. dioxane =0.
>
> Initial rate = $k[K_2S_2O_8]$ Average $k = 6.65 \cdot 10^{-3}$ min⁻¹
>
> Change in dioxane concentration: $(40.00 - 0.35)$ µg·dm⁻³ / 88.1 g·mol⁻¹ = 0.450 µmol·dm⁻³
>
> $[K_2S_2O_8]_0 = 5.00$ µmol dm⁻³; $[K_2S_2O_8]_t = 4.55$ µmol dm⁻³
>
> $4.55 = 5.00 \exp(-6.65 \cdot 10^{-3} t)$
>
> $t = 14.2$ minutes
>
> 5p (1p for each order, 1 p for k, 2p for final answer)

Oxidation time:

4.1.2. Assuming Ag(III) to be in steady state, deduce the rate equation for the oxidation of dioxane.

Your work:

$$k_1[S_2O_8^{-2}][Ag^+] - k_2[SO_4^{-2}]^2[Ag^{+3}] - k_3[Ag^{+3}][D] = 0$$

$$[Ag^{+3}] = \frac{k_1[S_2O_8^{-2}][Ag^+]}{k_2[SO_4^{-2}] + k_3[D]}$$

$$rate\ of\ oxidation = \frac{k_1 k_3[S_2O_8^{-2}][D][Ag^+]}{k_2[SO_4^{-2}]^2 + k_3[D]}$$

3p (1p for each step)

4.1.3. | A,C | 2p, (1p penalty for every mistake)

4.2.1. Write an expression for k_{obs} in terms of k_H, k_0, k_{OH} and $[H^+]$.

Your work:

$$k_{obs} = k_H[H^+] + k_0 + k_{OH}\frac{K_w}{[H^+]}$$

1p, (0.5p if $[OH^-]$ is included in the expression)

4.2.2. | B, D | 2p, (1p penalty for every mistake)

4.2.3. Using the diagram and the data in the table, calculate k_H, k_0 and k_{OH}. Make sure to specify the units.

Your work:

At pH = 5.30, k_0 is dominant
$\log(k_{obs}/\text{min}^{-1}) = -4.000 \Rightarrow k_{obs} = k_0 = 1.00 \cdot 10^{-4}\ \text{min}^{-1}$

At pH = 12.18, $[OH^-] = 0.01514\ \text{mol dm}^{-3}$
$\log(k_{obs}/\text{min}^{-1}) = -1.726 \Rightarrow k_{obs} = 1.88 \cdot 10^{-2}\ \text{min}^{-1}$
$k_{obs} = k_0 + k_{OH}[OH^-]$ k_0 can be neglected

$k_{OH} = k_{obs}/[OH^-] = 1.24\ \text{dm}^3 \cdot \text{mol}^{-1} \cdot \text{min}^{-1}$

At pH = 1.30, $[H^+] = 0.0501\ \text{mol dm}^{-3}$
$\log(k_{obs}/\text{min}^{-1}) = -3.886 \Rightarrow k_{obs} = 1.30 \cdot 10^{-4}\ \text{min}^{-1}$
$k_{obs} = k_H[H^+] + k_0$ k_0 cannot be neglected

$$k_H = \frac{k_{obs} - k_0}{[H^+]} = \frac{3.0 \cdot 10^{-5}\text{min}^{-1}}{0.0501\text{mol} \cdot \text{dm}^{-3}}$$

$k_H = 6.0 \cdot 10^{-4}\ \text{dm}^3 \cdot \text{mol}^{-1} \cdot \text{min}^{-1}$

6p (1p for k_0, 2p for k_{OH}, 3p for k_H, 0.5p penalty for wrong or no units)

k_0: k_{OH}: k_H:

4.3.1. [   ]   [b, c]   [2p, (1p penalty for every mistake)]

4.3.2. Assuming that only reactions I, II and III occur, <u>calculate</u> the value of the pH at the minimum of k_{obs}.

Your work:

$$k_{obs} = k_H[H^+] + k_0 + k_{OH}\frac{K_w}{[H^+]}$$

This is a minimum if

$$\frac{dk_{obs}}{d[H^+]} = k_H - k_{OH}\frac{K_w}{[H^+]^2} = 0$$

$$[H^+]_{min} = \sqrt{\frac{k_{OH}K_w}{k_H}} \qquad pH_{min} = \frac{1}{2}pK_W + \frac{1}{2}\log\frac{k_H}{k_{OH}} = 2.40$$

or see alternative solution without calculus

4p (3p for expression of [H+] at minimum, 1p for numerical result)

k_{obs} is a minimum if $k_H[H^+] + k_{OH}\frac{k_w}{[H^+]}$ is minimal.

The minimum happens when the two terms are equal. So at minimum:

$$k_H[H^+] = k_{OH}\frac{K_w}{[H^+]}$$

$$[H^+]_{min} = \sqrt{\frac{k_{OH}K_w}{k_H}} \qquad pH_{min} = \frac{1}{2}pK_W + \log\frac{k_H}{k_{OH}} = 2.40$$

pH at minimum:

Problem 5   8% of the total

5.1.1.	5.1.2.	5.1.3.	5.1.4.	5.1.5.	5.1.6.	5.2.1.	5.2.2.	5.3.	Sum
1	3	2	2	5	2	1	1	2	19

5.1.1. <u>Find</u> the mass of the gaseous mixture formed upon heating of **A** with **B** and SiO_2.

Your work:

> $m = 10.0 + 21.7 + 9.05 - 34.0 = 6.75$ g
>
> 1 p

5.1.2. <u>Determine</u> the quantitative composition of this gas mixture.

Your work:

> At 850°C, the number of moles of gaseous products is:
>
> $$n_1 = \frac{pV}{RT} = \frac{101325 \text{ Pa} \cdot 0.0167 \text{ m}^3}{8.314 \text{ Jmol}^{-1}\text{K}^{-1} \cdot (850\text{K} + 273\text{K})} = 0.181 \text{ mol}$$
>
> while at 0°C
>
> $$n_2 = \frac{pV}{RT} = \frac{101325 \text{ Pa} \cdot 0.00304 \text{ m}^3}{8.314 \text{ Jmol}^{-1}\text{K}^{-1} \cdot 273 \text{ K}} = 0.136 \text{ mol}$$
>
> The difference of 0.045 moles is probably water that has condensed. Hence, the mass of the gas at 0°C is $m = 6.75 - 0.045 \cdot 18 = 5.94$ g, and the molar mass is $m/n_2 \approx 44$ g/mol. Taken into account that we dealt with minerals, and the temperature was high, we can conclude that the rest of the gas is CO_2.
>
> The gas formed at 850°C contains 0.045 mol of H_2O and 0.136 mol of CO_2.
>
> 3p (0.5p for finding each compound, 1p for the quantity of each compound)

The gaseous mixture formed at 850°C contains ……… mol of ………. and ……… mol of ………

5.1.3. <u>Calculate</u> the molar mass and determine the formula of mineral **B**. Hint: it is an ionic solid insoluble in water and containing no water of crystallization.

Your work:

> Heating of mineral **A** with SiO_2 alone produces half of the gases evolved in the presence of **B**. Thus, **B** should form the rest $0.181/2 = 0.0905$ moles of gases and is a carbonate of some metal. If it forms pure CO_2, the molar mass of **B** per carbonate group is 9.05 g $/ 0.0905$ mol $= 100$ g mol^{-1}. The molar mass of CO_3 group is
> 60 g mol^{-1}, so the mass of metal per carbonate group is 40 g mol^{-1}.
>
> This corresponds to Ca, **B** – $CaCO_3$
>
> 2p

B is:

5.1.4. <u>Determine</u> the formula of mineral **C**.

Your work:

> Similar to the previous question, the molar mass of **C** per carbonate group is 17.8 g $/ 0.0905$ mol $= 197$ g mol^{-1}. The mass of metal per carbonate group is 137 g mol^{-1}.
>
> This corresponds to Ba, **C** – $BaCO_3$.
>
> 2p

C is:

5.1.5. <u>Determine</u> the formulae of Egyptian blue and Chinese blue.

Your work:

> Taking into account the molar ratios of known compounds, we can write a general equation of formation of Egyptian blue:
>
> $$\textbf{A} + 2\ CaCO_3 + 8\ SiO_2 = pigment + 3\ CO_2 + H_2O$$
>
> The composition of Egyptian blue can be written as $2CaO \cdot 8SiO_2 \cdot nMe_xO_y$. Oxide Me_xO_y forms from mineral **A**. Let us find the molar mass of nMe_xO_y:
>
> $$M(\text{pigment}) = M(2CaO \cdot 8SiO_2) + M(nMe_xO_y)$$
>
> $$M(\text{pigment}) = 2M(CaCO_3)\frac{m(\text{pigment})}{m(CaCO_3)}$$
>
> $$M(nMe_xO_y) = 2M(CaCO_3)\frac{34.0\ \text{g}}{9.05\ \text{g}} - M(2CaO \cdot 8SiO_2) \approx 159\ \text{g/mol}$$
>
> Trying different values (at least from 1 to 3) of n, x, and y, we ensure that the only possibility is $n = 2$, $x = y = 1$, Me is Cu. This is supported by a blue color of a pigment.
>
> The formula of Egyptian blue is then $CaCuSi_4O_{10}$.
>
> The formula of Chinese blue is $BaCuSi_4O_{10}$.
>
> 3p for proving presence of Cu (1.5 p for correct molar mass of oxide without further advances)
>
> 2p for formulas of the pigments
>
> Any correct way of calculation is fully marked
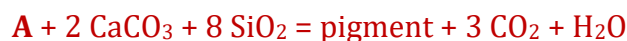
Egyptian blue is: Chinese blue is:

5.1.6. <u>Determine</u> the formula of mineral **A**.

Your work:

> Upon heating **A** turns into 2 CuO, 1 CO_2 and 1 H_2O.
>
> It means that **A** is malachite $Cu_2CO_3(OH)_2$.
>
> 2p

A is:

5.2.1. <u>Suggest</u> the formula of the mineral used in place of **C**.

> $BaSO_4$ (the most stable compound containing Ba and S, mineral barite)
>
> 1p (BaS is soluble and reactive, can not be a mineral.)

5.2.2. <u>Could</u> the temperature of synthesis of Chinese blue be decreased if this mineral is used instead of **C**?

☐ Yes ☐ No

> No. $BaSO_4$ is more stable than $BaCO_3$.
>
> 1p

5.3. <u>Write down</u> a formula of a binary compound that forms under the conditions required for Chinese violet and is responsible for the change of the color.

> Cu_2O (mixing red with blue gives purple)
>
> 2p
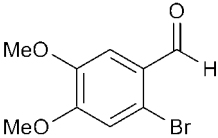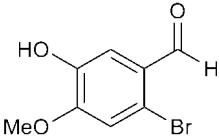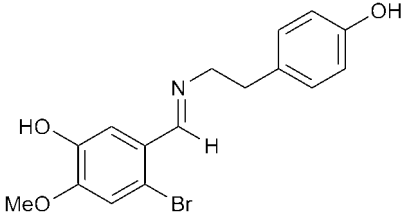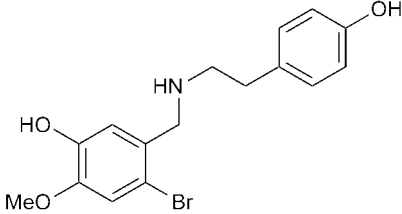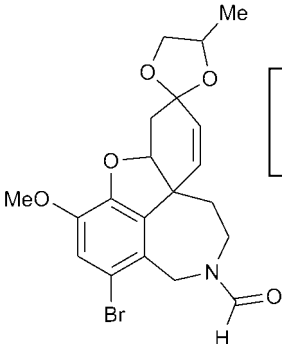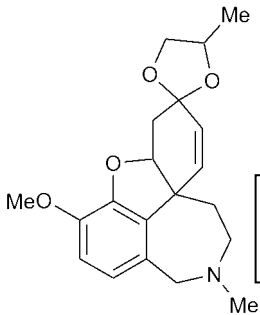
Problem 6   7% of the total

6.1.1.	6.1.2	6.2.1.	6.2.2.	6.2.3.	6.3.1	6.3.2.	Sum
24	4	3	6	2	2	8	49

6.1.1. Suggest structures for **A**, **B**, **C**, **D**, **F**, and **G**. None of the reactions except for the final transformation with L-selectride are stereoselective. Therefore, stereochemistry does not need to be indicated in your answers.

A

0p if lacks 2 para protons

B

C

D

F

2p penalty if Br removed

G

2p penalty if Br present

6.1.2. Give the formula for a possible reagent, **X**, to convert compound **D** to **E**.

X

CH₃CH₂OCOH or any other reasonable reagent. 4p (3p for formyl chloride)

Formic acid = 0p

6.2.1. <u>What</u> is the enantiomeric excess of the resolved compound prepared by the industrial route?

Your work:

> If x is the percentage of the (−) enantiomer:
>
> $x(-415) + (1 - x)(415) = -400$
>
> $x = 815/830$
>
> $ee = (815/830) - (15/830) = 800/830 = 0.964$ or 96.4%
>
> 3p (2p enantiomer composition, 1p ee calculation)

ee:

6.2.2. <u>Assign</u> the labelled stereocentres (α, β, γ) in (−)-**1** as R or S.

α	β	γ
S	R	S

6.2.3. <u>Give</u> the formula for a reagent that carries out the same reaction as L-selectride, the conversion of **H** to **1**. You need not worry about stereoselectivity.
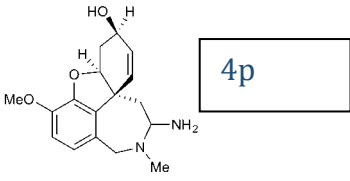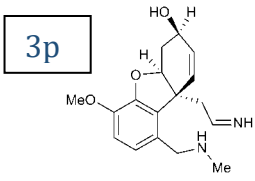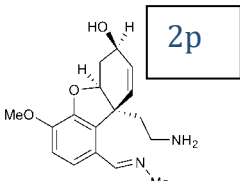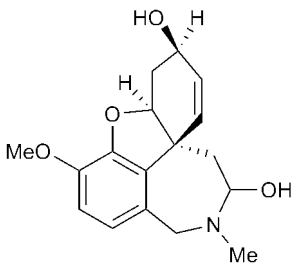
> $NaBH_4$, $LiAlH_4$, etc. 2p

6.3.1. <u>Give</u> the formula for compound **Y** to carry out the first step of the route.

Y
> CH_3NH_2 2p

6.3.2. <u>Suggest</u> structures for **J** and **K**.

J   4p

3p   2p

K   0p for J and K if not in agreement with the formula, full marks for open form of K.

Problem 7 — 8% of the total

7.1.	7.2.	7.3.1.	7.3.2.	7.4.	Sum
2	36	16	8	4	66
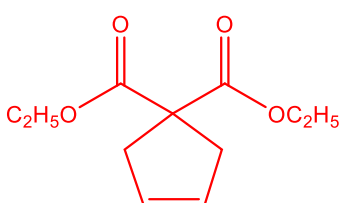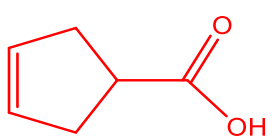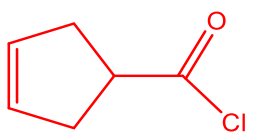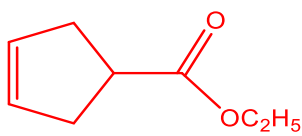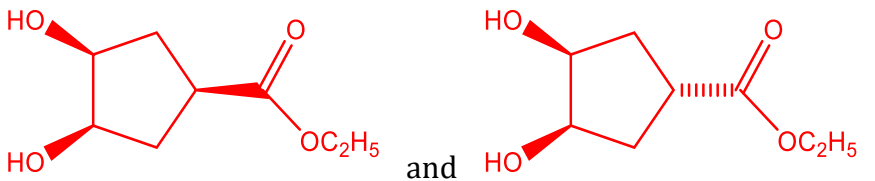
7.1. Determine the empirical formula of **G** from the percentage masses given.

Your work:

> C_2H_3O
>
> 2p (1p for molecular formula)

7.2. Give the structures of **A**, **B**, **C**, **D**, **E1**, **E2**, **F1**, **F2** and **G**.

A

4p (0pt if still contains Cl)
(2p penalty if H⁻ is used as reducing agent)

B

4p (2pt if no de-carboxylation)
(2p in mono-ester)

C

4p (allow carry forward from **B**)

D

4p (0p if remade **A**)
(1p if pyridinium intermediate)

E1 and **E2**

and

4p each (1p if OHs on different sides)
(2p if no de-carboxylation; 1p if osmate ester)

F1 and **F2**

and
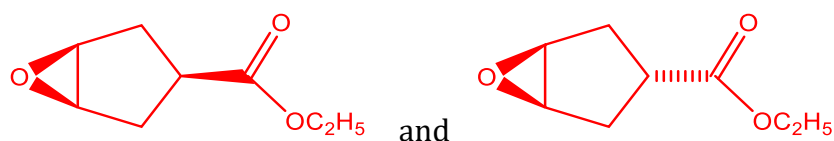
4p each
(1p if no de-carboxylation; 1p for trans-diol; 0p if no de-carboxylation and diol)

G
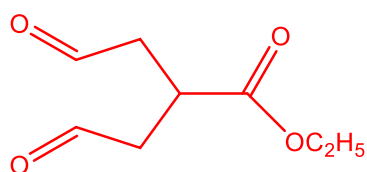
4p
(0p if does not fit formula)

7.3.1. <u>Give</u> the structures of **H**, **I**, and **J**. There is no need to show the different diastereoisomers formed.

H
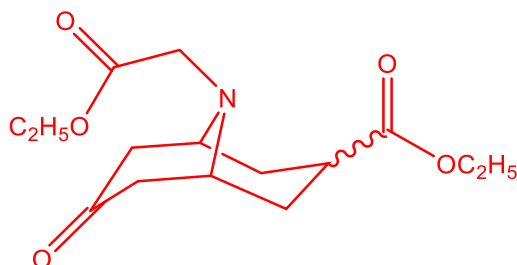
8p
(points for fitting formula, sensible chemistry, correct number of possible diastereomers, and being achiral)

I
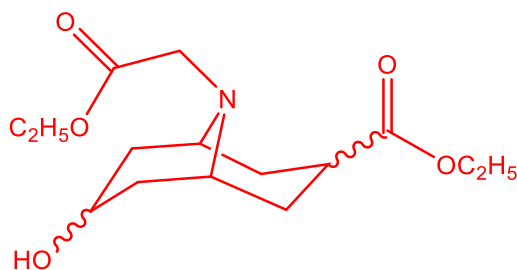
4p
(points for reduction of ketone, sensible chemistry, correct number of possible diastereomers, and being achiral)

J
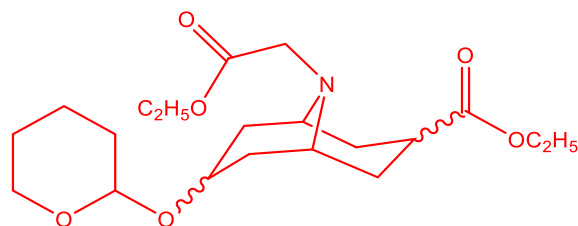
4p

(points for fitting formula, sensible chemistry, forming acetal, sensible number of possible diastereomers)

7.3.2   Give the structures of diastereoisomers **K1**, and **K2**.

K1
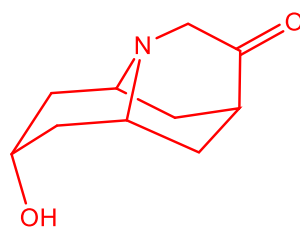
4p (2p if answer is **K2**)

(answer must fit formula and be sensible)

K2

4 pt (2pt if answer is **K1**)

(answer must fit formula and be sensible)

7.4.   Give the structure of **N**.

N
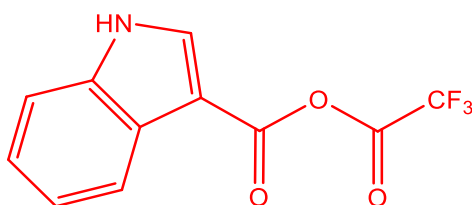
4p

(full marks for anhydride of **L**)

Problem 8   7% of the total

8.1.	8.2.1.	8.2.2.	8.3.1.	8.3.2.	8.3.3.	Sum
4	10	1	4	1	2	22

8.1.1. Which of the following sentences is true?

(x)□ **A** is an α isomer.   □ **A** is neither α nor β.
□ **A** is a β isomer.   □ **A** is a mixture of α and β isomers.

8.1.2. Which of the following sentences is true?

□ We can get product **A** only if we use α-D glucose as starting material.
□ We can get product **A** only if we use β-D glucose as starting material.
(x)□ We can get product **A** either from α- or from β-D glucose as starting material.

8.1.3. Which one of these reagents can be utilized as **X** for the selective hydrolysis of **A**?

(x)□ 50% acetic acid   □ concentrated H_2SO_4
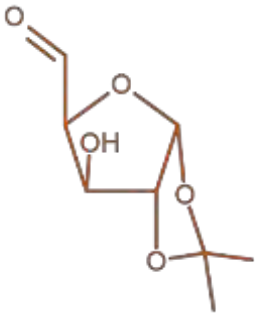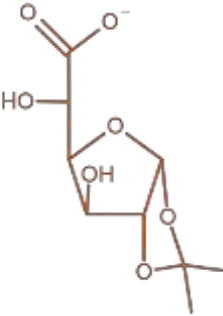□ 6M HCl in water   □ 1M NaOH in water
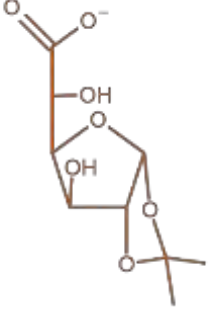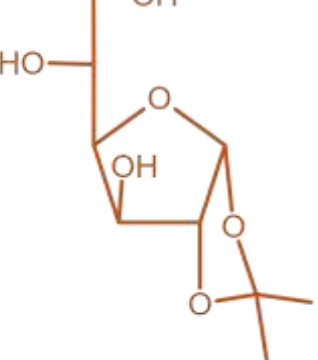□ 6M HCl in acetic acid

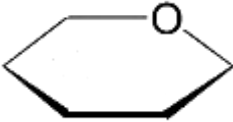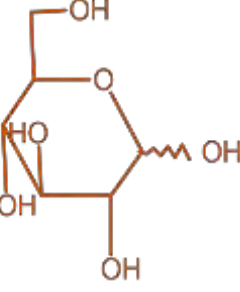**8.1.4.** Which is the stereochemically correct structure for compound **B**?

Neither of these

□   (x) □   □
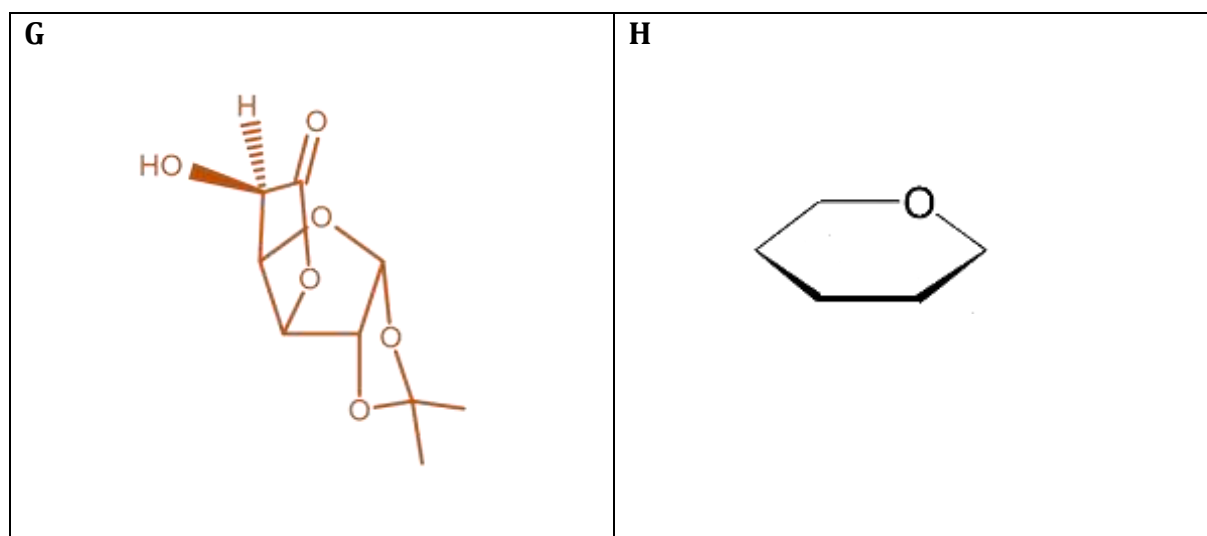
8.2.1. <u>Draw</u> the structures of **C**, **D**$_1$, **D**$_2$, **E** and **F** including stereochemical information. <u>Show</u> **F** as the more stable 6-membered ring containing isomer using the ring skeleton. <u>Indicate</u> with a wavy line if absolute chirality around a carbon is not known.

C	D$_1$

D$_2$	E

F	
	2p for each correct structure 1p for structures with one minor error (e.g. wrong configuration) 0p for more minor mistakes or a more serious one (COOH->COH, unidentifiable chiral center) 1-1p if D$_1$ and D$_2$ swapped 2p if –COOH in D

8.2.2. The reaction sequence from glucose to **F** does not seem to be useful. In some cases, however, this is the most economical way to produce **F**. <u>In which case</u>?

(x)☐ ^{13}C labelling at carbon 6 of **F**
☐ ^{13}C labelling at carbon 5 of **F**
☐ ^{13}C labelling at carbon 1 of **F**
☐ ^{15}O labelling at glycosidic OH of **F**
☐ synthesis of an uncommon isomer of **F**

8.3.1. Draw the structure of **G** including stereochemistry.
Draw **H** as the more stable 6-membered ring containing isomer using the ring skeleton. Indicate with a wavy line if absolute chirality around a carbon is not known.

G	H

8.3.2. How are the rings of **G** fused together?

(x)☐ both junctions cis
☐ one cis and one trans junction
☐ both junctions trans
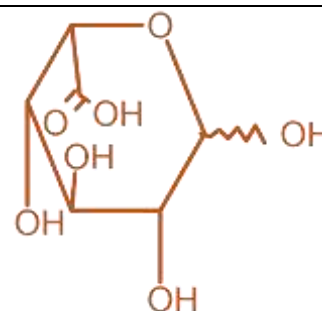
8.3.3. Which of the following is true for **H**? (You can choose more than one option.)

(x)☐ **H** is a reducing sugar (reacts with Fehling's reagent)
☐ **H** is an aldaric acid (dicarboxylic derivative of an aldose)
☐ **H** is an aldonic acid (C1 is a carboxyl group)
(x)☐ **H** is a uronic acid (C5 or C6 is a carboxyl group)
☐ **H** is a ketose
☐ **H** is a lactone
☐ **H** is a D sugar
☐ **H** is achiral
☐ **H** is a meso compound

> 2p, 1p with only one mistake (extra or missing letter), 0p with 2 or more mistakes

References

This appears only in the published version, it is not printed for the students.

Problem 1

Christe, Karl O., and William W. Wilson. 1982. "Perfluoroammonium and Alkali-Metal Salts of the heptafluoroxenon(VI) and octafluoroxenon(VI) Anions." *Inorganic Chemistry* 21 (12): 4113–17. doi:10.1021/ic00142a001.

Problem 2

Figure is from:

Gan, J., V. Venkatachalapathy, B.G. Svensson, and E.V. Monakhov. 2015. "Influence of Target Power on Properties of Cu_xO Thin Films Prepared by Reactive Radio Frequency Magnetron Sputtering." *Thin Solid Films* 594 (November): 250–55. doi:10.1016/j.tsf.2015.05.029.

Problem 4

Figures are adapted from:

Kamal, Oussama, Abderazzak Benlyamani, Farid Serdaoui, Mohammed Riri, Abdelmjid Cherif, and Miloudi Hlaïbi. 2012. "Stability Studies of Lysine Acetylsalicylate (Aspirin Derivative): Mechanisms of Hydrolysis." *Open Journal of Physical Chemistry* 2 (2): 81–87. doi:10.4236/ojpc.2012.22011.

Marrs, Peter S. 2004. "Class Projects in Physical Organic Chemistry: The Hydrolysis of Aspirin." *Journal of Chemical Education* 81 (6): 870. doi:10.1021/ed081p870.

Problem 6

Küenburg, Bernhard, Laszlo Czollner, Johannes Fröhlich, and Ulrich Jordis. 1999. "Development of a Pilot Scale Process for the Anti-Alzheimer Drug (−)-Galanthamine Using Large-Scale Phenolic Oxidative Coupling and Crystallisation-Induced Chiral Conversion." *Organic Process Research & Development* 3 (6): 425–31. doi:10.1021/op990019q.

Trost, Barry M., Weiping Tang, and F. Dean Toste. 2005. "Divergent Enantioselective Synthesis of (-)-Galanthamine and (-)-Morphine." *Journal of the American Chemical Society* 127 (42): 14785–803. doi:10.1021/ja054449+.

Problem 8

Shafizadeh, F., and M. L. Wolfrom. 1955. "Synthesis1 of L-Iduronic Acid and an Improved Production of L -Glucose-6-C14." *Journal of the American Chemical Society* 77 (9): 2568–69. doi:10.1021/ja01614a072.