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. On which electrode does nitrogen trifluoride form?

☐ Cathode ☐ Anode

Write a balanced chemical equation for 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. Which of NF_3, NHF_2 or NH_2F compound is expected to condense at the lowest temperature?

☐ NF_3 ☐ NHF_2 ☐ NH_2F

NF_3

1.3. Assign 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. Write 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. Propose a suitable reagent for the formation of NF_4^+ and write 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.

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

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 $1/2 \cdot 427.0\ \text{pm} \cdot \sqrt{3} = 369.8$ pm.

Cu-O: 1/4th of the cell body diagonal $1/4 \cdot 427.0\ \text{pm} \cdot \sqrt{3} = 184.9$ pm.

Cu-Cu: half of the face diagonal: $1/2 \cdot 427.0\ \text{pm} \cdot \sqrt{2} = 301.9$ 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 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. 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: $2/1002 \approx 0.2\%$

1 p

percentage:

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

Reaction 1:

(1) $2\ Cu_2O + O_2 \longrightarrow 4\ CuO$ (copper(II)-hydroxides and carbonates accepted)

Reactio

(2) $Cu_2O + 2\ H^+ \longrightarrow Cu + Cu^{2+} + H_2O$

(3) $Cu_2O + H_2SO_4 + 4\ H^+ \longrightarrow 2\ Cu^{2+} + SO_2 + 3\ H_2O$

Reactio

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:

$\Delta_f G(CuO) = -156000\ J\ mol^{-1} + 84\ J\ mol^{-1}\ K^{-1}\ T$
$\Delta_f G(Cu_2O) = -170000\ J\ mol^{-1} + 72\ J\ mol^{-1}\ K^{-1}\ T$

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_2O or CuO)

2.5. Write 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.

Cathode

Anode:

C: $2\ H_2O + 2\ e^- \longrightarrow H_2 + 2\ OH^-$

A: $2\ Cu + 2\ OH^- \longrightarrow Cu_2O + H_2O + 2e^-$

2p

2.6.1. Write the half reaction equation of the cathode process giving Cu_2O in acidic medium.

$2\ Cu^{2+} + H_2O + 2\ e^- \longrightarrow Cu_2O + 2\ H^+$

1p

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

Your work:

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

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

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

maximum pH:

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

Your work:

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

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

$Cu_2O(s) + H_2O(l) + 2e^- \longrightarrow 2\ Cu(s) + 2\ OH^-(aq)$ $\Delta G^o{}_1 = -2F(-0.36\ V)$
$Cu^{2+}(aq) + 2\ e^- \longrightarrow Cu(s)$ $\Delta G^o{}_2 = -2F(+0.337\ V)$
$H_2O(l) \longrightarrow H^+(aq) + OH^-(aq)$ $\Delta G^o{}_3 = -RT \ln K_w$

For $2\ Cu^{2+}(aq) + H_2O(l) + 2\ e^- \longrightarrow Cu_2O(s) + 2\ H^+(aq)$:

$\Delta G^o = -\Delta G^o{}_1 + 2\Delta G^o{}_2 + 2\Delta G^o{}_3$

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

The concentration dependence of the cathodic Cu_2O production potential:

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

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

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

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

pH = 2.69

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

Many other routes possible – all correct ones accepted.

minimum pH:

Problem 3 9% of the total

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

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

$IO_3^- + 8\ I^- + 6\ H^+ \rightarrow 3\ I_3^- + 3\ H_2O$ or $IO_3^- + 5\ I^- + 6\ H^+ \rightarrow 3\ I_2 + 3\ H_2O$

2p (1p species, 1p coefficients, 0.5p penalty if spectator ions are included.)

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

$I_3^- + 2\ S_2O_3^{2-} \rightarrow 3\ I^- + S_4O_6^{2-}$ or $I_2 + 2\ S_2O_3^{2-} \rightarrow 2\ I^- + S_4O_6^{2-}$

2p (1p species, 1p coefficients, 0.5p penalty if spectator ions are included.)

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

Your work:

$(0.00750\ \text{dm}^3\ \text{titrant})\cdot(0.00235\ \text{mol dm}^{-3}\ S_2O_3^{2-}) = 1.76\cdot10^{-5}\ \text{mol}\ S_2O_3^{2-}$

$(1.76\cdot10^{-5}\ \text{mol}\ S_2O_3^{2-})\cdot(1\ \text{mol}\ IO_3^-/6\ \text{mol}\ S_2O_3^{2-}) = 2.94\cdot10^{-6}\ \text{mol}\ IO_3^-$

$(2.94\cdot10^{-6}\ \text{mol}\ IO_3^-)\cdot(126.90\ \text{g/mol}) = 3.73\cdot10^{-4}\ \text{g iodine}$

$\{(3.73\cdot10^{-4}\ \text{g iodine})/(10.00\ \text{g salt})\}\cdot10^6\ \text{ppm} = 37.3\ \text{ppm iodine}$

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(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. 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 $[Cl^-] = 0.100$ 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. 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/dm³, $[Cl^-] = 0.100$ mol/dm³ (see above).
Almost all of the originally present $1.0 \cdot 10^{-5}$ mol/dm³ iodide has been precipitated out as 9.9 μmol AgI, since $[I^-] = K_{spI}/[Ag^+] = 1.0 \cdot 10^{-7}$ mol/dm³

Total Ag in solution = 11.8 μmol – 9.9 μmol = 1.9 μmol

$[AgCl_2^-] = 1.9 \cdot 10^{-6}$ mol/dm³ (since free $[Ag^+]$ is only $1.6 \cdot 10^{-9}$ mol/dm³)

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

Same approach works for 11 μmol Ag^+ added.

2p for selecting a data point between 10-12.0 μmol

3p for reasonable method of calculating K_f

2p for value of K_f

An alternative approach is to look at the equivalence point, where

$|E| = 0.558 \text{ V} = -0.0591 \cdot \log[Ag^+] \Rightarrow [Ag^+] = 3.62 \cdot 10^{-10}$ mol/dm³

Since AgI(*s*) is present, $[I^-] = K_{spI}/[Ag^+] = 4.42 \cdot 10^{-7}$ mol/dm³

The amount of dissolved iodine and silver is equivalent:

$[I^-] = [Ag^+] + [AgCl_2^-] \Rightarrow [AgCl_2^-] = 4.42 \cdot 10^{-7}$ mol/dm³

$$K_f = \frac{[AgCl_2^-]}{[Ag^+][Cl^-]^2} = \frac{4.42 \cdot 10^{-7}}{3.62 \cdot 10^{-10} \cdot 0.100^2} = 1.2 \cdot 10^5 \quad [7.6 \cdot 10^5 \text{ given const.}]$$

K_f:

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

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

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

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

So $n = 1$.

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

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

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

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

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

$m =$ $n =$ $p =$ $k =$

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

Your work:

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

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

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

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

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

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

ppm I =

Problem 4 8% of the total

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

4.1.1. Calculate the time in minutes the oxidation process has to continue in order to reach the accepted level of dioxane at 303.15 K if the initial concentration of $K_2S_2O_8$ is $5.0\cdot10^{-6}$ 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 $k = 6.65\cdot10^{-3}\ \text{min}^{-1}$

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

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

$4.55 = 5.00 \exp(-6.65\cdot10^{-3}\ t)$

$t = 14.2$ 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, deduce the rate equation for the oxidation of dioxane.

Your work:

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

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

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

3p (1p for each step)

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

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

Your work:

$$k_{\mathrm{obs}} = k_{\mathrm{H}}[\mathrm{H^+}] + k_0 + k_{\mathrm{OH}}\frac{K_{\mathrm{w}}}{[\mathrm{H^+}]}$$

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

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

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

Your work:

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

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

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

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

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

$k_{\mathrm{H}} = 6.0 \cdot 10^{-4}\ \mathrm{dm^3 \cdot mol^{-1} \cdot min^{-1}}$

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. Find 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. Determine the quantitative composition of this gas mixture.

Your work:

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

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

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. 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:

$$\mathbf{A} + 2\ CaCO_3 + 8\ SiO_2 = \text{pigment} + 3\ CO_2 + H_2O$$

The composition of Egyptian blue can be written as $2CaO{\cdot}8SiO_2{\cdot}nMe_xO_y$. Oxide Me_xO_y forms from mineral **A**. Let us find the molar mass of nMe_xO_y:

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

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

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

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 $CaCuSi_4O_{10}$.

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. Determine 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.

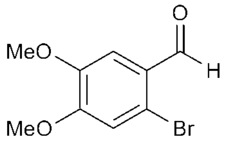
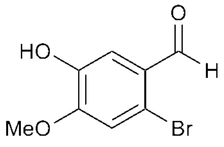
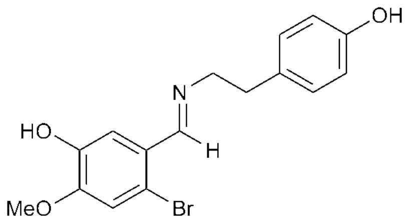
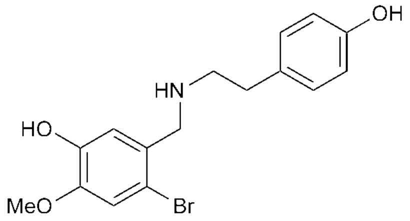
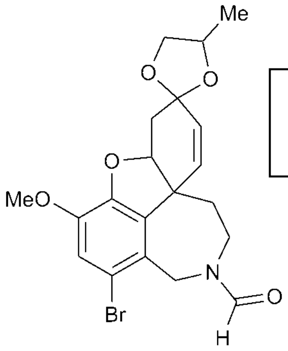
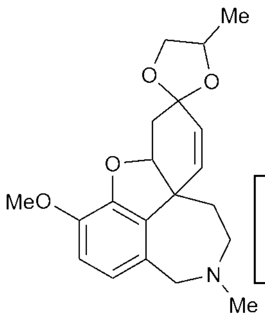
Cu_2O (mixing red with blue gives purple)

2p

Problem 6 7% of the total

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

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

A  0p if lacks 2 para protons	**B** 
C 	**D** 
F  2p penalty if Br removed	**G**  2p penalty if Br present

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

X

CH_3CH_2OCOH 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:

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

$x = 815/830$

$ee = (815/830) - (15/830) = 800/830 = 0.964$ or 96.4%

3p (2p enantiomer composition, 1p *ee* calculation)

ee:

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

α	β	γ
S	R	S

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.

$NaBH_4$, $LiAlH_4$, etc. 2p

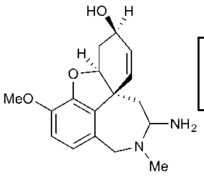
6.3.1. Give the formula for compound **Y** to carry out the first step of the route.

Y

CH_3NH_2 2p

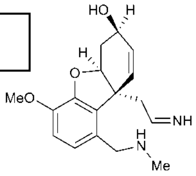
6.3.2. Suggest structures for **J** and **K**.

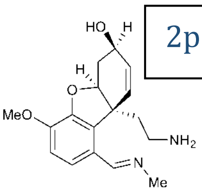
J



4p

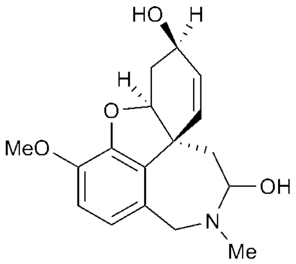
3p





2p

K



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

Problem 7 8% of the total

7.1.	7.2.	7.3.1.	7.3.2.	7.4.	Sum
2	36	16	8	4	66

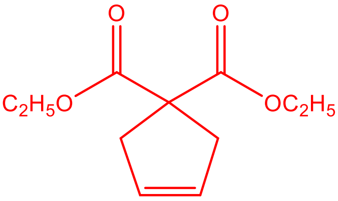
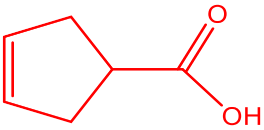
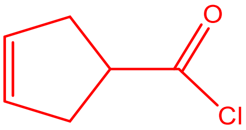
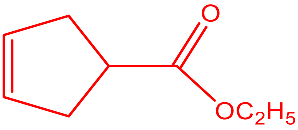
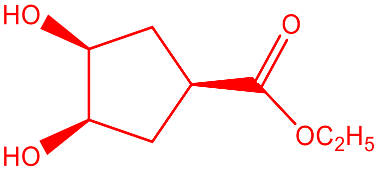
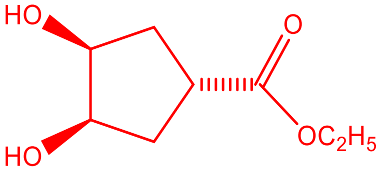
7.1. Determine the empirical formula of **G** from the percentage masses given.

Your work:

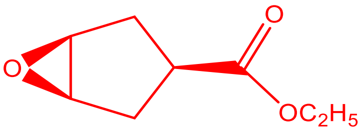
C_2H_3O

2p (1p for molecular formula)

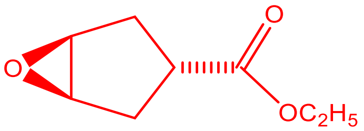
7.2. Give the structures of **A**, **B**, **C**, **D**, **E1**, **E2**, **F1**, **F2** and **G**.

<table>
<tr><td>A

4p (0pt if still contains Cl)
(2p penalty if H^- is used as reducing agent)</td><td>B

4p (2pt if no de-carboxylation)
(2p in mono-ester)</td></tr>
<tr><td>C

4p (allow carry forward from B)</td><td>D

4p (0p if remade A)
(1p if pyridinium intermediate)</td></tr>
<tr><td colspan="2">E1 and E2
 and 
4p each (1p if OHs on different sides)
(2p if no de-carboxylation; 1p if osmate ester)</td></tr>
</table>

F1 and **F2**



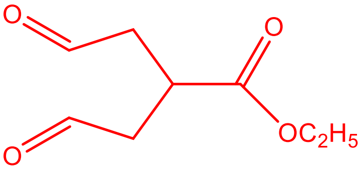
and



4p each

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

G

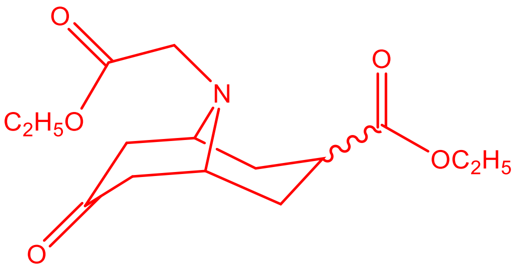


4p

(0p if does not fit formula)

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

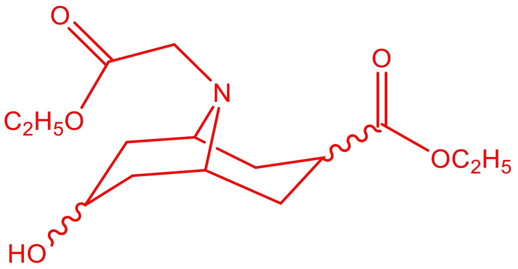
H



8p

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

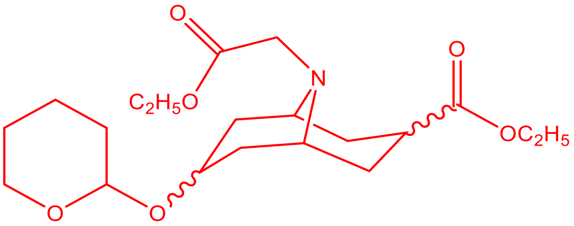
I



4p

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

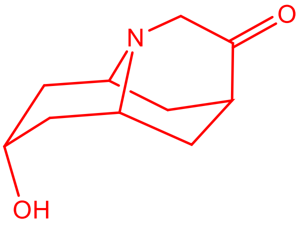
J



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

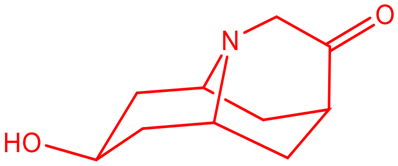
7.3.2 Give the structures of diastereoisomers **K1**, and **K2**.

K1



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

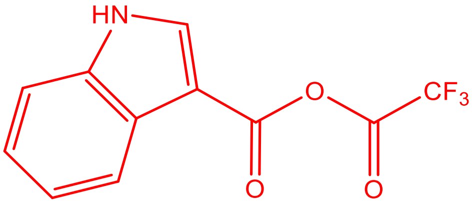
K2



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

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

N



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

Problem 8 7% of the total

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

8.1.1. Which of the following sentences is true?

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

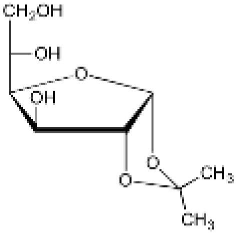
8.1.2. Which of the following sentences is true?

☐ 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.

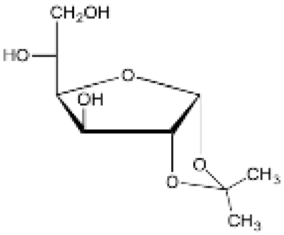
8.1.3. Which one of these reagents can be utilized as **X** for the selective hydrolysis of **A**?

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

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



☐

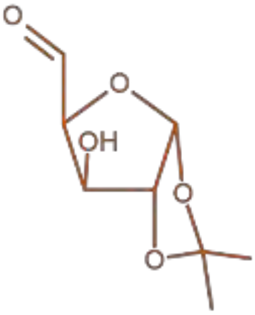
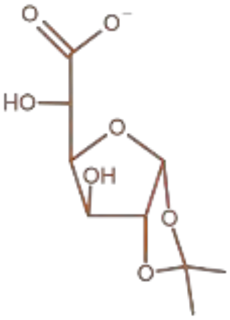
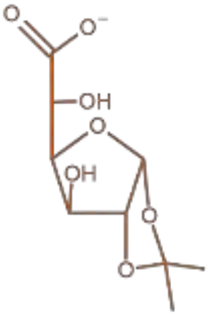
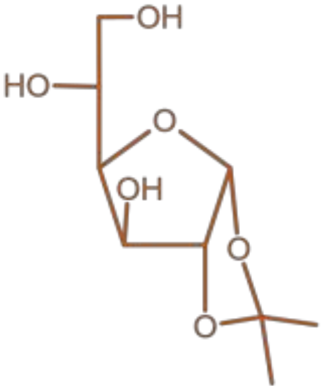
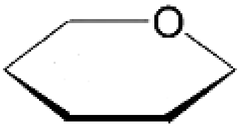
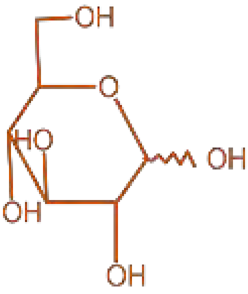


(x) ☐

Neither of these

☐

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.

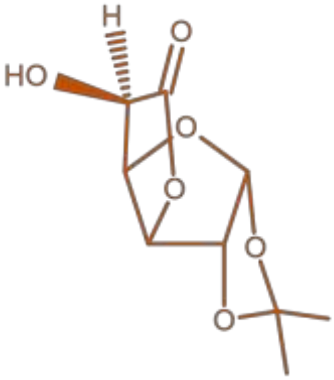
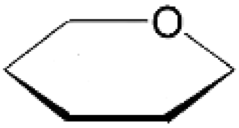
C 	**D**$_1$ 
D$_2$ 	**E** 
F 	

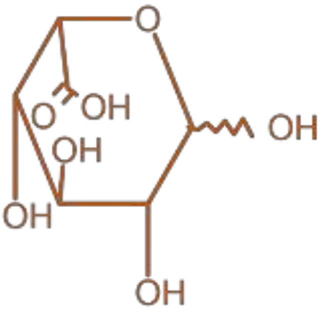
2p for each correct structure
1p for structures with one minor error (e.g. wrong configuration)
0p for more minor mistakes or a more serious one (COOH->COH, unidentifiable chiral center)
1-1p if D$_1$ and D$_2$ swapped
2p if –COOH in D

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

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

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

G	**H**
	



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

(x)☐ both junctions cis
☐ one cis and one trans junction
☐ both junctions trans

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

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

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

References

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

Problem 1

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

Problem 2

Figure is from:

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

Problem 4

Figures are adapted from:

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

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

Problem 6

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

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

Problem 8

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