



48<sup>th</sup> 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  $\text{NF}_3$ .



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

1.2. Which of  $\text{NF}_3$ ,  $\text{NHF}_2$  or  $\text{NH}_2\text{F}$  compound is expected to condense at the lowest temperature?

$\text{NF}_3$       $\text{NHF}_2$       $\text{NH}_2\text{F}$       $\text{NF}_3$

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

Molecule	$\text{NH}_2\text{F}$	$\text{NHF}_2$	$\text{NF}_3$
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.



2p (1p  $\text{N}_2\text{F}_2$ , 1p equation)

1.5. Propose a suitable reagent for the formation of  $\text{NF}_4^+$  and write a balanced chemical equation for the reaction.



2p (1p species, 1p coefficients)

1.6. Write a balanced chemical equation for the hydrolysis of  $\text{NF}_4^+$ .



2p (1p species, 1p coefficients)

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



2p (1p species, 1p coefficients)

1.7. Determine the formula of the salt in question.

Your work:

From the  $\text{NF}_3:\text{F}_2$  ratio it is clear that the anion also contains fluorine. Moreover, the starting  $\text{NF}_4^+$ : liberated  $\text{F}_2$  ratio is 1:2, and all fluorine content is released. With a  $(\text{NF}_4)_x\text{AF}_y$  composition,  $x:y = 1:4$ .

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

With  $x=1$ , the atomic mass of **A** is close to zinc, but not all fluorine would be released with Zn. If  $x=2$ , then the element is xenon, and the formula is  $(\text{NF}_4)_2\text{XeF}_8$

3p (1.5p for Zn)

Formula:



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  $\text{Cu}_{2-x}\text{O}$  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)  $2 \text{Cu}_2\text{O} + \text{O}_2 \rightarrow 4 \text{CuO}$  (copper(II)-hydroxides and carbonates accepted)

Reaction

(2)  $\text{Cu}_2\text{O} + 2 \text{H}^+ \rightarrow \text{Cu} + \text{Cu}^{2+} + \text{H}_2\text{O}$

Reaction

(3)  $\text{Cu}_2\text{O} + \text{H}_2\text{SO}_4 + 4 \text{H}^+ \rightarrow 2 \text{Cu}^{2+} + \text{SO}_2 + 3 \text{H}_2\text{O}$

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

$\Delta_r G = 142000 \text{ J mol}^{-1} - 96 \text{ J mol}^{-1} \text{ K}^{-1} T$

The Gibbs energy of the reaction is negative above 1480 K.

CuO is stable below 1480 K,  $\text{Cu}_2\text{O}$  above 1480 K.

6 p (1 for each  $\Delta G$  or equivalent calculation, 1 for each conclusion)

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Temperature range between 500-1500K	The most stable form (Cu, Cu <sub>2</sub> O or CuO)

- 2.5. Write the half reaction equations for the electrode processes during the anodic production of Cu<sub>2</sub>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: $2 \text{Cu} + 2 \text{OH}^- \rightarrow \text{Cu}_2\text{O} + \text{H}_2\text{O} + 2\text{e}^-$
	2p

- 2.6.1. Write the half reaction equation of the cathode process giving Cu<sub>2</sub>O in acidic medium.

$2 \text{Cu}^{2+} + \text{H}_2\text{O} + 2 \text{e}^- \rightarrow \text{Cu}_2\text{O} + 2 \text{H}^+$
1p

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

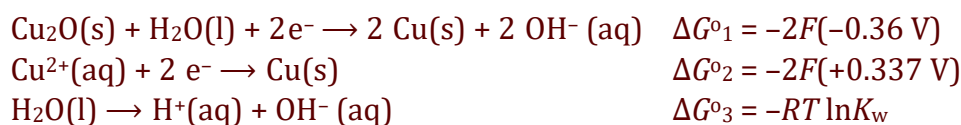
<p>Your work:</p> <div style="border: 1px solid black; padding: 10px; margin: 10px 0;"> <p style="color: red;">If the pH is too high, Cu(OH)<sub>2</sub> precipitates.</p> <p style="color: red;"><math>K_{\text{sp}} \geq 0.1[\text{OH}^-]^2 \quad \Rightarrow \quad \text{pH} \leq 5.15</math></p> <p style="color: blue;">3 p (1p realizing that precipitation occurs, 1p equation, 1p result)</p> </div> <p>maximum pH</p>
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2.6.3. What is the minimum pH at which the cathodic production of Cu<sub>2</sub>O in a 0.100 mol dm<sup>-3</sup> Cu<sup>2+</sup> solution is still possible?

Your work:

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

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



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

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

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

The concentration dependence of the cathodic Cu<sub>2</sub>O production potential:

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

This potential has to be higher than the potential of the reduction of Cu<sup>2+</sup>.

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

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

$$\text{pH} = 2.69$$

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.



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.



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:

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

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

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

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

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,  $5.0 \mu\text{mol}$  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  $n(Ag^+) \leq 10.0 \mu\text{mol}$

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

$K_{spI}$ :

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

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  $\text{AgCl}(s)$  first precipitates (estimated at  $11.8 \mu\text{mol Ag}^+$  added) to calculate  $K_f$ . At this point,  $[\text{Ag}^+] = 1.6 \cdot 10^{-9} \text{ mol/dm}^3$ ,  $[\text{Cl}^-] = 0.100 \text{ mol/dm}^3$  (see above).

Almost all of the originally present  $1.0 \cdot 10^{-5} \text{ mol/dm}^3$  iodide has been precipitated out as  $9.9 \mu\text{mol AgI}$ , since  $[\text{I}^-] = K_{spI}/[\text{Ag}^+] = 1.0 \cdot 10^{-7} \text{ mol/dm}^3$

Total Ag in solution =  $11.8 \mu\text{mol} - 9.9 \mu\text{mol} = 1.9 \mu\text{mol}$

$[\text{AgCl}_2^-] = 1.9 \cdot 10^{-6} \text{ mol/dm}^3$  (since free  $[\text{Ag}^+]$  is only  $1.6 \cdot 10^{-9} \text{ mol/dm}^3$ )

$$K_f = \frac{[\text{AgCl}_2^-]}{[\text{Ag}^+][\text{Cl}^-]^2} = \frac{1.9 \cdot 10^{-6}}{1.6 \cdot 10^{-9} \cdot 0.100^2} = 1.2 \cdot 10^5 \quad [1.9 \cdot 10^4 \text{ given const.}]$$

Same approach works for  $11 \mu\text{mol Ag}^+$  added.

2p for selecting a data point between  $10\text{-}12.0 \mu\text{mol}$

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

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

Since  $\text{AgI}(s)$  is present,  $[\text{I}^-] = K_{spI}/[\text{Ag}^+] = 4.42 \cdot 10^{-7} \text{ mol/dm}^3$

The amount of dissolved iodine and silver is equivalent:

$$[\text{I}^-] = [\text{Ag}^+] + [\text{AgCl}_2^-] \Rightarrow [\text{AgCl}_2^-] = 4.42 \cdot 10^{-7} \text{ mol/dm}^3$$

$$K_f = \frac{[\text{AgCl}_2^-]}{[\text{Ag}^+][\text{Cl}^-]^2} = \frac{4.42 \cdot 10^{-7}}{3.62 \cdot 10^{-10} \cdot 0.100^2} = 1.2 \cdot 10^5 \quad [7.6 \cdot 10^5 \text{ given const.}]$$

$K_f$ :

- 3.3.1.** Write balanced net ionic equations for the reaction of cerium(IV) with  $\text{H}_3\text{AsO}_3$  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:



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:



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

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



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

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

- 3.3.2.** 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  $-\ln(A/A_0) \cdot (1/t)$ , which should be a constant ( $k_{\text{obs}}$ ) if the reaction is first-order:

$t, \text{s}$	$k_{\text{obs}}, \text{s}^{-1}, \text{Run 1}$	$k_{\text{obs}}, \text{s}^{-1}, \text{Run 2}$	$k_{\text{obs}}, \text{s}^{-1}, \text{Run 3}$
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  $k_{\text{obs}}$  is unchanged (within 10%) from run 1 to run 2 despite decreasing  $[\text{H}_3\text{AsO}_3]$  by a factor of two,  $m = 0$ .

In contrast, decreasing  $[\text{I}^-]$  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  $p = 1$ .

$k = k_{\text{obs}}/[\text{I}^-]$ , 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

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

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

Your work:

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

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

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

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  
 $(3.51 \cdot 10^{-7} \text{ mol iodine})(126.90 \text{ g/mol}) = 4.45 \cdot 10^{-5} \text{ g iodine}$   
 $\{(4.45 \cdot 10^{-5} \text{ g iodine})/(1.000 \text{ g salt})\} \cdot 10^6 \text{ ppm} = 44.5 \text{ ppm I}$

2p for calculating  $k_{\text{obs}}$ , 1p for  $[\text{I}^-]$  from  $k_{\text{obs}}$ , 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  $\text{K}_2\text{S}_2\text{O}_8$  is  $5.0 \cdot 10^{-6} \text{ mol/dm}^3$ . Assume that the rate law obtained from the data above is valid under these conditions.

Your work:

Trial1 and 2  $\Rightarrow$  the rate doubles when concentration of  $\text{K}_2\text{S}_2\text{O}_8$  is doubled.  
Order w.r.t.  $\text{K}_2\text{S}_2\text{O}_8 = 1$ .

Trial3 and 4  $\Rightarrow$  the rate does not change with concentration of dioxane.  
Order w.r.t. dioxane = 0.

Initial rate =  $k[\text{K}_2\text{S}_2\text{O}_8]$       Average  $k = 6.65 \cdot 10^{-3} \text{ min}^{-1}$

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

$[\text{K}_2\text{S}_2\text{O}_8]_0 = 5.00 \mu\text{mol dm}^{-3}$ ;  $[\text{K}_2\text{S}_2\text{O}_8]_t = 4.55 \mu\text{mol dm}^{-3}$

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

$t = 14.2$  minutes

5p (1p for each order, 1 p for  $k$ , 2p for final answer)

Oxidation time:

- 4.1.2. Assuming  $\text{Ag(III)}$  to be in steady state, deduce the rate equation for the oxidation of dioxane.

Your work:

$$k_1[\text{S}_2\text{O}_8^{2-}][\text{Ag}^+] - k_2[\text{SO}_4^{-2}]^2[\text{Ag}^{+3}] - k_3[\text{Ag}^{+3}][\text{D}] = 0$$

$$[\text{Ag}^{+3}] = \frac{k_1[\text{S}_2\text{O}_8^{2-}][\text{Ag}^+]}{k_2[\text{SO}_4^{-2}]^2 + k_3[\text{D}]}$$

$$\text{rate of oxidation} = \frac{k_1 k_3 [\text{S}_2\text{O}_8^{2-}][\text{D}][\text{Ag}^+]}{k_2 [\text{SO}_4^{-2}]^2 + k_3 [\text{D}]}$$

3p (1p for each step)

4.1.3.

A,C

2p, (1p penalty for every mistake)

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

Your work:

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

1p, (0.5p if  $[\text{OH}^-]$  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  $k_{\text{H}}$ ,  $k_0$  and  $k_{\text{OH}}$ . 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,  $[\text{OH}^-] = 0.01514 \text{ mol dm}^{-3}$

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

$$k_{\text{obs}} = k_0 + k_{\text{OH}}[\text{OH}^-] \quad k_0 \text{ can be neglected}$$

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

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

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

$$k_{\text{obs}} = k_{\text{H}}[\text{H}^+] + k_0 \quad k_0 \text{ cannot be neglected}$$

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

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

6p (1p for  $k_0$ , 2p for  $k_{\text{OH}}$ , 3p for  $k_{\text{H}}$ , 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

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

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

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:

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

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

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  $\text{SiO}_2$ .

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  $850^\circ\text{C}$ , 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  $0^\circ\text{C}$

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

The difference of 0.045 moles is probably water that has condensed. Hence, the mass of the gas at  $0^\circ\text{C}$  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  $\text{CO}_2$ .

The gas formed at  $850^\circ\text{C}$  contains 0.045 mol of  $\text{H}_2\text{O}$  and 0.136 mol of  $\text{CO}_2$ .

3p (0.5p for finding each compound, 1p for the quantity of each compound)

The gaseous mixture formed at  $850^\circ\text{C}$  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  $\text{SiO}_2$  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  $\text{CO}_2$ , the molar mass of **B** per carbonate group is  $9.05 \text{ g} / 0.0905 \text{ mol} = 100 \text{ g mol}^{-1}$ . The molar mass of  $\text{CO}_3$  group is  $60 \text{ g mol}^{-1}$ , so the mass of metal per carbonate group is  $40 \text{ g mol}^{-1}$ .

This corresponds to Ca, **B** –  $\text{CaCO}_3$

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  $17.8 \text{ g} / 0.0905 \text{ mol} = 197 \text{ g mol}^{-1}$ . The mass of metal per carbonate group is  $137 \text{ g mol}^{-1}$ .

This corresponds to Ba, **C** –  $\text{BaCO}_3$ .

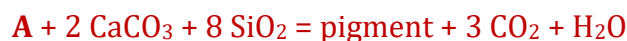
2p

**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:



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:

Chinese blue is:

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

Your work:

Upon heating **A** turns into 2 CuO, 1 CO<sub>2</sub> and 1 H<sub>2</sub>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.

BaSO<sub>4</sub> (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<sub>4</sub> is more stable than BaCO<sub>3</sub>.

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<sub>2</sub>O (mixing red with blue gives purple)

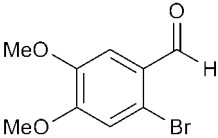
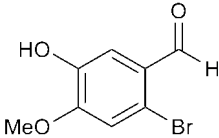
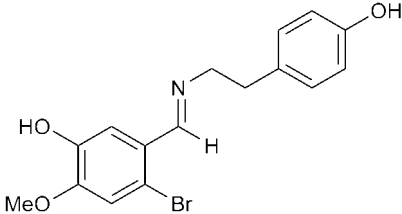
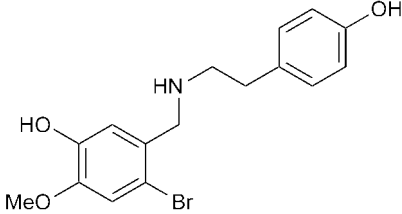
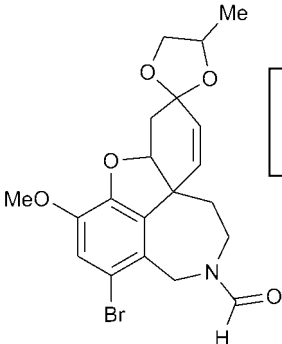
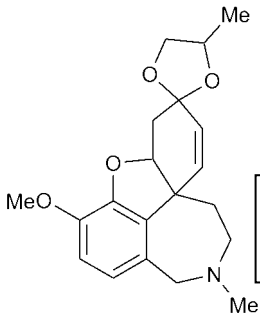
2p

# 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.

<p><b>A</b></p>  <div style="border: 1px solid black; padding: 5px; margin-top: 10px; color: red;">       0p if lacks 2 para protons     </div>	<p><b>B</b></p> 
<p><b>C</b></p> 	<p><b>D</b></p> 
<p><b>F</b></p>  <div style="border: 1px solid black; padding: 5px; margin-top: 10px; color: red;">       2p penalty if Br removed     </div>	<p><b>G</b></p>  <div style="border: 1px solid black; padding: 5px; margin-top: 10px; color: red;">       2p penalty if Br present     </div>

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

<p><b>X</b></p> <div style="border: 1px solid black; padding: 10px; margin-top: 10px; color: red;"> <math>\text{CH}_3\text{CH}_2\text{OCOH}</math> or any other reasonable reagent. 4p (3p for formyl chloride)            Formic acid = 0p         </div>
--

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:

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

$$x = 815/830$$

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

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

*ee*:

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

$\alpha$	$\beta$	$\gamma$
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.

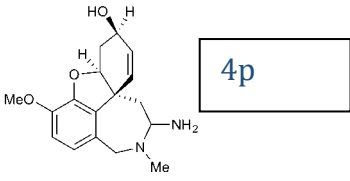
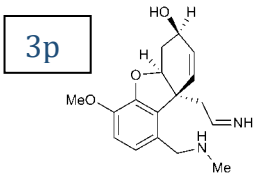
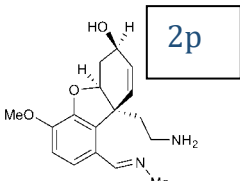
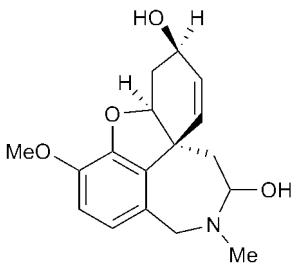
$\text{NaBH}_4$ ,  $\text{LiAlH}_4$ , etc. 2p

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

**Y**

$\text{CH}_3\text{NH}_2$  2p

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

<b>J</b>	<b>K</b>
  	

# 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

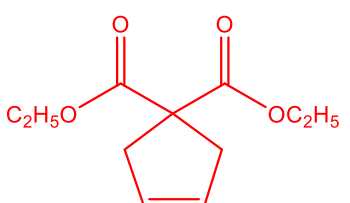
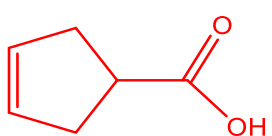
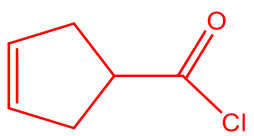
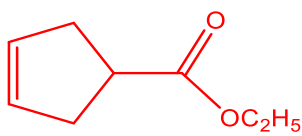
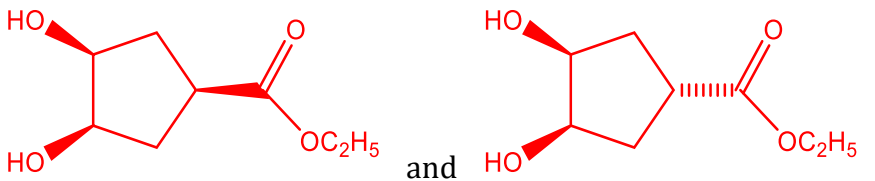
7.1. Determine the empirical formula of **G** from the percentage masses given.

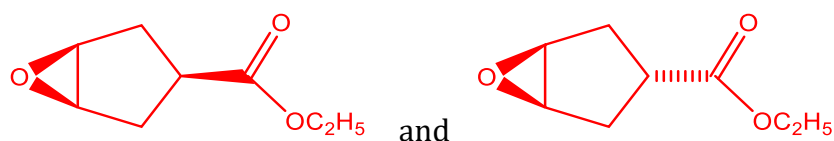
Your work:



2p (1p for molecular formula)

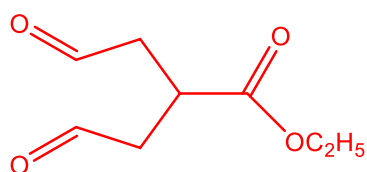
7.2. Give the structures of **A**, **B**, **C**, **D**, **E1**, **E2**, **F1**, **F2** and **G**.

<p><b>A</b></p>  <p>4p (0pt if still contains Cl) (2p penalty if H<sup>-</sup> is used as reducing agent)</p>	<p><b>B</b></p>  <p>4p (2pt if no de-carboxylation) (2p in mono-ester)</p>
<p><b>C</b></p>  <p>4p (allow carry forward from <b>B</b>)</p>	<p><b>D</b></p>  <p>4p (0p if remade <b>A</b>) (1p if pyridinium intermediate)</p>
<p><b>E1 and E2</b></p>  <p>4p each (1p if OHs on different sides) (2p if no de-carboxylation; 1p if osmate ester)</p>	

**F1 and F2**

4p each

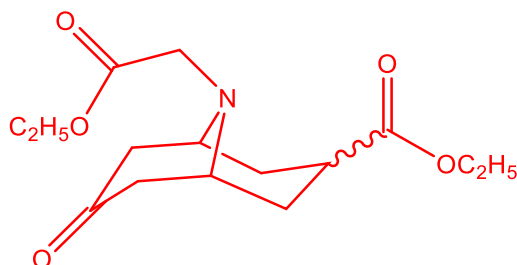
(1p if no de-carboxylation; 1p for trans-diol; 0p if no de-carboxylation and diol)

**G**

4p

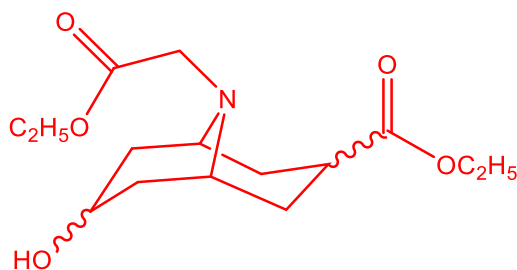
(0p if does not fit formula)

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

**H**

8p

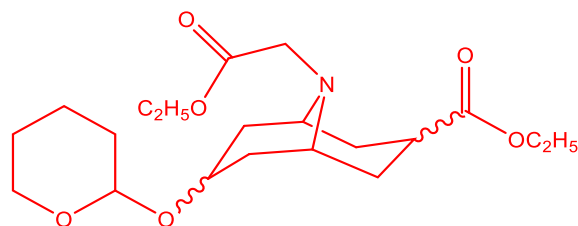
(points for fitting formula, sensible chemistry, correct number of possible diastereomers, and being achiral)

**I**

4p

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

J

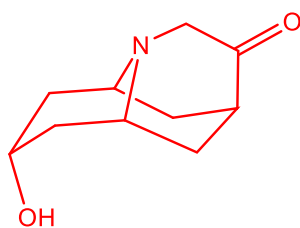


4p

(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)

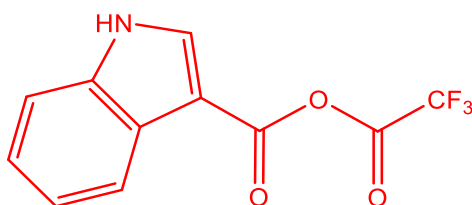
K2

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?

- A** is an  $\alpha$  isomer.                       **A** is neither  $\alpha$  nor  $\beta$ .  
 **A** is a  $\beta$  isomer.                                       **A** is a mixture of  $\alpha$  and  $\beta$  isomers.

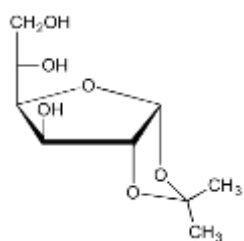
8.1.2. Which of the following sentences is true?

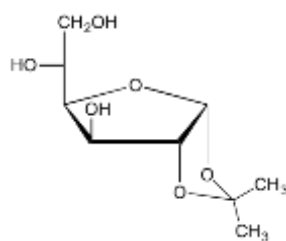
- We can get product **A** only if we use  $\alpha$ -D glucose as starting material.  
 We can get product **A** only if we use  $\beta$ -D glucose as starting material.  
 We can get product **A** either from  $\alpha$ - or from  $\beta$ -D glucose as starting material.

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

- 50% acetic acid                                       concentrated  $\text{H}_2\text{SO}_4$   
 6M HCl in water     1M NaOH in water  
 6M HCl in acetic acid

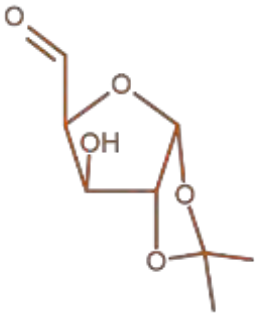
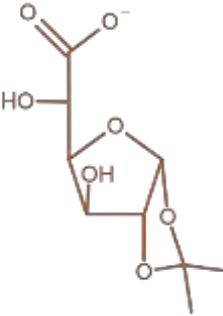
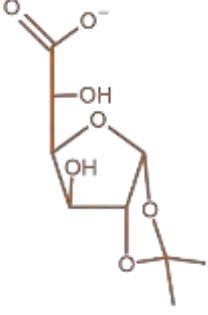
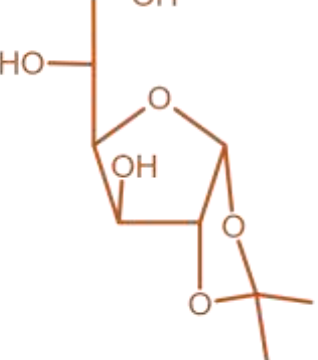
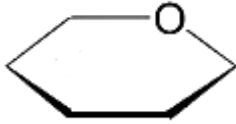
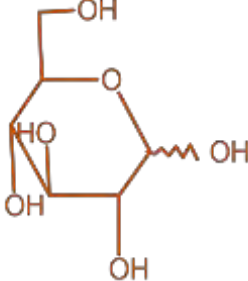
8.1.4. Which is the stereochemically correct structure for compound **B**?






Neither of these

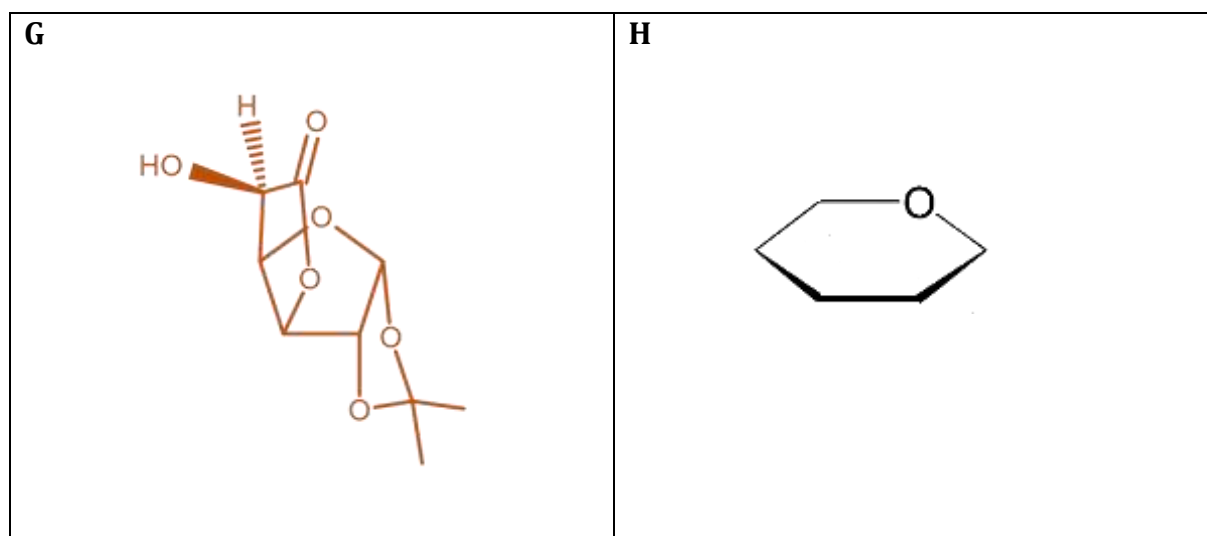
8.2.1. Draw the structures of **C**, **D**<sub>1</sub>, **D**<sub>2</sub>, **E** and **F** including stereochemical information. Show **F** as the more stable 6-membered ring containing isomer using the ring skeleton. Indicate with a wavy line if absolute chirality around a carbon is not known.

<p><b>C</b></p> 	<p><b>D1</b></p> 
<p><b>D2</b></p> 	<p><b>E</b></p> 
<p><b>F</b></p> 	 <p>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-&gt;COH, unidentifiable chiral center)  1-1p if D1 and D2 swapped  2p if -COOH in D</p>

**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?

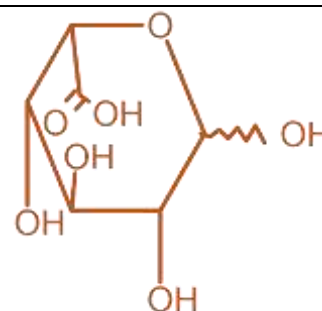
- (x)   $^{13}\text{C}$  labelling at carbon 6 of **F**  
  $^{13}\text{C}$  labelling at carbon 5 of **F**  
  $^{13}\text{C}$  labelling at carbon 1 of **F**  
  $^{15}\text{O}$  labelling at glycosidic OH of **F**  
 synthesis of an uncommon isomer of **F**

- 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?

- 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

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  $\text{Cu}_x\text{O}$  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. "Synthesis of L-Iduronic Acid and an Improved Production of L-Glucose-6-C<sup>14</sup>." *Journal of the American Chemical Society* 77 (9): 2568–69. doi:10.1021/ja01614a072.