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.
Consider all gases ideal throughout the exam.

### Constants and formulae

<table>
<thead>
<tr>
<th>Constants and formulae</th>
</tr>
</thead>
<tbody>
<tr>
<td>Avogadro constant: $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$</td>
</tr>
<tr>
<td>Zero of the Celsius scale: $273.15 \text{ K}$</td>
</tr>
<tr>
<td>Gas constant: $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$</td>
</tr>
<tr>
<td>Faraday constant: $F = 96485 \text{ C mol}^{-1}$</td>
</tr>
<tr>
<td>Ideal gas equation: $pV = nRT$</td>
</tr>
<tr>
<td>Gibbs energy: $G = H - TS$</td>
</tr>
<tr>
<td>Nernst equation: $E = E^o + \frac{RT}{nF} \ln \frac{c_{ox}}{c_{red}} = E^o + \frac{0.059 V}{n} \log \frac{c_{ox}}{c_{red}}$</td>
</tr>
<tr>
<td>or $E = E^o - \frac{RT}{nF} \ln Q = E^o - \frac{0.059 V}{n} \log Q$</td>
</tr>
<tr>
<td>Beer-Lambert law: $A = \log \frac{I_0}{I} = \varepsilon cl$</td>
</tr>
</tbody>
</table>

### Periodic table with relative atomic masses

<table>
<thead>
<tr>
<th>1</th>
<th>2</th>
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<th>4</th>
<th>5</th>
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<tbody>
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<tr>
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<td>36 Kr</td>
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<td>37 Rb</td>
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<td>38 Sr</td>
<td>87.620</td>
<td>39 Y</td>
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<td>229.000</td>
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<td>231.000</td>
<td>92 U</td>
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<td>95 Am</td>
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<td>97 Bk</td>
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<td>102 No</td>
<td>259.000</td>
<td>103 Lr</td>
<td>262.000</td>
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48th IChO Theoretical Problems, Official English version 3
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. On which electrode does nitrogen trifluoride form? Write a balanced chemical equation for the electrode half reaction for the formation of NF₃.

Interestingly the related fluoroamine (NH₂F) and difluoroamine (NHF₂) 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. Which of NF₃, NHF₂ or NH₂F compound is 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. Assign the N-F bond lengths (136, 140, 142 pm) to the molecules.

When NHF₂ 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. Write a balanced chemical equation for the formation of the binary nitrogen-fluorine compound.

Tetrafluoroammonium ion (NF₄⁺) and its corresponding salt can form from NF₃ with elementary fluorine in the presence of an appropriate reagent.

1.5. Propose a suitable reagent and write a balanced chemical equation for the reaction.

NF₄⁺ ions form stable salts with a number of anions. These are very sensitive to humidity, because NF₄⁺ ion hydrolyzes forming NF₃ and O₂. Interestingly nitrogen trifluoride always forms quantitatively, while the quantity of oxygen is often less than expected due to side reactions.

1.6. Write a balanced chemical equation for the hydrolysis of NF₄⁺. Write a balanced chemical equation for a possible side reaction that can decrease the theoretically expected O₂:NF₃ mole ratio.

Tetrafluoroammonium salts were investigated for use as solid rocket fuels, because NF₃ and F₂ are released from them on heating. One of them has a fluorine content of 65.6 m/m%, all of which is converted into NF₃ and F₂ upon decomposition. During the decomposition 2.5 times as many moles of F₂ are formed as of NF₃.

1.7. Determine 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 Cu₂O crystal. The lattice constant of the structure is 427.0 pm.

2.1.1. Which of the atoms (A or B) is copper? 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? What are the coordination numbers of the atoms?

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

2.1.3. What 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. What percentage of normal copper sites are empty in the crystal sample? What is x in the empirical formula Cu₂₋ₓO 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. Write 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 Cu₂O. In a pure oxygen atmosphere, the three species containing copper (Cu(s), Cu₂O(s) or CuO(s)) can potentially interconvert.

Suppose that the ΔfH° and S° data given for 10⁵ Pa are independent of temperature:

<table>
<thead>
<tr>
<th></th>
<th>ΔfH° / kJ mol⁻¹</th>
<th>S° / J mol⁻¹ K⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(s)</td>
<td>0</td>
<td>65</td>
</tr>
<tr>
<td>O₂(g)</td>
<td>0</td>
<td>244</td>
</tr>
<tr>
<td>CuO(s)</td>
<td>−156</td>
<td>103</td>
</tr>
<tr>
<td>Cu₂O(s)</td>
<td>−170</td>
<td>180</td>
</tr>
</tbody>
</table>

2.4. **Determine** the temperature ranges, if any, of thermodynamic stability of copper and its oxides between 500 and 1500 K in a 10⁵ Pa oxygen atmosphere.

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

\[
K_p(Cu(OH)_2) = 2 \cdot 10^{-19} \\
Cu₂O(s) + H₂O(l) + 2e⁻ → 2Cu(s) + 2OH⁻(aq) \quad E^o = -0.360 \text{ V} \\
Cu^{2+}(aq) + e⁻ → Cu⁺(aq) \quad E^o = +0.159 \text{ V} \\
Cu^{2+}(aq) + 2e⁻ → Cu(s) \quad E^o = +0.337 \text{ V}
\]

One possibility for producing Cu₂O 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. **Write** the half reaction equations for the electrode processes during the anodic production of Cu₂O in NaOH solution with a platinum cathode and copper anode.

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

2.6.1. **Write** the half reaction equation of the cathode process giving Cu₂O in acidic medium.

Let us use 0.100 mol dm⁻³ Cu²⁺ solution and carry out electrolysis with platinum electrodes.

2.6.2. **What** 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. **What** is the minimum pH at which the cathodic production of Cu₂O in a 0.100 mol dm⁻³ Cu²⁺ 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 (KIO₃). 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. Write a balanced net ionic equation for the reaction when iodate reacts with excess iodide in acidic solution.

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

3.1.3. Calculate 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 AgNO₃. 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) \([K_{spl}]\) and AgCl(s) \([K_{spCl}]\) and the formation of AgCl₂⁻(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).

\[
\begin{align*}
AgI(s) &\rightleftharpoons Ag^{+}(aq) + I^{-}(aq) & K_{spl} \\
AgCl(s) &\rightleftharpoons Ag^{+}(aq) + Cl^{-}(aq) & K_{spCl} \\
Ag^{+}(aq) + 2 Cl^{-}(aq) &\rightleftharpoons AgCl_2^{-}(aq) & K_f
\end{align*}
\]
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 dm$^3$ of solution containing $1.00\cdot10^{-5}$ mol/dm$^3$ iodide and no chloride ion. Experiment B (open circles) was done using 1.000 dm$^3$ of solution containing $1.00\cdot10^{-5}$ mol/dm$^3$ iodide and $1.00\cdot10^{-1}$ mol/dm$^3$ 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           |

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

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

3.2.3. Select an appropriate data point from the experiments and use it to calculate $K_f$. 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 $K_{spI} = 1.00\cdot10^{-15}$ and $K_{spCl} = 1.00\cdot10^{-9}$ 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 $\text{H}_3\text{AsO}_3$ with $\text{Ce(IV)}$ to give $\text{Ce(III)}$ 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 $\text{H}_3\text{AsO}_3$ in acidic solution, as well as reactions of cerium(IV) with a species containing the element iodine and $\text{H}_3\text{AsO}_3$ with a species containing the element iodine, that could reasonably account for the catalysis of the net reaction by iodide.

The reaction of $\text{Ce(IV)}$ with $\text{H}_3\text{AsO}_3$ can be monitored by measuring the absorbance at 405 nm, as $\text{Ce(IV)}$ 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/dm$^3$ $\text{H}_2\text{SO}_4$ at 25.0°C using the following initial concentrations:

<table>
<thead>
<tr>
<th>Run</th>
<th>$[\text{H}_3\text{AsO}_3]_0$, mol dm$^{-3}$</th>
<th>$[\text{Ce(IV)}]_0$, mol dm$^{-3}$</th>
<th>$[\text{I}^-]_0$, mol dm$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.01250</td>
<td>0.00120</td>
<td>$1.43\cdot10^{-6}$</td>
</tr>
<tr>
<td>2</td>
<td>0.00625</td>
<td>0.00060</td>
<td>$1.43\cdot10^{-6}$</td>
</tr>
<tr>
<td>3</td>
<td>0.01250</td>
<td>0.00120</td>
<td>$7.16\cdot10^{-7}$</td>
</tr>
</tbody>
</table>

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:

Under these conditions (0.5 mol/dm$^3$ $\text{H}_2\text{SO}_4$, 25.0°C), the rate law for the reaction can be written as

\[
\text{Rate} = k[\text{H}_3\text{AsO}_3]^m[\text{Ce(IV)}]^n[\text{I}^-]^p
\]

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 cm$^3$ of solution. A 0.0500 cm$^3$ aliquot of this solution is added to a mixture of 1.000 cm$^3$ 0.025 mol/dm$^3$ H$_3$AsO$_3$ in 0.5 mol/dm$^3$ H$_2$SO$_4$ and 0.800 cm$^3$ 0.5 mol/dm$^3$ H$_2$SO$_4$. To this mixture is added 0.200 cm$^3$ 0.0120 mol/dm$^3$ Ce(NH$_4$)$_2$(NO$_3$)$_6$ in 0.5 mol/dm$^3$ H$_2$SO$_4$ and the absorbance at 405 nm is measured as a function of time at 25.0°C:

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 (C₄H₈O₂), 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 (K₂S₂O₈) as oxidant and AgNO₃ as catalyst at T = 303.15 K are given below. The reaction was monitored by the estimation of unreacted peroxodisulfate. The concentration of AgNO₃ used in this study was 1.00·10⁻³ mmol·dm⁻³.

<table>
<thead>
<tr>
<th>Trial</th>
<th>Dioxane mmol·dm⁻³</th>
<th>K₂S₂O₈ mmol·dm⁻³</th>
<th>Initial rate mmol·dm⁻³·min⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0100</td>
<td>2.50</td>
<td>1.661·10⁻²</td>
</tr>
<tr>
<td>2</td>
<td>0.0100</td>
<td>5.10</td>
<td>3.380·10⁻²</td>
</tr>
<tr>
<td>3</td>
<td>0.00500</td>
<td>13.8</td>
<td>9.200·10⁻²</td>
</tr>
<tr>
<td>4</td>
<td>0.0110</td>
<td>13.8</td>
<td>9.201·10⁻²</td>
</tr>
</tbody>
</table>

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 AgNO₃ used in this study was 1.00·10⁻³ 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 K₂S₂O₈ is 5.0·10⁻⁶ 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:

\[
S₂O₈^{2-} + Ag^+ \xrightleftharpoons[k₂]{k₁} Ag^{3+} + 2SO₄^{2-}
\]

\[
Ag^{3+} + D (dioxane) \rightarrow D' (dioxane oxidised) + 2H^+ + Ag^+
\]

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 $\text{dm}^3\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ at very high concentrations of dioxane.

D) The units of the observed rate constant are $\text{dm}^3\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ 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.

\[
\text{LAS} \rightarrow \text{Lysine salicylate} + \text{Acetic acid}
\]

Hydrolysis of LAS can proceed via three different pathways (a) acid catalysed, (b) uncatalysed and (c) base catalysed.

If $[\text{LAS}]$ denotes the concentration of LAS at time ‘$t$’, the overall rate of the hydrolysis reaction can be written as

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

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

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) $k_{\text{obs}} \equiv k_0$ at pH = 12
   B) $k_{\text{obs}} \equiv k_0$ 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, calculate $k_\text{H}$, $k_0$ and $k_{\text{OH}}$. Make sure to specify the units.

<table>
<thead>
<tr>
<th>pH</th>
<th>$\log(k_{\text{obs}}/\text{min}^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.300</td>
<td>-3.886</td>
</tr>
<tr>
<td>5.30</td>
<td>-4.000</td>
</tr>
<tr>
<td>12.180</td>
<td>-1.726</td>
</tr>
</tbody>
</table>
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. \( \text{CH}_3\text{COOC}_6\text{H}_4\text{COOH} + \text{H}_3\text{O}^+ \rightarrow \text{HOC}_6\text{H}_4\text{COO}^- + \text{CH}_3\text{COOH} + \text{H}^+ \)
- II. \( \text{CH}_3\text{COOC}_6\text{H}_4\text{COOH} + \text{H}_2\text{O} \rightarrow \text{HOC}_6\text{H}_4\text{COO}^- + \text{CH}_3\text{COOH} \)
- III. \( \text{CH}_3\text{COOC}_6\text{H}_4\text{COOH} + \text{OH}^- \rightarrow \text{HOC}_6\text{H}_4\text{COO}^- + \text{CH}_3\text{COOH} \)
- IV. \( \text{CH}_3\text{COOC}_6\text{H}_4\text{COO}^- + \text{H}_3\text{O}^+ \rightarrow \text{HOC}_6\text{H}_4\text{COO}^- + \text{CH}_3\text{COOH} \)
- V. \( \text{CH}_3\text{COOC}_6\text{H}_4\text{COO}^- + \text{H}_2\text{O} \rightarrow \text{HOC}_6\text{H}_4\text{COO}^- + \text{CH}_3\text{COOH} \)
- VI. \( \text{CH}_3\text{COOC}_6\text{H}_4\text{COO}^- + \text{OH}^- \rightarrow \text{HOC}_6\text{H}_4\text{COO}^- + \text{CH}_3\text{COO}^- \)

4.3.1. Using the pH-rate profile diagram and the reactions given above, state 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 \( k_{\text{obs}} \) 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:

\[
\begin{array}{ccc}
  k_H & k_0 & k_{OH} \\
  1.99 \text{ dm}^3\text{ mol}^{-1}\text{ day}^{-1} & 2.29 \times 10^{-4} \text{ day}^{-1} & 3.18 \times 10^9 \text{ dm}^3\text{ mol}^{-1}\text{ day}^{-1}
\end{array}
\]

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

4.3.2. Assuming that only reactions I, II and III occur, calculate the value of the pH at the minimum of \( k_{\text{obs}} \).
Problem 5

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 \( \text{SiO}_2 \) 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∙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. **Find** the mass of the gaseous mixture formed upon heating of \( A \) with \( B \) and \( \text{SiO}_2 \).

5.1.2. **Determine** the quantitative composition of this gas mixture.

When 10.0 g of mineral \( A \) is heated with 21.7 g of \( \text{SiO}_2 \) in the absence of \( B \), it forms 8.34 dm\(^3\) of gaseous products (measured at 850°C and 1.013∙10\(^5\) Pa = 1.013 bar pressure). Mineral \( A \) contains only one metal.

5.1.3. **Calculate** 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 SiO₂ 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

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

The optical rotation of the material obtained by resolution was \(-400^\circ \text{ cm}^2 \text{ g}^{-1}\), while that of the enantiomerically pure compound is \(-415^\circ \text{ cm}^2 \text{ g}^{-1}\) 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. **What** 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. **Assign** the labelled stereocentres (\( \alpha \), \( \beta \), \( \gamma \)) in \((-)-1\) as \( R \) or \( S \).

6.2.3. **Give** 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.

6.3.1. **Give** the formula for compound \( Y \) to carry out the first step of the route.

6.3.2. **Suggest** structures for \( J \) and \( K \).
Problem 7

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 OsO₄, 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. Give 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. Give 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.

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 H₂SO₄
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 $D_1$ and $D_2$. These compounds can be separated by column chromatography.

\[
\begin{align*}
1. \text{NaCN} & \\
\text{IO}_4^- & \\
\text{NaOH/H}_2\text{O} & \\
\begin{array}{ccc}
\text{B} & \rightarrow & \text{C} \\
188.2 \text{ g/mol} & \\
\text{C} & \rightarrow & \text{D}_1 + \text{D}_2
\end{array}
\end{align*}
\]

Reaction of $D_1$ with LiAlH$_4$ followed by heating with 1M HCl solution gives sugar $F$ that is the hydrolysis product of the most abundant natural polysaccharide.

\[
\begin{align*}
\text{LiAlH}_4 & \\
1\text{M HCl/H}_2\text{O} & \\
\begin{array}{ccc}
\text{D}_1 & \rightarrow & \text{E} \\
\text{E} & \rightarrow & \text{F}
\end{array}
\end{align*}
\]

8.2.1. Draw the structures of $C$, $D_1$, $D_2$, $E$, and $F$ including stereochemical information. Show $F$ 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.

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 $F$. In which case?

- $^{13}$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 $D_2$ 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.

\[
\begin{align*}
1. \text{Equimolar HCl} & \\
2. \text{Heat, toluene} & \\
\text{D}_2 & \rightarrow \text{G} \\
\text{G} & \rightarrow \text{H}
\end{align*}
\]

8.3.1. Draw the structure of $G$ including the 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.
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
Theoretical Problems
Answer sheets

28 July 2016
Tbilisi, Georgia
Problem 1 5% of the total

<table>
<thead>
<tr>
<th></th>
<th>1.1.</th>
<th>1.2.</th>
<th>1.3.</th>
<th>1.4.</th>
<th>1.5.</th>
<th>1.6.</th>
<th>1.7.</th>
<th>Sum</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3</td>
<td>1</td>
<td>2</td>
<td>2</td>
<td>4</td>
<td>3</td>
<td>17</td>
<td></td>
</tr>
</tbody>
</table>

1.1. On which electrode does nitrogen trifluoride form?
- [ ] Cathode  [ ] Anode

Write a balanced chemical equation for the electrode half reaction for the formation of NF₃.

\[ \text{NH}_4^+ + 3 \text{F}^- \rightarrow \text{NF}_3 + 4 \text{H}^+ + 6 \text{e}^- \text{ or } \text{NH}_4\text{F} + 2 \text{HF} \rightarrow \text{NF}_3 + 6 \text{H}^+ + 6 \text{e}^- \text{ or equ.} \]

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

1.2. Which of NF₃, NHF₂ or NH₂F compound is expected to condense at the lowest temperature?
- [ ] NF₃  [ ] NHF₂  [ ] NH₂F  [ ] NF₃

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

<table>
<thead>
<tr>
<th>Molecule</th>
<th>NH₂F</th>
<th>NHF₂</th>
<th>NF₃</th>
<th>The partial positive charge on N increases in this order, so the attraction also increases between the N and F.</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-F bond length, pm</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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

\[ 2 \text{NHF}_2 + 2 \text{KF} \rightarrow \text{N}_2\text{F}_2 + 2 \text{KHF}_2 \text{ or } 2 \text{NHF}_2 \rightarrow \text{N}_2\text{F}_2 + 2 \text{HF} \]

2p (1p N₂F₂, 1p equation)

1.5. Propose a suitable reagent for the formation of NF₄⁺ and write a balanced chemical equation for the reaction.

\[ \text{NF}_3 + \text{F}_2 + \text{SbF}_5 \rightarrow \text{NF}_4^+ + \text{SbF}_6^- \text{ any strong fluoride acceptor (AsF}_5, \text{BF}_3 \]

2p (1p species, 1p coefficients)
1.6. Write a balanced chemical equation for the hydrolysis of NF$_4^+$.

\[
2 \text{NF}_4^+ + 2 \text{H}_2\text{O} \rightarrow 2 \text{NF}_3 + \text{O}_2 + 2 \text{HF} + 2 \text{H}^+ \Rightarrow n(\text{O}_2):n(\text{NF}_3) = 1:2
\]

Write a balanced chemical equation for a possible side reaction that can decrease the theoretically expected O$_2$:NF$_3$ mole ratio.

\[
e.g.: \text{NF}_4^+ + 2 \text{H}_2\text{O} \rightarrow \text{NF}_3 + \text{H}_2\text{O}_2 + \text{HF} + \text{H}^+ \quad \text{HOF, O}_3, \text{OF}_2 \text{ also accepted.}
\]

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$_4$)$_x$AF$_y$ composition, \(x:y = 1:4\).

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

With \(x=1\), the atomic mass of \(\text{A}\) 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$_8$.

Formula:

\[
3\text{p (1.5p for Zn)}
\]
Problem 2

2.1.1. Which of the atoms (A or B) is copper?

Copper: 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?

<table>
<thead>
<tr>
<th></th>
<th>pr. cubic</th>
<th>fcc</th>
<th>bcc</th>
<th>diamond</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

B: fcc  A: bcc

What are the coordination numbers of the atoms?

A: 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: half of the cell body diagonal 1/2·427.0 pm·√3 = 369.8 pm.
Cu-O: 1/4th of the cell body diagonal 1/4·427.0 pm·√3 = 184.9 pm.
Cu-Cu: half of the face diagonal: 1/2·427.0 pm·√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 pm)³.
The mass of a unit cell is (4M_{Cu} + 2 M_{O})/ N_{A}. The density is 6.106 g/cm³.

2p
2.2. What percentage 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 ≈ 0.2%

What is $x$ in the empirical formula $\text{Cu}_2x\text{O}$ of the crystal?

Your work:

0.2% of 2 coppers is missing. That is 0.004.

$x$:

2.3. Write balanced chemical equations for reactions (1-3).

Reaction 1:

(1) $2\text{Cu}_2\text{O} + \text{O}_2 \rightarrow 4\text{CuO}$ (copper(II)-hydroxides and carbonates accepted)
(2) $\text{Cu}_2\text{O} + 2\text{H}^+ \rightarrow \text{Cu} + \text{Cu}^{2+} + \text{H}_2\text{O}$
(3) $\text{Cu}_2\text{O} + \text{H}_2\text{SO}_4 + 4\text{H}^+ \rightarrow 2\text{Cu}^{2+} + \text{SO}_2 + 3\text{H}_2\text{O}$

Reaction 3p (non-ionic equations also accepted)

2.4. Determine 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:

$\Delta_f G(\text{CuO}) = -156000 \text{ J mol}^{-1} + 84 \text{ J mol}^{-1} \text{ K}^{-1} T$
$\Delta_f G(\text{Cu}_2\text{O}) = -170000 \text{ J mol}^{-1} + 72 \text{ J mol}^{-1} \text{ K}^{-1} T$

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: $2\text{CuO} = \text{Cu}_2\text{O} + 0.5\text{O}_2$

$\Delta_r G = 1420000 \text{ J mol}^{-1} - 96 \text{ J mol}^{-1} \text{ K}^{-1} T$

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 $\Delta G$ or equivalent calculation, 1 for each conclusion)
Temperature range between 500-1500K | The most stable form (Cu, Cu$_2$O or CuO) |
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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:  
\[
C: 2 \text{H}_2\text{O} + 2 \text{e}^- \rightarrow \text{H}_2 + 2 \text{OH}^-
\]

Anode:  
\[
A: 2 \text{Cu} + 2 \text{OH}^- \rightarrow \text{Cu}_2\text{O} + \text{H}_2\text{O} + 2\text{e}^-
\]

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

\[
2 \text{Cu}^{2+} + \text{H}_2\text{O} + 2 \text{e}^- \rightarrow \text{Cu}_2\text{O} + 2 \text{H}^+
\]

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.

\[
K_{sp} \geq 0.1[\text{OH}^-]^2 \quad \Rightarrow \quad \text{pH} \leq 5.15
\]

3 p (1p realizing that precipitation occurs, 1p equation, 1p result)
Your work:

The potential of the cathodic process (2 Cu$^{2+}$ + H$_2$O + 2 e$^-$ = Cu$_2$O + 2 H$^+$) depends on the pH.

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

- \[ \text{Cu}_2\text{O}(s) + \text{H}_2\text{O}(l) + 2 \text{e}^- \rightarrow 2 \text{Cu}(s) + 2 \text{OH}^- (\text{aq}) \quad \Delta G_{\text{e}_1} = -2F(-0.36 \text{ V}) \]
- \[ \text{Cu}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Cu}(s) \quad \Delta G_{\text{e}_2} = -2F(+0.337 \text{ V}) \]
- \[ \text{H}_2\text{O}(l) \rightarrow \text{H}^+ (\text{aq}) + \text{OH}^- (\text{aq}) \quad \Delta G_{\text{e}_3} = -RT \ln K_w \]

For 2 Cu$^{2+}$(aq) + H$_2$O(l) + 2 e$^-$ → Cu$_2$O(s) + 2 H$^+$(aq):

\[ \Delta G^0 = -\Delta G_{\text{e}_1} + 2\Delta G_{\text{e}_2} + 2\Delta G_{\text{e}_3} \]

\[ E^0 = \frac{-\Delta G^0}{2F} = 0.36 \text{ V} + 2 \cdot 0.337 \text{ V} - \left(\frac{RT}{F}\right) \cdot \ln K_w = 0.208 \text{ V} \]

The concentration dependence of the cathodic Cu$_2$O production potential:

\[ E = 0.208 \text{ V} + 0.059/2 \log \left(\frac{[\text{Cu}^{2+}]^2}{[\text{H}^+]^2}\right) \]

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

\[ 0.337 + \frac{0.059}{2} \log [\text{Cu}^{2+}] = 0.208 + \frac{0.059}{2} \log \left(\frac{[\text{Cu}^{2+}]^2}{[\text{H}^+]^2}\right) \]

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

pH = 2.69

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

Many other routes possible – all correct ones accepted.

minimum pH:
Problem 3

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

\[
\text{IO}_3^- + 8 \text{I}^- + 6 \text{H}^+ \rightarrow 3 \text{I}_3^- + 3 \text{H}_2\text{O} \text{ or } \text{IO}_3^- + 5 \text{I}^- + 6 \text{H}^+ \rightarrow 3 \text{I}_2 + 3 \text{H}_2\text{O}
\]

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.

\[
\text{I}_3^- + 2 \text{S}_2\text{O}_3^{2-} \rightarrow 3 \text{I}^- + \text{S}_4\text{O}_6^{2-} \text{ or } \text{I}_2 + 2 \text{S}_2\text{O}_3^{2-} \rightarrow 2 \text{I}^- + \text{S}_4\text{O}_6^{2-}
\]

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:

\[
(0.00750 \text{ dm}^3 \text{ titrant}) \times (0.00235 \text{ mol dm}^{-3} \text{ S}_2\text{O}_3^{2-}) = 1.76 \times 10^{-5} \text{ mol S}_2\text{O}_3^{2-}
\]

\[
(1.76 \times 10^{-5} \text{ mol S}_2\text{O}_3^{2-}) \times (1 \text{ mol} \text{ IO}_3^- / 6 \text{ mol S}_2\text{O}_3^{2-}) = 2.94 \times 10^{-6} \text{ mol} \text{ IO}_3^-
\]

\[
(2.94 \times 10^{-6} \text{ mol} \text{ IO}_3^-) \times (126.90 \text{ g/mol}) = 3.73 \times 10^{-4} \text{ g iodine}
\]

\[
(3.73 \times 10^{-4} \text{ g iodine}) / (10.00 \text{ g salt}) \times 10^6 \text{ ppm} = 37.3 \text{ ppm iodine}
\]

2p for calculating mol thiosulfate
2p for calculating mol iodate
2p for converting to ppm

ppm iodine =
3.2.1. **Select** an appropriate data point from the experiments and **use it to calculate** 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 $n(\text{added } Ag^+) = n (I^- \text{ initially present})$ 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 $\mu$mol added Ag$^+$, then

$[I^-] = [I^-]_0 - 5.0 \cdot 10^{-6} \text{ mol/dm}^3 = 5.0 \cdot 10^{-6} \text{ mol/dm}^3$

$|E| = 0.622 \text{ V} = -0.0591 \cdot \log[Ag^+] \Rightarrow [Ag^+] = 3.2 \cdot 10^{-11} \text{ mol/dm}^3$

$K_{spI} = [Ag^+] [I^-] = 1.6 \cdot 10^{-16}$

2p for relationship between $E$ and $[Ag^+]$ (full credit if used even if not stated explicitly)

1p for selecting a data point with $n(\text{Ag}^+) \leq 10.0 \mu$mol

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

---

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

**Your work:**

In the titration with $[Cl^-] = 0.100 \text{ mol/dm}^3$ (experiment B), the fact that the potential stops changing at $n(\text{added } Ag^+) \geq 11.8 \mu$mol 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:

$|E| = 0.517 \text{ V} = -0.0591 \cdot \log[Ag^+] \Rightarrow [Ag^+] = 1.6 \cdot 10^{-9} \text{ mol/dm}^3$

$K_{spCl} = [Ag^+] [Cl^-] = 1.6 \cdot 10^{-10}$

1p for selecting a data point with $n(\text{Ag}^+) > 11.8 \mu$mol

3p for calculation of $K_{spCl}$

---
3.2.3. Select an appropriate data point from the experiments and use it to calculate $K_f$. 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$^3$)

$K_f = \frac{[AgCl_2^-]}{[Ag^+] [Cl^-]^2} = \frac{1.9 \cdot 10^{-6}}{1.6 \cdot 10^{-9} \cdot 0.100^2} = 1.2 \cdot 10^5 \ [1.9 \cdot 10^4 \ \text{given const.} ]$

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

$|E| = 0.558 \text{ V} = -0.0591 \cdot \log[Ag^+] \Rightarrow [Ag^+] = 3.62 \cdot 10^{-10}$ 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$^3$

$K_f = \frac{[AgCl_2^-]}{[Ag^+] [Cl^-]^2} = \frac{4.42 \cdot 10^{-7}}{3.62 \cdot 10^{-10} \cdot 0.100^2} = 1.2 \cdot 10^5 \ [7.6 \cdot 10^5 \ \text{given const.} ]$
3.3.1. **Write** balanced net ionic equations for the reaction of cerium(IV) with $\text{H}_3\text{AsO}_3$ in acidic solution, as well as reactions of cerium(IV) with a species containing the element iodine and $\text{H}_3\text{AsO}_3$ 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 $\text{H}_3\text{AsO}_3$ in acidic solution:**

$$2 \text{Ce}^{4+} + \text{H}_3\text{AsO}_3 + \text{H}_2\text{O} \rightarrow 2 \text{Ce}^{3+} + \text{H}_3\text{AsO}_4 + 2 \text{H}^+$$

2p (1p for $\text{H}_3\text{AsO}_3/\text{H}_3\text{AsO}_4$ couple, 1p balanced)

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

$$2 \text{Ce}^{4+} + 2 \text{I}^- \rightarrow 2 \text{Ce}^{3+} + \text{I}_2$$

2p (1p species, 1p balanced). Full marks for $\text{I}_3^-$ or $\text{I}^-$ as products

**Reaction of $\text{H}_3\text{AsO}_3$ with an iodine-containing species:**

$$\text{H}_3\text{AsO}_3 + \text{I}_2 + \text{H}_2\text{O} \rightarrow \text{H}_3\text{AsO}_4 + 2 \text{I}^- + 2 \text{H}^+$$

2p (1p species, 1p balanced). Full marks for $\text{I}_3^-$ or $\text{I}^-$ as products

Two iodine-containing reactions must add up to the net reaction, otherwise $-2p$ for the iodine-containing reactions

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

**Your work:**

The limiting reactant is Ce(IV) which is $< 10\%$ of the concentration of $\text{H}_3\text{AsO}_3$, so only the concentration of Ce(IV) changes appreciably over the course of the reaction. ($\text{I}^-$ 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 \(-\ln(A/A_0)/(1/t)\), which should be a constant \((k_{\text{obs}})\) if the reaction is first-order:

<table>
<thead>
<tr>
<th>(t), s</th>
<th>(k_{\text{obs}}, \text{s}^{-1}, \text{Run 1})</th>
<th>(k_{\text{obs}}, \text{s}^{-1}, \text{Run 2})</th>
<th>(k_{\text{obs}}, \text{s}^{-1}, \text{Run 3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.0290</td>
<td>0.0328</td>
<td>0.0148</td>
</tr>
<tr>
<td>40</td>
<td>0.0286</td>
<td>0.0310</td>
<td>0.0147</td>
</tr>
<tr>
<td>60</td>
<td>0.0284</td>
<td>0.0305</td>
<td>0.0146</td>
</tr>
<tr>
<td>80</td>
<td>0.0284</td>
<td>0.0305</td>
<td>0.0146</td>
</tr>
<tr>
<td>100</td>
<td>0.0282</td>
<td>0.0302</td>
<td>0.0145</td>
</tr>
<tr>
<td><strong>avg.</strong></td>
<td>0.0285</td>
<td>0.0310</td>
<td>0.0146</td>
</tr>
</tbody>
</table>

So \(n = 1\).

Since \(k_{\text{obs}}\) 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 \(p = 1\).

\[ k = k_{\text{obs}}/[I^-], \] giving values of \(1.99 \cdot 10^4\), \(2.17 \cdot 10^4\), and \(2.04 \cdot 10^4\) \(\text{dm}^3\text{mol}^{-1}\text{s}^{-1}\) for runs 1-3; average \(k = 2.07 \cdot 10^4\) \(\text{dm}^3\text{mol}^{-1}\text{s}^{-1}\).

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

3.3.3. Calculate the iodization level, in ppm, of the salt sample.

Your work:

<table>
<thead>
<tr>
<th>(t), s</th>
<th>(-\ln(A/A_0)/(1/t), \text{s}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
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</tr>
<tr>
<td>40</td>
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</tr>
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<tr>
<td>80</td>
<td>0.0176</td>
</tr>
<tr>
<td>100</td>
<td>0.0177</td>
</tr>
</tbody>
</table>

So \(k_{\text{obs}} = 0.0177 \text{s}^{-1} = k[I^-] = (2.07 \cdot 10^4 \text{dm}^3\text{mol}^{-1}\text{s}^{-1})[I^-]\)

\([I^-] = 8.55 \cdot 10^{-7} \text{mol/dm}^3\)

Since the salt solution was diluted by a factor of \((2.05 \text{ cm}^3)/(0.050 \text{ cm}^3) = 41\), the concentration in the original salt solution was

\(41 \cdot (8.55 \cdot 10^{-7} \text{ mol/dm}^3) = 3.51 \cdot 10^{-5}\) \(\text{mol/dm}^3\).

\((3.51 \cdot 10^{-5} \text{ mol dm}^{-3})(0.01000 \text{ dm}^3) = 3.51 \cdot 10^{-7} \text{ mol I in the salt sample}\)

\((3.51 \cdot 10^{-5} \text{ mol iodine})(126.90 \text{ g/mol}) = 4.45 \cdot 10^{-5} \text{ g iodine}\)

\((4.45 \cdot 10^{-5} \text{ g iodine})/(1.000 \text{ g salt})\cdot 10^6 \text{ ppm} = 44.5 \text{ ppm I}\)

2p for calculating \(k_{\text{obs}}, 1p\) for \([I^-]\) from \(k_{\text{obs}}, 2p\) for converting to ppm
Problem 4 8% of the total

<table>
<thead>
<tr>
<th>4.1.1</th>
<th>4.1.2</th>
<th>4.1.3</th>
<th>4.2.1</th>
<th>4.2.2</th>
<th>4.2.3</th>
<th>4.3.1</th>
<th>4.3.2</th>
<th>Sum</th>
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</thead>
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<td>2</td>
<td>6</td>
<td>2</td>
<td>4</td>
<td>25</td>
</tr>
</tbody>
</table>

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 \( 5.0 \times 10^{-6} \) mol/dm\(^3\). Assume that the rate law obtained from the data above is valid under these conditions.

**Your work:**

Trial 1 and 2 ⇒ the rate doubles when concentration of \( K_2S_2O_8 \) is doubled.  
Order w.r.t. \( K_2S_2O_8 = 1 \).

Trial 3 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 \( k = 6.65 \times 10^{-3} \) min\(^{-1}\)

Change in dioxane concentration: \((40.00 - 0.35) \mu g \cdot dm^{-3} / 88.1 \text{ g} \cdot \text{mol}^{-1} = 0.450 \mu \text{mol} \cdot dm^{-3} \)

\[ [ K_2S_2O_8]_0 = 5.00 \mu \text{mol dm}^{-3} ; [ K_2S_2O_8]_t = 4.55 \mu \text{mol dm}^{-3} \]

\[ 4.55 = 5.00 \exp(-6.65 \times 10^{-3} \cdot t) \]

\[ t = 14.2 \text{ minutes} \]

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:**
4.2.1. Write an expression for \(k_{\text{obs}}\) in terms of \(k_H\), \(k_0\), \(k_{OH}\) and \([H^+]\).

Your work:

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

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

4.2.2. 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

\[
\log(k_{\text{obs}}/\text{min}^{-1}) = -4.000 \Rightarrow k_{\text{obs}} = k_0 = 1.00 \cdot 10^{-4} \text{ min}^{-1}
\]

At pH = 12.18, \([OH^-]\) = 0.01514 mol dm\(^{-3}\)

\[
\log(k_{\text{obs}}/\text{min}^{-1}) = -1.726 \Rightarrow k_{\text{obs}} = 1.88 \cdot 10^{-2} \text{ min}^{-1}
\]

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

At pH = 1.30, \([H^+]\) = 0.0501 mol dm\(^{-3}\)

\[
\log(k_{\text{obs}}/\text{min}^{-1}) = -3.886 \Rightarrow k_{\text{obs}} = 1.30 \cdot 10^{-4} \text{ min}^{-1}
\]

\(k_0\) can be neglected

\[
k_{OH} = \frac{k_{\text{obs}}/[OH^-]}{[H^+]} = 3.0 \cdot 10^{-5} \text{ min}^{-1}
\]

\[
k_H = \frac{k_{\text{obs}} - k_0}{[H^+]} = \frac{3.0 \cdot 10^{-5} \text{ min}^{-1}}{0.0501 \text{ mol dm}^{-3}} = 6.0 \cdot 10^{-4} \text{ dm}^3\cdot\text{mol}^{-1}\cdot\text{min}^{-1}
\]

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

Your work:

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

This is a minimum if
$$\frac{dk_{\text{obs}}}{d[H^+]} = k_{\text{H}} - k_{\text{OH}} \frac{K_w}{[H^+]^2} = 0$$

$$[H^+]_{\text{min}} = \sqrt{\frac{k_{\text{OH}}K_w}{k_{\text{H}}}}$$

$$\text{pH}_{\text{min}} = \frac{1}{2} pK_w + \frac{1}{2} \log \frac{k_{\text{H}}}{k_{\text{OH}}} = 2.40$$

or see alternative solution without calculus

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

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

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

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

$$[H^+]_{\text{min}} = \sqrt{\frac{k_{\text{OH}}K_w}{k_{\text{H}}}}$$

$$\text{pH}_{\text{min}} = \frac{1}{2} pK_w + \log \frac{k_{\text{H}}}{k_{\text{OH}}} = 2.40$$

pH at minimum:
Problem 5  8% of the total

<table>
<thead>
<tr>
<th>5.1.1</th>
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<th>5.1.5</th>
<th>5.1.6</th>
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</tbody>
</table>

5.1.1. Find the mass of the gaseous mixture formed upon heating of A with B and SiO₂.

Your work:

\[ m = 10.0 + 21.7 + 9.05 - 34.0 = 6.75 \text{ g} \]

1 p

5.1.2. Determine the quantitative composition of this gas mixture.

Your work:

At 850°C, the number of moles of gaseous products is:

\[ n_1 = \frac{pV}{RT} = \frac{101325 \text{ Pa} \cdot 0.0167 \text{ m}^3}{8.314 \text{ J mol}^{-1}\text{K}^{-1} \cdot (850 \text{K} + 273 \text{K})} = 0.181 \text{ mol} \]

while at 0°C

\[ n_2 = \frac{pV}{RT} = \frac{101325 \text{ Pa} \cdot 0.00304 \text{ m}^3}{8.314 \text{ J mol}^{-1}\text{K}^{-1} \cdot 273 \text{ K}} = 0.136 \text{ mol} \]

The difference of 0.045 moles is probably water that has condensed. Hence, the mass of the gas at 0°C is \( m = 6.75 - 0.045 \cdot 18 = 5.94 \text{ g} \), and the molar mass is \( m/n_2 \approx 44 \text{ g/mol} \). Taken into account that we dealt with minerals, and the temperature was high, we can conclude that the rest of the gas is CO₂.

The gas formed at 850°C contains 0.045 mol of H₂O and 0.136 mol of CO₂.

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. **Calculate** 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. **Determine** 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. **Determine** 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:

\[ A + 2 \text{CaCO}_3 + 8 \text{SiO}_2 = \text{pigment} + 3 \text{CO}_2 + \text{H}_2\text{O} \]

The composition of Egyptian blue can be written as \(2\text{CaO} \cdot 8\text{SiO}_2 \cdot n\text{Me}_x\text{O}_y\). Oxide \(\text{Me}_x\text{O}_y\) forms from mineral \(A\). Let us find the molar mass of \(n\text{Me}_x\text{O}_y\):

\[
M(\text{pigment}) = M(2\text{CaO} \cdot 8\text{SiO}_2) + M(n\text{Me}_x\text{O}_y)
\]

\[
M(\text{pigment}) = 2M(\text{CaCO}_3) \frac{m(\text{pigment})}{m(\text{CaCO}_3)}
\]

\[
M(n\text{Me}_x\text{O}_y) = 2M(\text{CaCO}_3) \frac{34.0 \text{ g}}{9.05 \text{ g}} - M(2\text{CaO} \cdot 8\text{SiO}_2) \approx 159 \text{ g/mol}
\]

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 \(\text{CaCuSi}_4\text{O}_{10}\).

The formula of Chinese blue is \(\text{BaCuSi}_4\text{O}_{10}\).

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:** \(\text{CaCuSi}_4\text{O}_{10}\) 

**Chinese blue is:** \(\text{BaCuSi}_4\text{O}_{10}\)

5.1.6. **Determine** the formula of mineral \(A\).

Your work:

Upon heating \(A\) turns into 2 CuO, 1 CO\(_2\) and 1 H\(_2\)O.

It means that \(A\) is malachite \(\text{Cu}_2\text{CO}_3(\text{OH})_2\).

2p

\(A\) is:
5.2.1. Suggest the formula of the mineral used in place of C.

BaSO₄ (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. BaSO₄ is more stable than BaCO₃.
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.

Cu₂O (mixing red with blue gives purple)
2p
Problem 6  7% of the total

<table>
<thead>
<tr>
<th>6.1.1</th>
<th>6.1.2</th>
<th>6.2.1</th>
<th>6.2.2</th>
<th>6.2.3</th>
<th>6.3.1</th>
<th>6.3.2</th>
<th>Sum</th>
</tr>
</thead>
<tbody>
<tr>
<td>24</td>
<td>4</td>
<td>3</td>
<td>6</td>
<td>2</td>
<td>2</td>
<td>8</td>
<td>49</td>
</tr>
</tbody>
</table>

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

X

CH₃CH₂COOH or any other reasonable reagent. 4p (3p for formyl chloride)
Formic acid = 0p
6.2.1. What is the enantiomeric excess of the resolved compound prepared by the industrial route?

Your work:

If $x$ is the percentage of the $(-)$ enantiomer:

$x(-415) + (1 - x)(415) = -400$

$x = \frac{815}{830}$

$ee = \frac{(815/830) - (15/830)}{800/830} = 0.964$ or 96.4%

$ee$: 3p (2p enantiomer composition, 1p ee calculation)

6.2.2. Assign the labelled stereocentres ($\alpha$, $\beta$, $\gamma$) in $(-)\cdot 1$ as $R$ or $S$.

<table>
<thead>
<tr>
<th>$\alpha$</th>
<th>$\beta$</th>
<th>$\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>R</td>
<td>S</td>
</tr>
</tbody>
</table>

6.2.3. Give 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.

NaBH₄, LiAlH₄, etc. 2p

6.3.1. Give the formula for compound $Y$ to carry out the first step of the route.

$Y$: CH₃NH₂ 2p

6.3.2. Suggest structures for $J$ and $K$.

$J$: 4p

$K$: 0p for $J$ and $K$ if not in agreement with the formula, full marks for open form of $K$. 2p
Problem 7

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.

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Structure A" /></td>
<td><img src="image" alt="Structure B" /></td>
</tr>
</tbody>
</table>

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

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

<table>
<thead>
<tr>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Structure C" /></td>
<td><img src="image" alt="Structure D" /></td>
</tr>
</tbody>
</table>

4p (allow carry forward from B)

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

<table>
<thead>
<tr>
<th>E₁ and E₂</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Structure E₁ and E₂" /></td>
</tr>
</tbody>
</table>

4p each (1p if OHs on different sides)
(2p if no de-carboxylation; 1p if osmate ester)
7.3.1. **Give** the structures of H, I, and J. There is no need to show the different diastereoisomers formed.

**H**

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

**I**

(points for reduction of ketone, sensible chemistry, correct number of possible diastereomers, and being achiral)
7.3.2  **Give** the structures of diastereoisomers \( K_1 \), and \( K_2 \).

**K1**

\[
\begin{align*}
\text{4p (2p if answer is } K_2) \\
(\text{answer must fit formula and be sensible)}
\end{align*}
\]

**K2**

\[
\begin{align*}
\text{4 pt (2pt if answer is } K_1) \\
(\text{answer must fit formula and be sensible)}
\end{align*}
\]

7.4.  **Give** the structure of \( N \).

**N**

\[
\begin{align*}
\text{4p} \\
(\text{full marks for anhydride of } L)
\end{align*}
\]
Problem 8  

8.1. 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 of these reagents can be utilized as X for the selective hydrolysis of A?

(x) □ 50% acetic acid  □ concentrated H₂SO₄  □ 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?

8.2.1. Draw the structures of C, D₁, D₂, E and F including stereochemical information. Show F 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.
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. In which case?

(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.

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


Problem 2

Figure is from:


Problem 4

Figures are adapted from:


Problem 6


Problem 8