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:	$G = H - TS$
$\Delta_r G^o = -RT \ln K = -nFE^o_{cell}$		Ionic product of water at 298.15K :	$K_w = 10^{-14}$
Nernst equation:	$E = E^o + \dfrac{RT}{nF} \ln \dfrac{c_{ox}}{c_{red}} = E^o + \dfrac{0.059\ \text{V}}{n} \log \dfrac{c_{ox}}{c_{red}}$ 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.
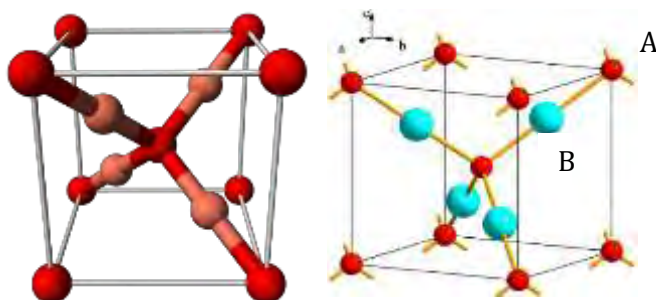
The two figures above depict the cubic unit cell of the Cu_2O crystal. The lattice constant of the structure is 427.0 pm.

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 Δ_fH^o and S^o data given for 10^5 Pa are independent of temperature:

	Δ_fH^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$_2$O(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:

$K_{sp}(Cu(OH)_2)=2·10^{-19}$
$Cu_2O(s) + H_2O(l) + 2e^- \longrightarrow 2Cu(s) + 2OH^-(aq)$ $\qquad E^o= -0.360$ V
$Cu^{2+}(aq) + e^- \longrightarrow Cu^+(aq)$ $\qquad E^o= +0.159$ V
$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$ $\qquad E^o= +0.337$ V
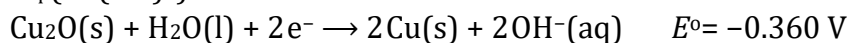
One possibility for producing Cu_2O is the anodic oxidation of copper. Electrolysis of an aqueous basic solution (e.g. NaOH) with a copper anode and platinum cathode can lead to formation of copper(I) oxide on the anode.

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 cm^3 of 1.0 mol/dm^3 aqueous HCl to which 1.0 g KI has been added. The solution is then titrated with 0.00235 mol/dm^3 aqueous sodium thiosulfate solution to a starch endpoint; this requires 7.50 cm^3 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/dm^3 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 dm^3 (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).

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

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

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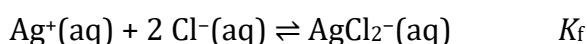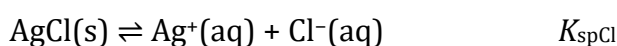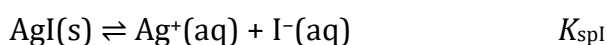
Below are shown the results of two experiments measuring the observed potential as a function of added number of moles of silver ion. Experiment **A** (solid circles) was carried out with 1.000 dm³ of solution containing $1.00 \cdot 10^{-5}$ mol/dm³ iodide and no chloride ion. Experiment **B** (open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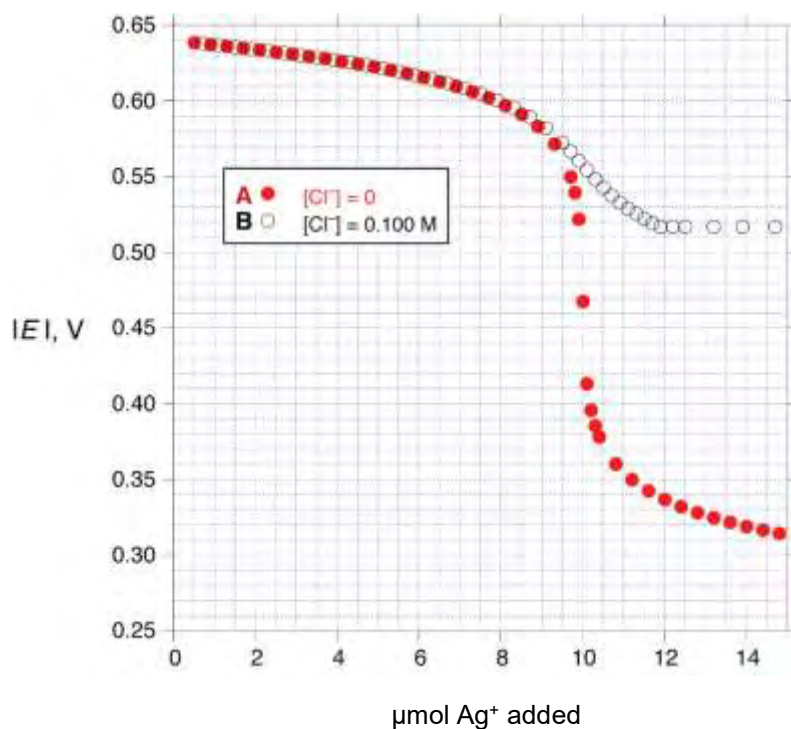
μmol Ag⁺ added	$\|E\|$, V exp. **A**	$\|E\|$, V exp. **B**
1.00	0.637	0.637
3.00	0.631	0.631
5.00	0.622	0.622
7.00	0.609	0.610
9.00	0.581	0.584
10.0	0.468	0.558
11.0	0.355	0.531
12.0	0.337	0.517
13.0	0.327	0.517
15.0	0.313	0.517

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. <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.

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:
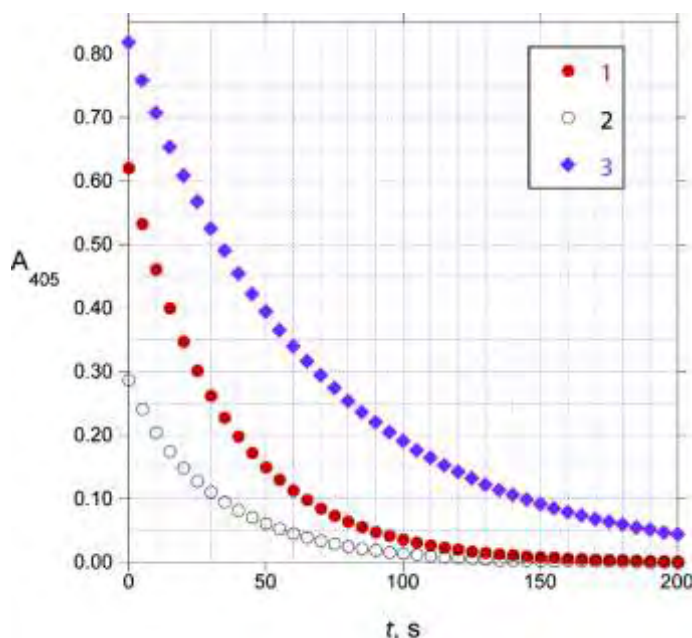
t, s	A_{405} Run **1**	A_{405} Run **2**	A_{405} Run **3**
0	0.621	0.287	0.818
20	0.348	0.149	0.608
40	0.198	0.083	0.455
60	0.113	0.046	0.340
80	0.064	0.025	0.254
100	0.037	0.014	0.191

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. <u>Determine</u> the values of m, n, and p and <u>calculate</u> the value of k (be sure to <u>specify</u> 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:
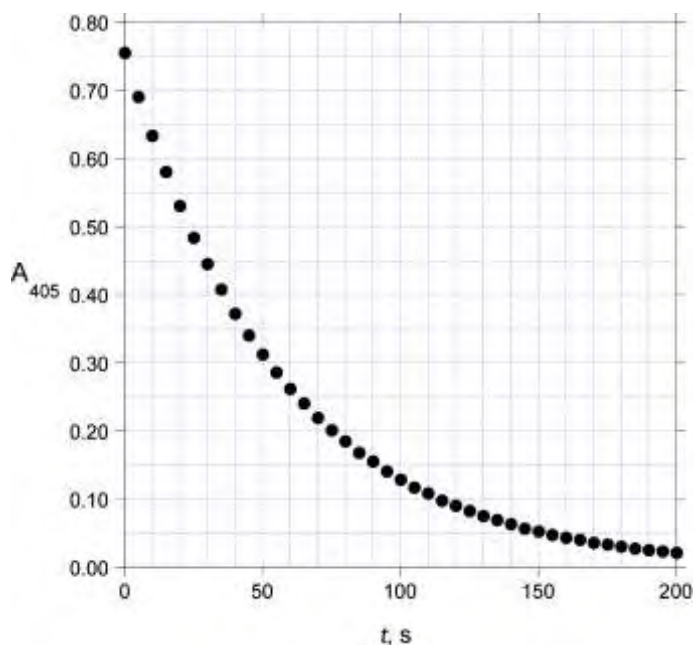
t, s	A_{405}
0	0.756
20	0.531
40	0.373
60	0.262
80	0.185
100	0.129

3.3.3. Calculate 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. 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 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:
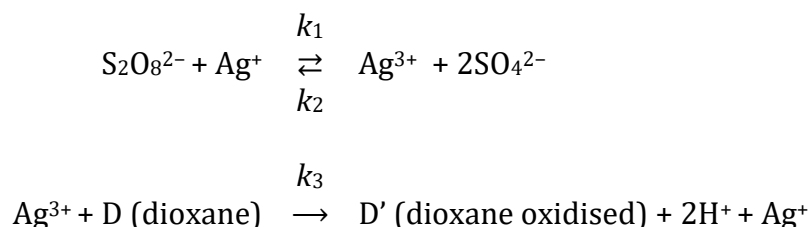
$$S_2O_8^{2-} + Ag^+ \underset{k_2}{\overset{k_1}{\rightleftarrows}} Ag^{3+} + 2SO_4^{2-}$$

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

4.1.2. Assuming Ag(III) to be in steady state, deduce 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.
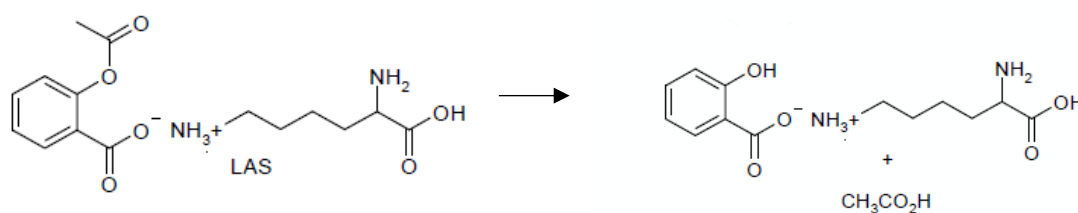
Hydrolysis of LAS can proceed via three different pathways (a) acid catalysed, (b) uncatalysed and (c) base catalysed.

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

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

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:

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

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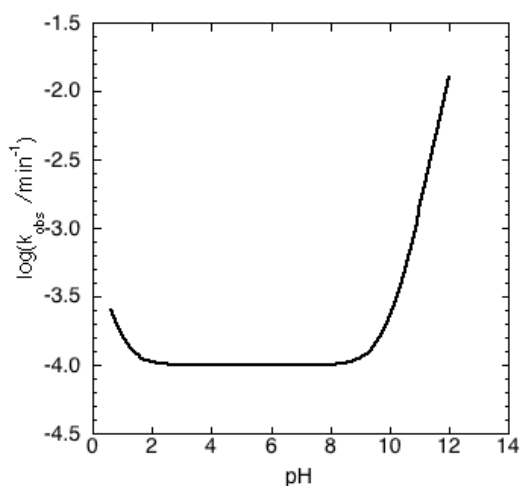
4.2.2. Which of the following is/are correct?
A) $k_{obs} \cong k_0$ at pH = 12
B) $k_{obs} \cong k_0$ at pH = 5.0
C) The rate of the reaction increases when the pH is changed from 0.50 to 1.0.
D) The rate of the reaction increases when the pH is changed from 10 to 12.

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:
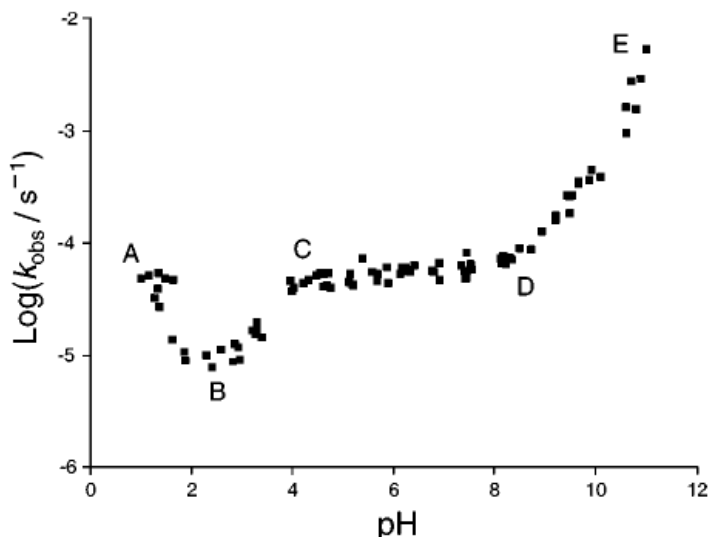
The following are possible reactions for the hydrolysis of aspirin. Depending on the pH, one or more of these reactions will predominate.

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 $dm^3 \cdot mol^{-1} \cdot day^{-1}$	$2.29 \cdot 10^{-4}$ day^{-1}	$3.18 \cdot 10^9$ $dm^3 \cdot mol^{-1} \cdot day^{-1}$

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

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 $1.013\cdot10^5$ 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 $1.013\cdot10^5$ 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. <u>Determine</u> the formula of mineral **C**.

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

5.1.6. <u>Determine</u> 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. <u>Suggest</u> a formula for the mineral used in place of **C**.

5.2.2. <u>Could</u> 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. <u>Write down</u> 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.
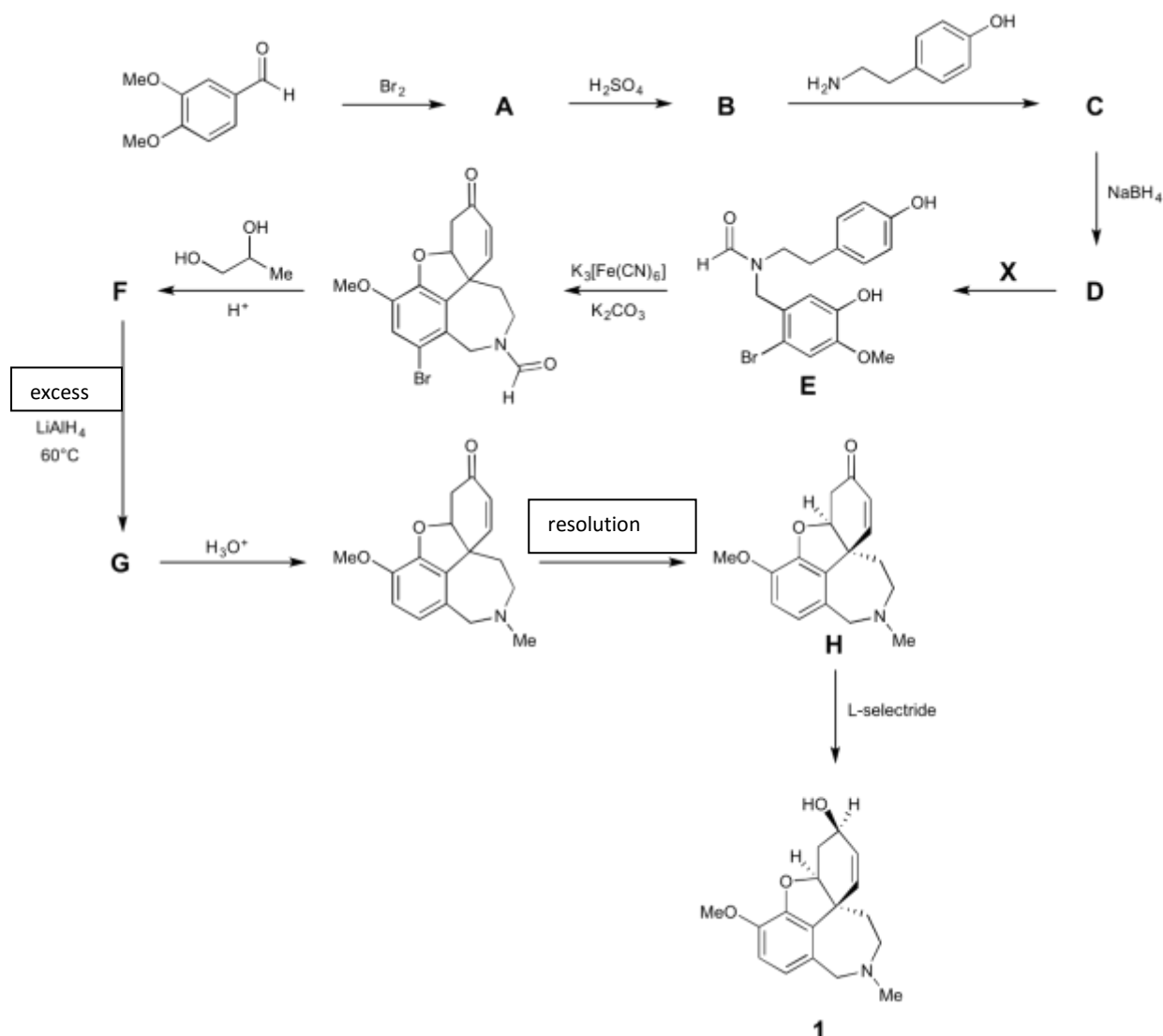
Notes about the synthesis:

- ^{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. <u>Suggest</u> 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° cm² g⁻¹, while that of the enantiomerically pure compound is −415° cm² 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.
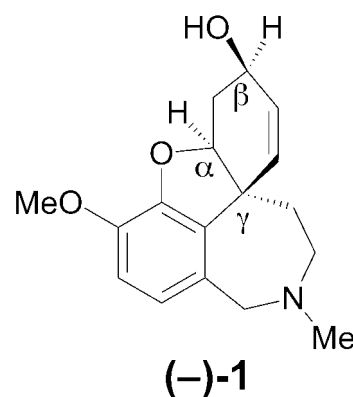
An alternative route to galantamine occurs with the seven-membered ring being the last ring to form.

(−)-1
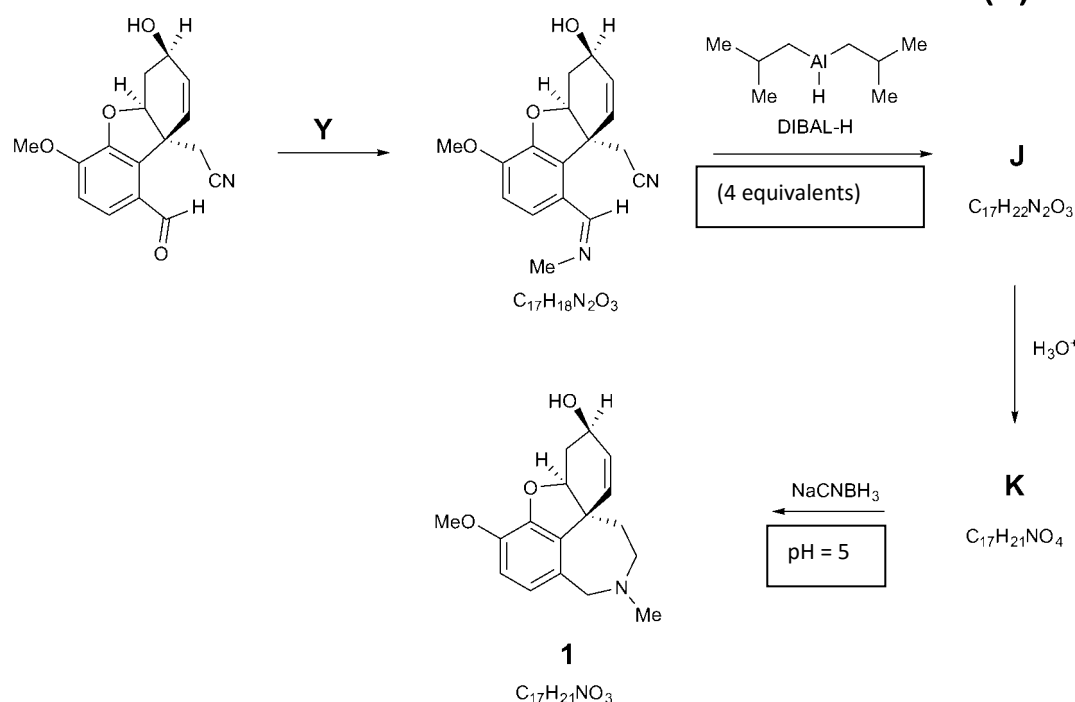
6.3.1. <u>Give</u> the formula for compound **Y** to carry out the first step of the route.

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.


Z
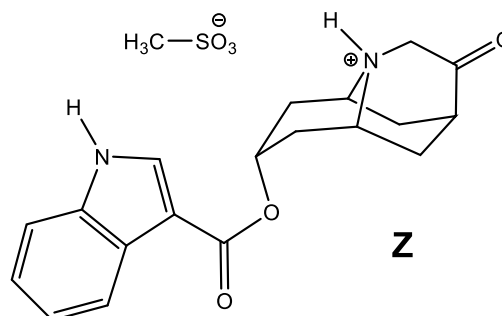
The synthesis begins as shown below.
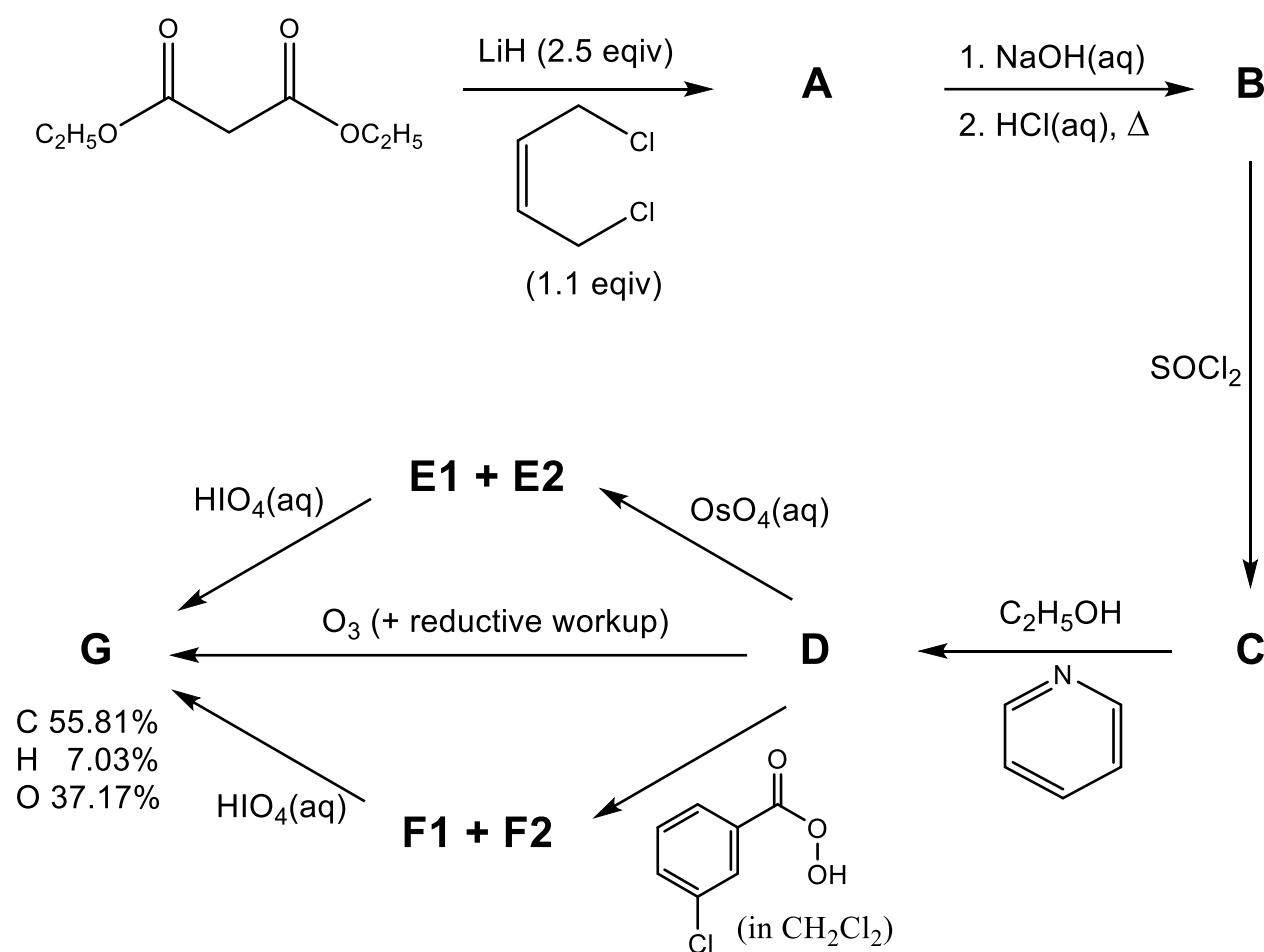
First cyclic compound **A** is made, which contains C, H, and O only. Compound **G** is achiral and can be prepared directly from **D** using ozone under reductive conditions, or via stereoisomers **E1** and **E2** using OsO_4, or via stereoisomers **F1** and **F2** using the peracid shown.

7.1. Determine the empirical formula of **G** from the percentage masses given.

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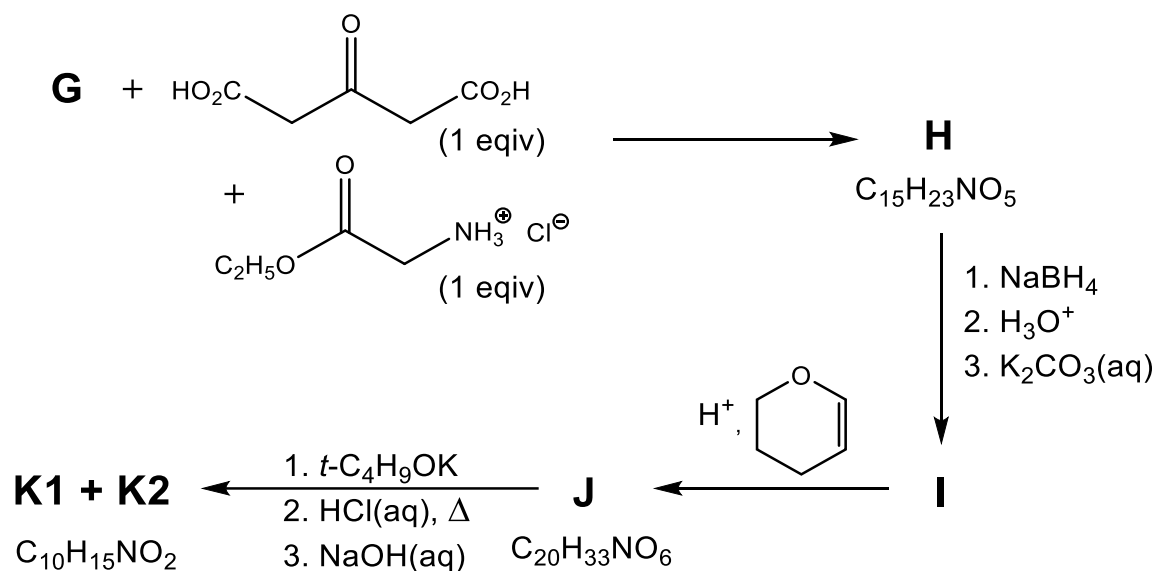
7.3.1. <u>Give</u> the structures of **H**, **I**, and **J**. There is no need to show the different diastereoisomers formed.

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.
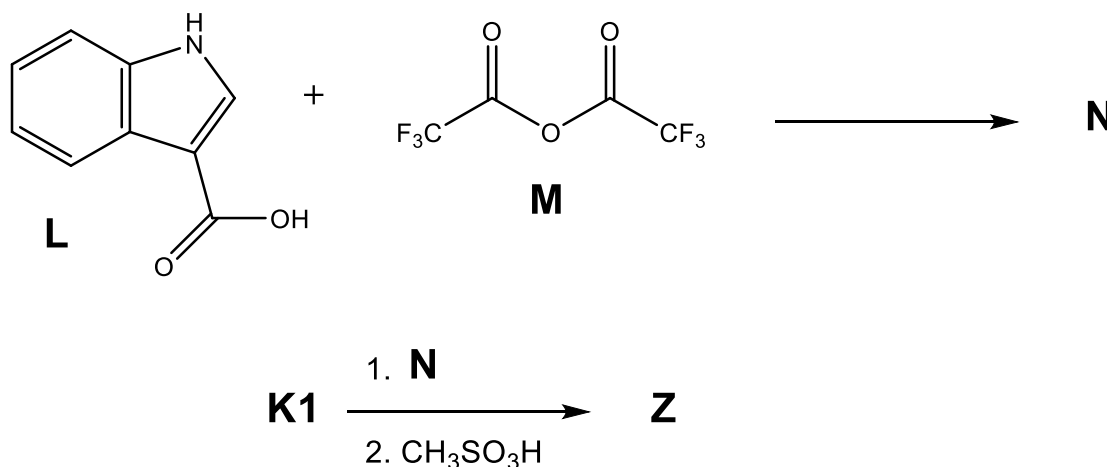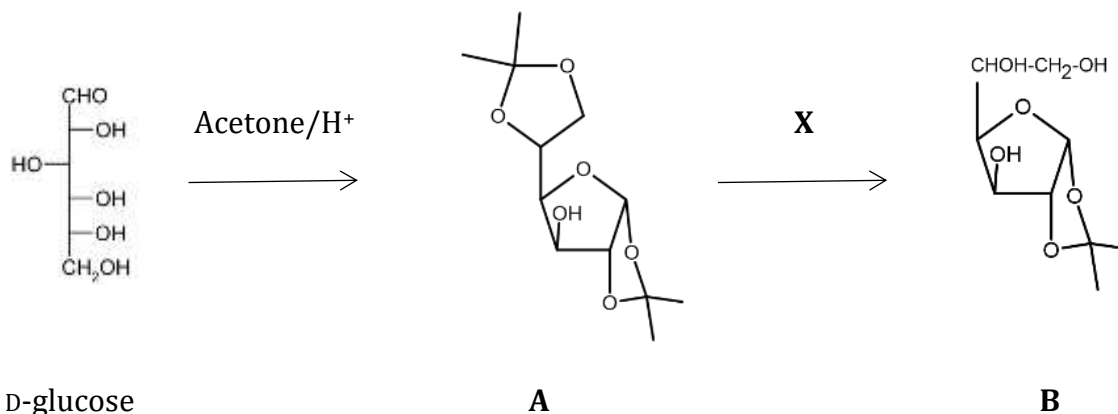

7.4. <u>Give</u> the structure of **N**.

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.

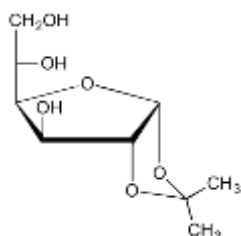**8.1.3.** Which one of these reagents can be utilized as **X** for the selective hydrolysis of **A**?

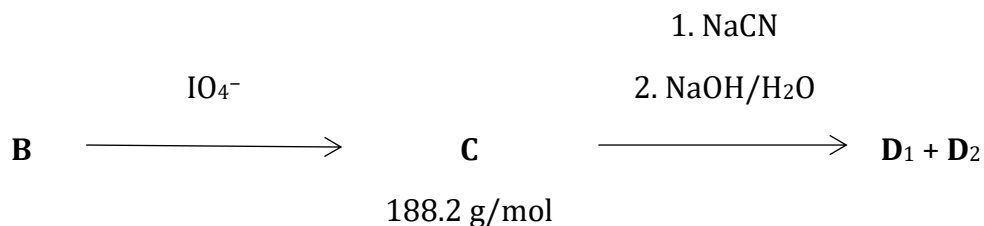|	
50% acetic acid	concentrated H_2SO_4
6 M HCl in water	1 M NaOH in water
6 M HCl in acetic acid	

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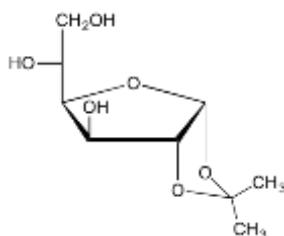

Neither of these

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.

$$\mathbf{B} \xrightarrow{\quad IO_4^- \quad} \underset{188.2 \text{ g/mol}}{\mathbf{C}} \xrightarrow[\quad 2.\ NaOH/H_2O \quad]{\quad 1.\ NaCN \quad} \mathbf{D_1 + D_2}$$

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.
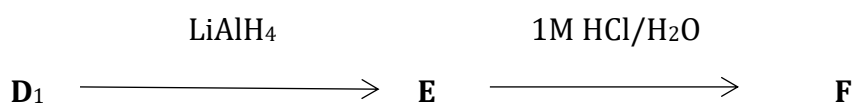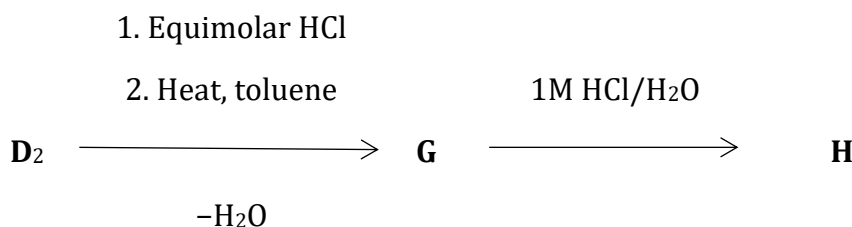
$$\mathbf{D_1} \xrightarrow{\quad LiAlH_4 \quad} \mathbf{E} \xrightarrow{\quad 1M\ HCl/H_2O \quad} \mathbf{F}$$

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}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**

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.

$$\mathbf{D_2} \xrightarrow[-H_2O]{\substack{1.\ \text{Equimolar HCl} \\ 2.\ \text{Heat, toluene}}} \mathbf{G} \xrightarrow{\quad 1M\ HCl/H_2O \quad} \mathbf{H}$$

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. Write 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)

Write 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. Determine 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 $(NF_4)_x\mathbf{A}F_y$ composition, $x{:}y = 1{:}4$.
>
> $$\frac{8xM(\mathrm{F})}{8xM(\mathrm{F})+xM(\mathrm{N})+M(\mathbf{A})} = 0.656 \Rightarrow \frac{M(\mathbf{A})}{x} = 65.7 \text{ g/mol}$$
>
> 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 $(NF_4)_2XeF_8$
>
> 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. Which of the atoms (A or B) is copper?

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

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

	pr. cubic	fcc	bcc	diamond
A				
B				

B: fcc   A: bcc

What are the coordination numbers of the atoms?

A: B:	B: 2 A: 4

2.1.2. Calculate the smallest O-O, Cu-O and Cu-Cu distances in the structure.

Your work:

O-O:

Cu-O:

Cu-Cu:

> O-O: half of the cell body diagonal $1/2 \cdot 427.0$ pm$\cdot\sqrt{3} = 369.8$ pm.
>
> Cu-O: $1/4^{th}$ 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.

2.1.3. What 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 $(4M_{Cu} + 2 M_O)/ N_A$. 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:

> $\Delta_f G(CuO) = -156000\ J\ mol^{-1} + 84\ J\ mol^{-1}\ K^{-1}\ T$
> $\Delta_f G(Cu_2O) = -170000\ J\ mol^{-1} + 72\ J\ mol^{-1}\ K^{-1}\ T$
>
> 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: $2\ CuO = Cu_2O + 0.5\ O_2$
> $\Delta_r G = 142000\ J\ mol^{-1} - 96\ J\ mol^{-1}\ K^{-1}\ T$
> The Gibbs energy of the reaction is negative above 1480 K.
> CuO is stable below 1480 K, Cu_2O 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. <u>Write</u> 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

C: 2 H$_2$O + 2 e$^-$ → H$_2$ + 2 OH$^-$

A: 2 Cu + 2 OH$^-$ → Cu$_2$O + H$_2$O + 2e$^-$

Anode:

2p

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

2 Cu^{2+} + H$_2$O + 2 e$^-$ → Cu$_2$O + 2 H$^+$

1p

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}?

Your work:

If the pH is too high, Cu(OH)$_2$ precipitates.

K$_{sp}$ ≥ 0.1[OH$^-$]^2 ⇒ pH ≤ 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 + 2·0.337 V – (RT/F) ·$\ln K_w$ = 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.
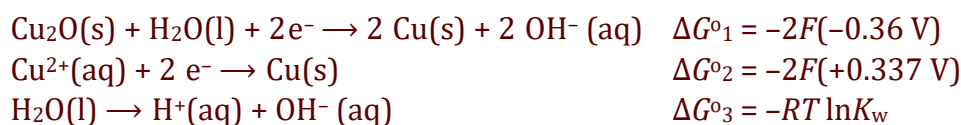
minimum pH:

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

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

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

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

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

Your work:

> (0.00750 dm^3 titrant)·(0.00235 mol dm^{-3} $S_2O_3^{2-}$) = 1.76·10^{-5} mol $S_2O_3^{2-}$
>
> (1.76·10^{-5} mol $S_2O_3^{2-}$)·(1 mol IO_3^-/6 mol $S_2O_3^{2-}$) = 2.94·10^{-6} mol IO_3^-
>
> (2.94·10^{-6} mol IO_3^-)·(126.90 g/mol) = 3.73·10^{-4} g iodine
>
> {(3.73·10^{-4} g iodine)/(10.00 g salt)} ·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
>
> $[I^-] = [I^-]_0 - 5.0\cdot10^{-6}$ mol/dm^3 = $5.0\cdot10^{-6}$ mol/dm^3
>
> $|E| = 0.622$ V = $-0.0591\cdot\log[Ag^+] \Rightarrow [Ag^+] = 3.2\cdot10^{-11}$ mol/dm^3
>
> $K_{spI} = [Ag^+][I^-] = 1.6\cdot10^{-16}$
>
> 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^+) ≥ 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 = $-0.0591\cdot\log[Ag^+] \Rightarrow [Ag^+] = 1.6\cdot10^{-9}$ mol/dm^3
>
> $K_{spCl} = [Ag^+][Cl^-] = 1.6\cdot10^{-10}$
>
> 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/dm^3, $[Cl^-] = 0.100$ mol/dm^3 (see above).
> Almost all of the originally present $1.0 \cdot 10^{-5}$ mol/dm^3 iodide has been precipitated out as 9.9 μmol AgI, since $[I^-] = K_{spI}/[Ag^+] = 1.0 \cdot 10^{-7}$ mol/dm^3
>
> Total Ag in solution = 11.8 μmol – 9.9 μmol = 1.9 μmol
>
> $[AgCl_2^-] = 1.9 \cdot 10^{-6}$ mol/dm^3 (since free $[Ag^+]$ is only $1.6 \cdot 10^{-9}$ mol/dm^3)
>
> $$K_f = \frac{[AgCl_2^-]}{[Ag^+][Cl^-]^2} = \frac{1.9 \cdot 10^{-6}}{1.6 \cdot 10^{-9} \cdot 0.100^2} = 1.2 \cdot 10^5 \quad [1.9 \cdot 10^4 \text{ given const.}]$$
>
> 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/dm^3
>
> Since AgI(s) is present, $[I^-] = K_{spI}/[Ag^+] = 4.42 \cdot 10^{-7}$ mol/dm^3
>
> The amount of dissolved iodine and silver is equivalent:
>
> $[I^-] = [Ag^+] + [AgCl_2^-] \Rightarrow [AgCl_2^-] = 4.42 \cdot 10^{-7}$ mol/dm^3
>
> $$K_f = \frac{[AgCl_2^-]}{[Ag^+][Cl^-]^2} = \frac{4.42 \cdot 10^{-7}}{3.62 \cdot 10^{-10} \cdot 0.100^2} = 1.2 \cdot 10^5 \quad [7.6 \cdot 10^5 \text{ given const.}]$$

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· 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·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 [H₃AsO₃] 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 $2.04\cdot10^4$ dm³ mol^{-1} s^{-1} for runs **1-3**; average $k = 2.07\cdot10^4$ dm³ 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} = $k[I^-]$ = $(2.07\cdot10^4$ dm³ mol^{-1} s$^{-1})[I^-]$

$[I^-] = 8.55\cdot10^{-7}$ mol/dm³

Since the salt solution was diluted by a factor of (2.05 cm³)/(0.050 cm³) = 41, the concentration in the original salt solution was $41\cdot(8.55\cdot10^{-7}$ mol/dm³) = $3.51\cdot10^{-5}$ mol/dm³.

$(3.51\cdot10^{-5}$ mol dm$^{-3})(0.01000$ dm³) = $3.51\cdot10^{-7}$ 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. <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 $5.0\cdot10^{-6}$ 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 $k = 6.65\cdot10^{-3}$ 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
>
> $4.55 = 5.00 \exp(-6.65\cdot10^{-3}\ t)$
>
> $t = 14.2$ 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, <u>deduce</u> the rate equation for the oxidation of dioxane.

Your work:

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

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

$$rate\ of\ oxidation = \frac{k_1k_3[S_2O_8^{-2}][D][Ag^+]}{k_2[SO_4^{-2}]^2 + k_3[D]}$$

3p (1p for each step)

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

4.2.1. <u>Write</u> 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, <u>calculate</u> k_H, k_0 and k_{OH}. Make sure to specify the units.

Your work:

At pH = 5.30, k_0 is dominant
$\log(k_{obs}/min^{-1}) = -4.000 \Rightarrow k_{obs} = k_0 = 1.00\cdot10^{-4}\ min^{-1}$

At pH = 12.18, $[OH^-] = 0.01514\ mol\ dm^{-3}$
$\log(k_{obs}/min^{-1}) = -1.726 \Rightarrow k_{obs} = 1.88\cdot10^{-2}\ min^{-1}$
$k_{obs} = k_0 + k_{OH}[OH^-]$ $\qquad$ k_0 can be neglected

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

At pH = 1.30, $[H^+] = 0.0501\ mol\ dm^{-3}$
$\log(k_{obs}/min^{-1}) = -3.886 \Rightarrow k_{obs} = 1.30\cdot10^{-4}\ min^{-1}$
$k_{obs} = k_H[H^+] + k_0$ $\qquad$ k_0 cannot be neglected

$$k_H = \frac{k_{obs} - k_0}{[H^+]} = \frac{3.0\cdot10^{-5} min^{-1}}{0.0501 mol\cdot dm^{-3}}$$

$k_H = 6.0\cdot10^{-4}\ dm^3\cdot mol^{-1}\cdot min^{-1}$

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, calculate 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 = 6.75−0.045·18 = 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 $2CaO \cdot 8SiO_2 \cdot n Me_x O_y$. Oxide $Me_x O_y$ forms from mineral **A**. Let us find the molar mass of $n Me_x O_y$:
>
> $$M(\text{pigment}) = M(2CaO \cdot 8SiO_2) + M(n Me_x O_y)$$
>
> $$M(\text{pigment}) = 2M(CaCO_3)\frac{m(\text{pigment})}{m(CaCO_3)}$$
>
> $$M(n Me_x O_y) = 2M(CaCO_3)\frac{34.0\ \text{g}}{9.05\ \text{g}} - M(2CaO \cdot 8SiO_2) \approx 159\ \text{g/mol}$$
>
> 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
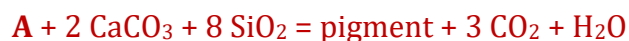
Egyptian blue is: Chinese blue is:

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. Suggest 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. Could 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. Write down 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
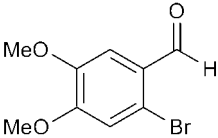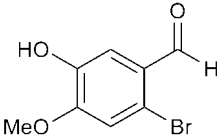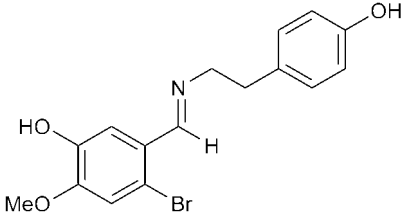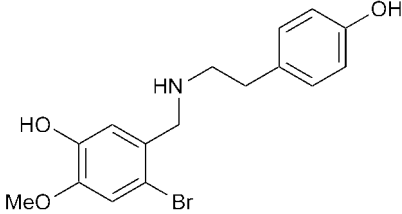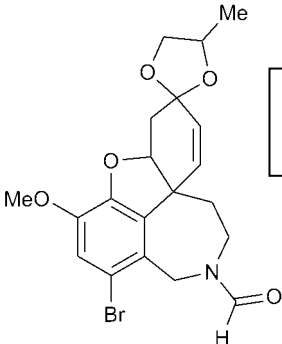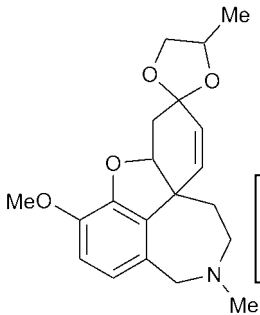
Problem 6 $\quad$ 7% of the total

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. <u>Suggest</u> 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	**B**
0p if lacks 2 para protons	
C	**D**
F	**G**
2p penalty if Br removed	2p penalty if Br present

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

X
CH_3CH_2OCOH 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.
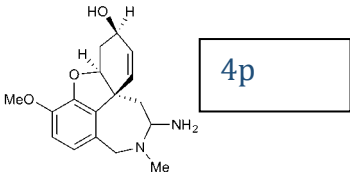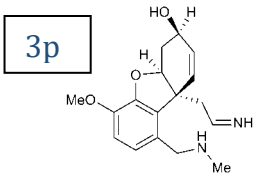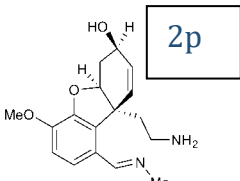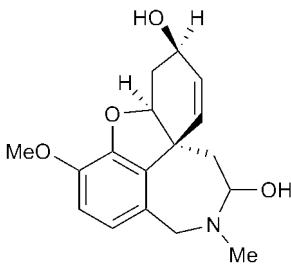
> $NaBH_4$, $LiAlH_4$, etc. 2p

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
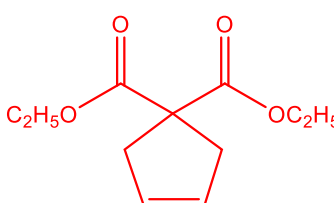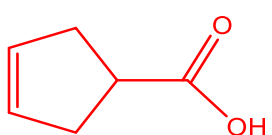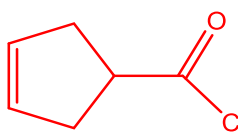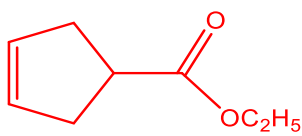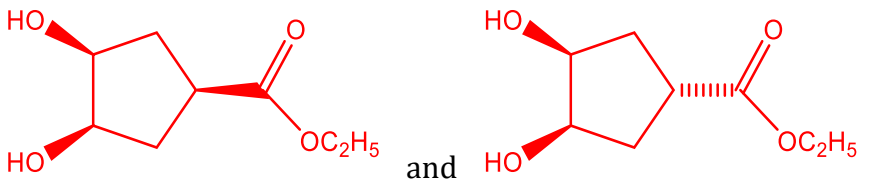
7.1.   Determine the empirical formula of **G** from the percentage masses given.

Your work:

C₂H₃O

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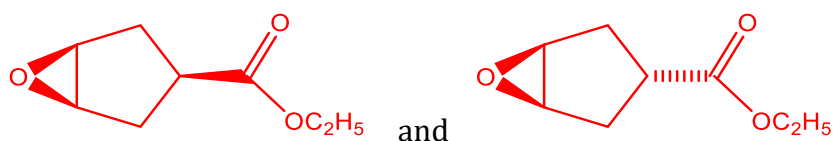
4p each
(1p if no de-carboxylation; 1p for trans-diol; 0p if no de-carboxylation and diol)

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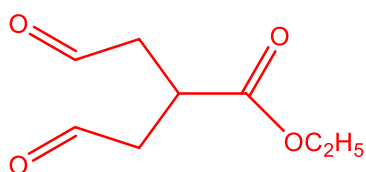
4p
(0p if does not fit formula)

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

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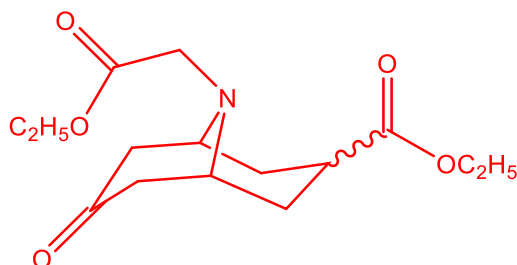
8p
(points for fitting formula, sensible chemistry, correct number of possible diastereomers, and being achiral)

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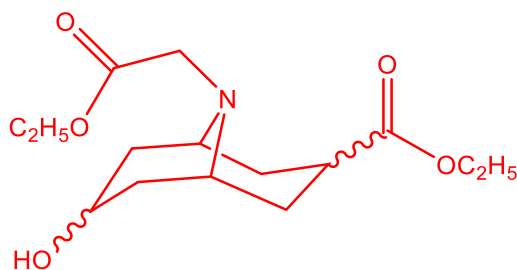
4p
(points for reduction of ketone, sensible chemistry, correct number of possible diastereomers, and being achiral)

J
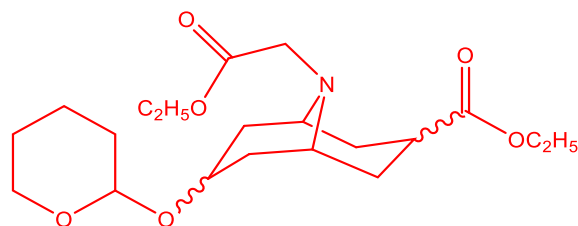
4p
(points for fitting formula, sensible chemistry, forming acetal, sensible number of possible diastereomers)

7.3.2 <u>Give</u> the structures of diastereoisomers **K1**, and **K2**.

K1
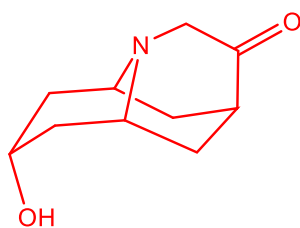
4p (2p if answer is **K2**)
(answer must fit formula and be sensible)

K2
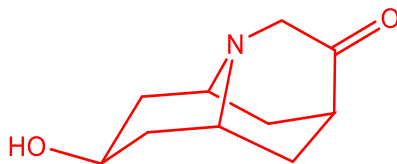
4 pt (2pt if answer is **K1**)
(answer must fit formula and be sensible)

7.4. <u>Give</u> the structure of **N**.

N
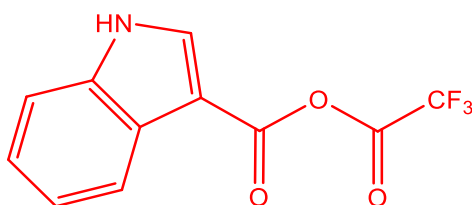
4p
(full marks for anhydride of **L**)

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
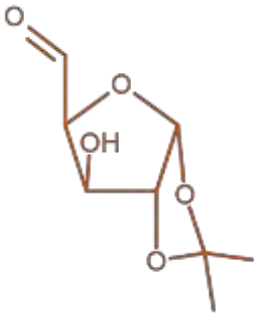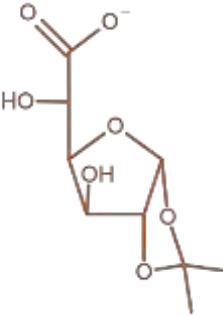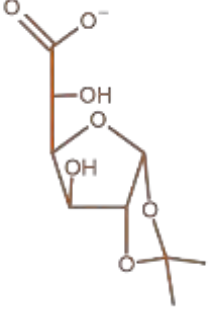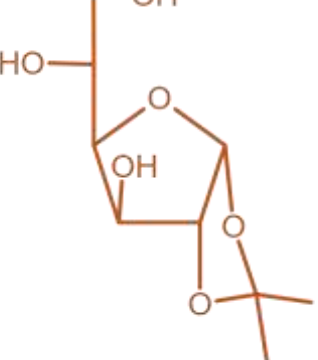☐ 6M HCl in acetic acid

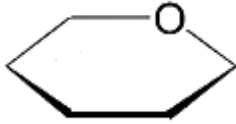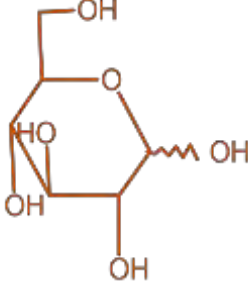**8.1.4.** Which is the stereochemically correct structure for compound **B**?

Neither of these

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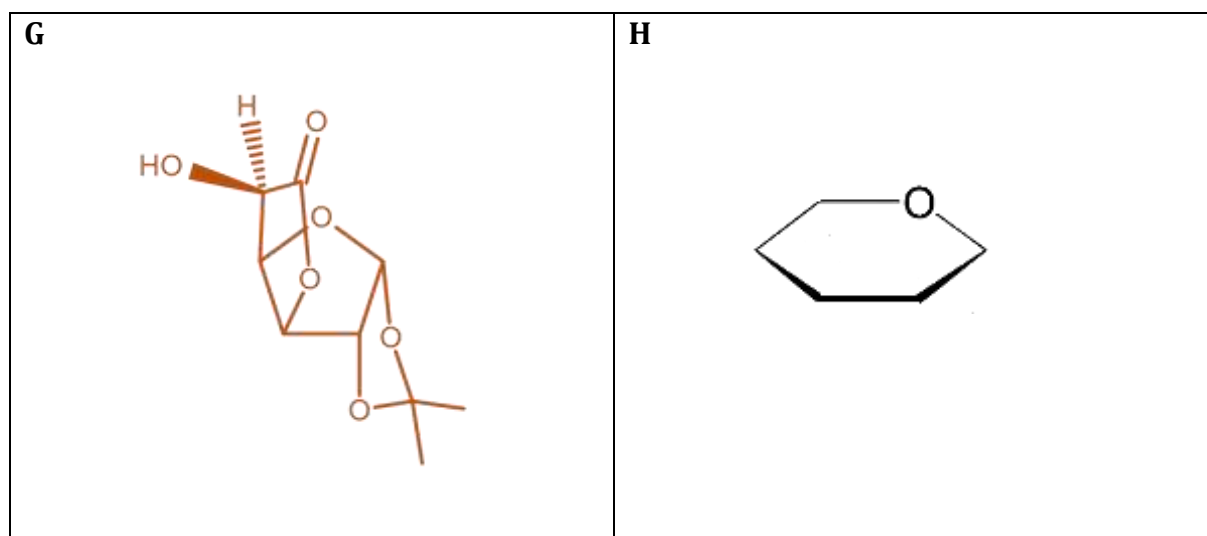
8.2.1. <u>Draw</u> the structures of **C**, **D**$_1$, **D**$_2$, **E** and **F** including stereochemical information.
<u>Show</u> **F** as the more stable 6-membered ring containing isomer using the ring
skeleton. <u>Indicate</u> with a wavy line if absolute chirality around a carbon is not
known.

C	D₁

D₂	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 D₁ and D₂ 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
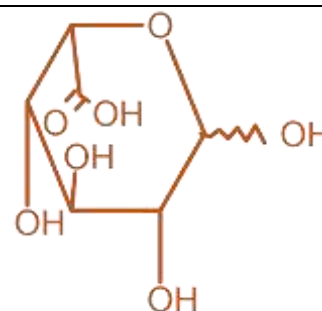
8.3.3. Which of the following is true for **H**? (You can choose more than one option.)

(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 ʟ-Iduronic Acid and an Improved Production of ʟ -Glucose-6-C14." *Journal of the American Chemical Society* 77 (9): 2568–69. doi:10.1021/ja01614a072.