

42nd INTERNATIONAL CHEMISTRY OLYMPIAD

2010

UK Round One

STUDENT QUESTION BOOKLET

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- The time allowed is 2 hours.
- Attempt all 6 questions.
- Write your answers in the special answer booklet.
- In your calculations, please write only the essential steps in the answer booklet.
- Always give the appropriate units and number of significant figures.
- You are provided with a copy of the Periodic Table.
- Do *NOT* write anything in the right hand margin of the answer booklet.

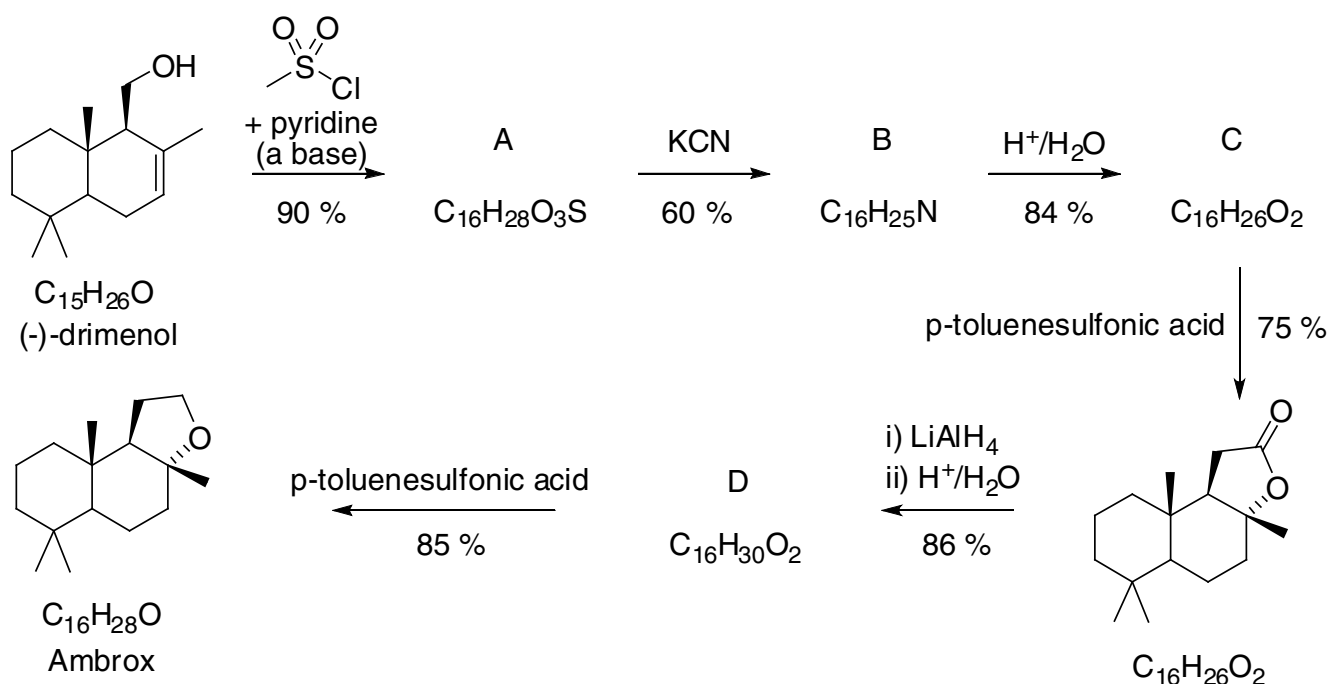
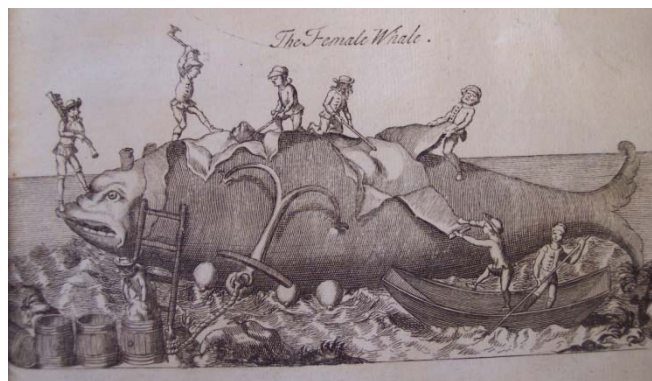
Some of the questions will contain material you will not be familiar with. However, by logically applying the skills you have learnt as a chemist, you should be able to work through the problems. There are different ways to approach the tasks – even if you cannot complete certain parts of a question, you may still find subsequent parts straightforward.

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<div>H</div> <div>1</div> <div>1.008</div>	2											13	14	15	16	17	<div>He</div> <div>2</div> <div>4.003</div>
<div>Li</div> <div>3</div> <div>6.94</div>	<div>Be</div> <div>4</div> <div>9.01</div>	<div>symbol</div> <div>atomic number</div> <div>relative atomic mass</div>										<div>B</div> <div>5</div> <div>10.81</div>	<div>C</div> <div>6</div> <div>12.01</div>	<div>N</div> <div>7</div> <div>14.01</div>	<div>O</div> <div>8</div> <div>16.00</div>	<div>F</div> <div>9</div> <div>19.00</div>	<div>Ne</div> <div>10</div> <div>20.18</div>
<div>Na</div> <div>11</div> <div>22.99</div>	<div>Mg</div> <div>12</div> <div>24.31</div>											3	4	5	6	7	8
<div>K</div> <div>19</div> <div>39.102</div>	<div>Ca</div> <div>20</div> <div>40.08</div>	<div>Sc</div> <div>21</div> <div>44.96</div>	<div>Ti</div> <div>22</div> <div>47.90</div>	<div>V</div> <div>23</div> <div>50.94</div>	<div>Cr</div> <div>24</div> <div>52.00</div>	<div>Mn</div> <div>25</div> <div>54.94</div>	<div>Fe</div> <div>26</div> <div>55.85</div>	<div>Co</div> <div>27</div> <div>58.93</div>	<div>Ni</div> <div>28</div> <div>58.71</div>	<div>Cu</div> <div>29</div> <div>63.55</div>	<div>Zn</div> <div>30</div> <div>65.37</div>	<div>Ga</div> <div>31</div> <div>69.72</div>	<div>Ge</div> <div>32</div> <div>72.59</div>	<div>As</div> <div>33</div> <div>74.92</div>	<div>Se</div> <div>34</div> <div>78.96</div>	<div>Br</div> <div>35</div> <div>79.904</div>	<div>Kr</div> <div>36</div> <div>83.80</div>
<div>Rb</div> <div>37</div> <div>85.47</div>	<div>Sr</div> <div>38</div> <div>87.62</div>	<div>Y</div> <div>39</div> <div>88.91</div>	<div>Zr</div> <div>40</div> <div>91.22</div>	<div>Nb</div> <div>41</div> <div>92.91</div>	<div>Mo</div> <div>42</div> <div>95.94</div>	<div>Tc</div> <div>43</div> <div></div>	<div>Ru</div> <div>44</div> <div>101.07</div>	<div>Rh</div> <div>45</div> <div>102.91</div>	<div>Pd</div> <div>46</div> <div>106.4</div>	<div>Ag</div> <div>47</div> <div>107.87</div>	<div>Cd</div> <div>48</div> <div>112.40</div>	<div>In</div> <div>49</div> <div>114.82</div>	<div>Sn</div> <div>50</div> <div>118.69</div>	<div>Sb</div> <div>51</div> <div>121.75</div>	<div>Te</div> <div>52</div> <div>127.60</div>	<div>I</div> <div>53</div> <div>126.90</div>	<div>Xe</div> <div>54</div> <div>131.30</div>
<div>Cs</div> <div>55</div> <div>132.91</div>	<div>Ba</div> <div>56</div> <div>137.34</div>	<div>La*</div> <div>57</div> <div>138.91</div>	<div>Hf</div> <div>72</div> <div>178.49</div>	<div>Ta</div> <div>73</div> <div>180.95</div>	<div>W</div> <div>74</div> <div>183.85</div>	<div>Re</div> <div>75</div> <div>186.2</div>	<div>Os</div> <div>76</div> <div>190.2</div>	<div>Ir</div> <div>77</div> <div>192.2</div>	<div>Pt</div> <div>78</div> <div>195.09</div>	<div>Au</div> <div>79</div> <div>196.97</div>	<div>Hg</div> <div>80</div> <div>200.59</div>	<div>Tl</div> <div>81</div> <div>204.37</div>	<div>Pb</div> <div>82</div> <div>207.2</div>	<div>Bi</div> <div>83</div> <div>208.98</div>	<div>Po</div> <div>84</div> <div></div>	<div>At</div> <div>85</div> <div></div>	<div>Rn</div> <div>86</div> <div></div>
<div>Fr</div> <div>87</div> <div></div>	<div>Ra</div> <div>88</div> <div></div>	<div>Ac⁺</div> <div>89</div> <div></div>															

*Lanthanides	Ce 58 140.12	Pr 59 140.91	Nd 60 144.24	Pm 61	Sm 62 150.4	Eu 63 151.96	Gd 64 157.25	Tb 65 158.93	Dy 66 162.50	Ho 67 164.93	Er 68 167.26	Tm 69 168.93	Yb 70 173.04	Lu 71 174.97
+Actinides	Th 90 232.01	Pa 91	U 92 238.03	Np 93	Pu 94	Am 95	Cm 96	Bk 97	Cf 98	Es 99	Fm 100	Md 101	No 102	Lr 103

1. This question is about a substitute for the perfume ingredient ambergris

Ambergris, a metabolic product of the sperm whale, was for many years one of the most valuable ingredients in fine fragrances. Recently, it has been replaced with synthetic equivalents such as Ambrox® which possesses a powerful amber-type fragrance. Many different research groups have proposed methods for synthesising Ambrox from natural products found in plants. A synthesis starting with (–)-drimenol extracted from the bark of the Chilean tree *Drimys winteri* is outlined below:



(a) Given that ten tonnes of Ambrox are produced every year, calculate the number of moles produced per year.

(b) Draw the structures of compounds **A** to **D**.

The yield of each step in the synthesis is shown beside the arrows in the scheme.

(c) (i) What is the overall percentage yield of Ambrox in this synthesis?

(ii) What mass of (–)-drimenol would be needed each year if all of the commercially synthesised Ambrox was made using this method?

(iii) Given that *Drimys winteri* bark contains 0.5 % by mass of (–)-drimenol calculate the mass of bark that would be needed each year if all of the commercially synthesised Ambrox was made using this method.

2. This question is about the analysis of a copper-containing complex.

In the practical exam for the 2009 International Chemistry Olympiad held in Cambridge, students were asked to analyse compound **X**, a compound containing copper(II). This compound consists of ions: the negatively charged ion is a complex ion containing copper, chlorine and oxygen. The positive counter ion in compound **X** is the tetramethylammonium ion, $(\text{CH}_3)_4\text{N}^+$. The students were asked to determine the formula of the negative ion, using two titrations.



The first titration was used to determine the proportion of copper ions in the complex. In this titration, the complex was reacted with EDTA solution. EDTA reacts with copper ions according to the equation:



The end-point of this titration was determined using an indicator called murexide, and one of the UK team found that 0.1000 g of **X** required 21.70 cm³ of 0.02000 mol dm⁻³ EDTA solution for complete reaction.

(a) Calculate the % by mass of copper in compound **X**.

The second titration determined the proportion of chloride ions in the complex. The chloride ions from the complex were titrated against 0.1000 mol dm⁻³ silver(I) nitrate solution, and the student found that 0.2000 g of **X** required 21.70 cm³ of silver nitrate.

(b) i) Give a balanced equation that shows the reaction that takes place in this titration.

ii) Calculate the % by mass of chlorine in compound **X**.

The proportions by mass of carbon, hydrogen and nitrogen in compound **X** were determined by combustion analysis. The results were found to be C 20.87%, H 5.17%, and N 5.96%.

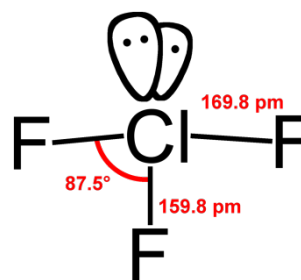
(c) i) Which of the six elements in compound **X** has the greatest percentage error in the determination of its proportion? Circle the element in the answer booklet.

ii) Ignoring this element, because of this uncertainty, determine the simplest whole number ratio of the remaining five elements in **X**.

iii) Hence determine the formula of the negative ion in **X**.

3. This question is about halogen fluorides

Chlorine trifluoride, ClF_3 , is one of the most reactive substances known: it causes sand and asbestos to explode and it reacts with xenon. It has been investigated as a rocket fuel; its reactions with every known fuel are so fast that no ignition delay has ever been measured.



- (a) ClF_3 is used to turn uranium into uranium hexafluoride, UF_6 , which is used to separate the isotopes of uranium. Chlorine monofluoride, ClF , is a side-product in this reaction. Write a balanced equation for the reaction between uranium and chlorine trifluoride.
- (b) ClF_3 is a powerful oxidising agent. In the answer booklet circle each atom / ion on the left hand side of the equation that is oxidised in the reaction between chlorine trifluoride and silver chloride.



Iodine forms the fluorides IF , IF_3 , IF_5 and IF_7 . Their standard enthalpy changes of formation are shown in the table.

	IF	IF_3	IF_5	IF_7
$\Delta_f H^\ominus / \text{kJ mol}^{-1}$	-95.4	-486	-843	-962.5

When the oxidation number of iodine is between 0 and +7 there is a possibility that it will disproportionate to the compound with iodine in its next highest oxidation number, and elemental iodine. For example, IF_3 might disproportionate to give IF_5 and I_2 .

- (c) i) Give the equations for the theoretical disproportionation reactions of IF , IF_3 and IF_5 .
- ii) Calculate the standard enthalpy change for each of these reactions.
- iii) Only one of IF , IF_3 and IF_5 , does not disproportionate – suggest which one.

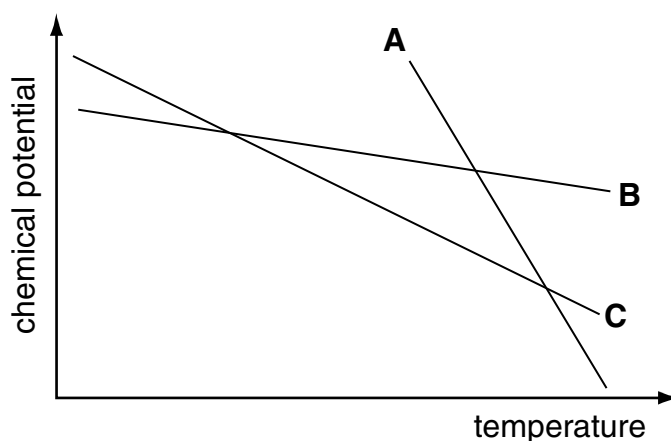
4. This question is about salting roads in winter

In winter in the U.K. a lot of money is spent on gritting roads to keep them safe during cold weather. The salt that is applied melts the ice. This question looks at the chemistry behind the salting.

The freezing point of a solution differs from that of pure water and is one of a number of so-called *colligative properties* of a solution. These are properties that, to a good approximation, depend only on the relative number of solute molecules or ions dissolved in the solution but not on their properties. Which phase exists at which temperature depends on a quantity called the chemical potential (μ). The phase with the lowest chemical potential is the most stable.



The graph below is a sketch of how the chemical potential of the three phases of pure water varies with temperature at standard pressure; each line shows how the chemical potential varies for one of the phases of water – solid, liquid, or gas.



(a) i) Which line corresponds to which phase of pure water?

ii) Mark in the appropriate places on the graph in the answer booklet the values of two temperatures that you know exactly.

The presence of salt affects the chemical potential. It is assumed that the salt dissolves only in the liquid phase of water and so the chemical potentials of the solid and gaseous phases are not affected by the salt. In the liquid phase, the chemical potential of a salt solution at a particular temperature is given by the expression below, where x_w is the fraction of water in the salt solution (in terms of moles), R is the gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$), and T is the temperature in Kelvin.

$$\mu_{\text{(solution)}} = \mu_{\text{(pure water)}} + RT \log_e x_w$$

- (b) i)** Sketch a line on a graph in the answer booklet that corresponds to the chemical potential of a salt solution.
- ii)** Hence circle in the answer booklet how the boiling point of a salt solution will compare to that of pure water:

lower than water

the same as water

higher than water

For the purpose of the following calculations, the mole fraction of ions, x_i , is given by:

$$x_i = \frac{\text{number of moles of anions} + \text{number of moles of cations}}{\text{number of moles of water} + \text{number of moles of cations} + \text{number of moles of anions}}$$

- (c) i)** Given the density of pure water is 1.00 g cm^{-3} , work out its concentration in mol dm^{-3} .
- ii)** Calculate the mole fraction of ions (x_i) in a 3.00 mol dm^{-3} solution of sodium chloride. You may assume there is no volume change upon dissolving the salt in water.

The freezing point of salt solutions of various concentrations can be estimated using the following expression,

$$\Delta T = \frac{x_i R T_m^2}{\Delta_m H^\circ}$$

where ΔT is the depression in freezing point

x_i is the mole fraction of ions

T_m is the melting point of pure water in Kelvin = 273 K

$\Delta_m H^\circ$ is the standard enthalpy change of melting for pure water = 6.01 kJ mol^{-1}

R is the gas constant = $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$.

- (d) i)** Calculate ΔT and hence the freezing point of a 3.00 mol dm^{-3} solution of sodium chloride.
- ii)** In reality, the salt is often present in excess on the roads and so the maximum freezing point depression is limited by the maximum solubility of the salt in water at low temperatures. The most concentrated solutions of sodium chloride remain liquid down to temperatures of -21.1°C . What concentration of sodium chloride is this?

In Russia, temperatures are so low that sodium chloride is unable to keep roads ice-free and calcium chloride is used instead. In a calcium chloride solution water molecules become strongly coordinated to the calcium ions and so are no longer free in solution. On average, 9 molecules of water are bound per calcium ion. These bound water molecules are no longer counted towards the number of moles of water in the mole fraction calculation but you may still assume there is no volume change upon dissolving the salt in water.

- (e)** Calculate the freezing point of a 3.00 mol dm^{-3} solution of calcium chloride.

5. This question is about the metal osmium in organic reactions

In 2004 it was reported that a terrorist attack that planned to use osmium tetroxide (OsO_4) had been foiled. However, although osmium tetroxide is highly toxic, it is unlikely to be used for such a purpose due to the high cost of this rare element (around £100 per gram of OsO_4). Nonetheless, osmium compounds are used in certain organic reactions.

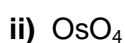
NATURAL HISTORY OF OSMIUM.

THIS is another new metal discovered by Mr. Tennant. The name of osmium is given to it on account of the oxid of it being exceedingly volatile, and diffusing, on being volatilized, a peculiar pungent odour. This metal likewise exists in the black powder, mixt with the ore of platina.

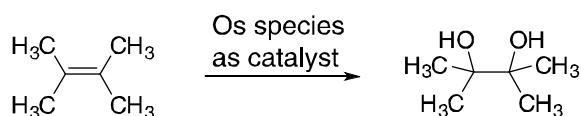
From "System of Theoretical and Practical Chemistry" by Fredrick Accum, 1808

In aqueous solution, osmium can exist as a number of species.

(a) Write down the oxidation number of the osmium atom in the following species:



An osmium species is able to catalyse the following transformation of an alkene into a diol where the two OH groups are on adjacent carbon atoms.

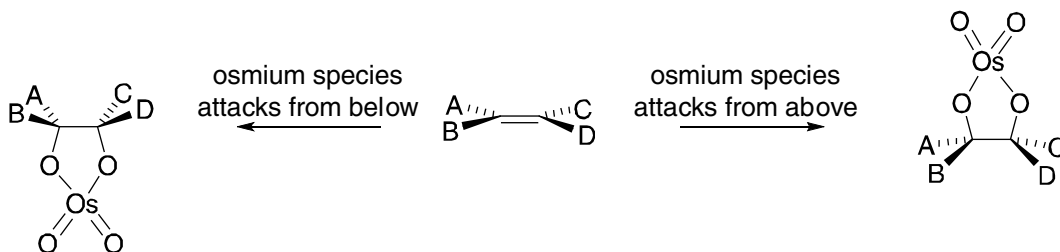


(b) How would you classify the reaction above? Circle the correct answer in the answer booklet.

Hydration Dehydration Oxidation Reduction Isomerisation

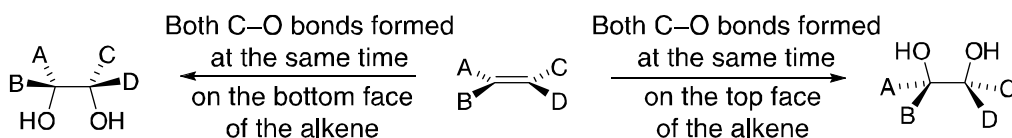
(c) Only one of the osmium species in part (a) is able to catalyse this reaction. Based on your classification of the reaction in part (b), which one of the osmium species do you think is used as the catalyst?

This reaction is very useful as there is a precise stereochemical outcome due to the way that the new C–O bonds are formed. Both new C–O bonds are formed simultaneously on the same face of the double bond. The first step is the formation of a cyclic compound where the osmium species can attack the double bond on either face.

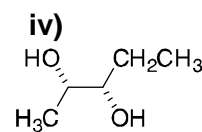
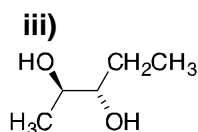
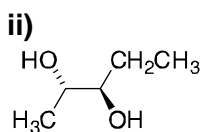
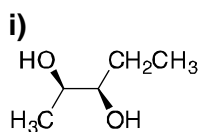


(d) What is the oxidation number of the osmium atom in the cyclic species?

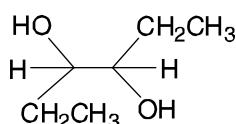
After hydrolysis, the new OH bonds end up either both on the top face, or both on the bottom face. This means that only certain stereoisomers can be formed.



- (e) The diol below can exist as four possible stereoisomers. For each one, draw the alkene that would need to be treated with the osmium species to form that stereoisomer.



- (f) i) How many stereoisomers are there for the following diol?

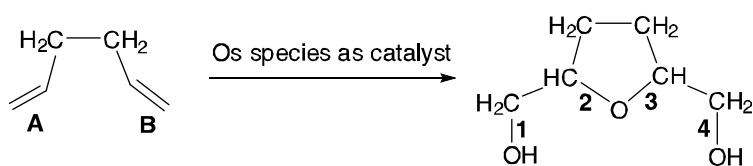


Circle in the answer booklet:

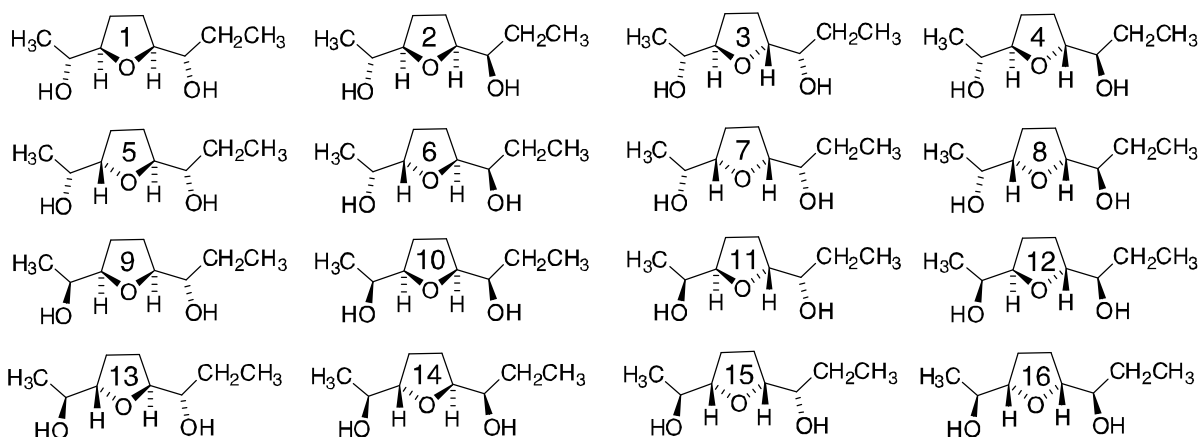
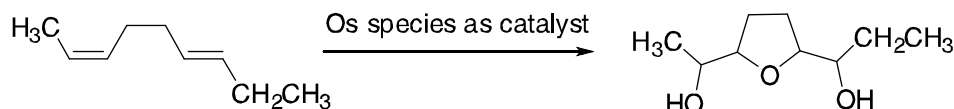
1 2 3 4

- ii) Draw the structure of each stereoisomer and the corresponding alkene needed to make it.

In certain molecules with two double bonds it is possible for one of the oxygens that is added to end up bonded to two carbon atoms, and in doing so form a ring. This reaction has a defined stereochemical outcome as well. Of the four new C-O bonds that are formed, bonds **1** and **2** are formed simultaneously on the same face of double bond **A**, and bonds **3** and **4** are formed simultaneously on the same face of double bond **B**.



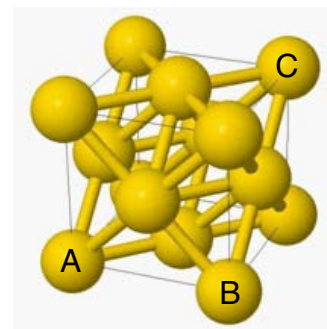
- (g) The cyclic product from the reaction of the following molecule with the appropriate osmium species can exist as 16 stereoisomers. In the answer booklet write the numbers of the stereoisomers that can be formed from this reaction given the information above.



6. This question is about gold leaf



Gold atoms crystallise in the cubic arrangement shown in the figure on the right. The gold atoms, which are assumed to be spherical, are shown at half-radius size (rather than touching their neighbours) to illustrate the structure more clearly. The lattice structure can be built up from these cubic 'building blocks' – known as unit cells. Atoms are located at the corner positions and in the centre of the faces. The cube is shown as a thin outline; the thicker 'bonds' indicate which atoms are, in reality, in contact.



Avogadro's constant is $6.02 \times 10^{23} \text{ mol}^{-1}$. Gold has only one isotope, which has a relative mass of 197. The density of gold is 19.3 g cm^{-3} .

- (a) Calculate the mass (in g) of one gold atom.

The cube shown in wireframe in the figure has its corners at the centre of the atoms occupying those corner positions. The faces of the cube pass through the centre of the atoms found in the centre of the faces.

- (b) By considering the fraction of each atom actually inside the unit cell, calculate the number of atoms within the unit cell.
- (c) Bearing in mind that the atoms are in contact across the diagonal of a face of the cube, find expressions, in terms of the radius of the gold atom, r , for :
- i) the length of the edge of the unit cell, i.e. the distance between the centres of atoms **A** and **B**;
 - ii) the volume of the unit cell;
 - iii) the length of the *unit cell body diagonal*, i.e. the distance between the centres of the atoms **A** and **C**.
- (d) Calculate the molar volume of gold in $\text{cm}^3 \text{ mol}^{-1}$.
- (e) Given that the volume of a sphere is $\frac{4}{3} \pi r^3$, calculate what fraction of the volume of the unit cell is occupied by gold atoms.
- (f) Bearing in mind your answer to part (e), calculate the radius of a gold atom.


A small mass of gold can be hammered out to cover an extremely large area with gold foil. The most efficient way of stacking layers of gold atoms has three layers in the length of the unit cell body diagonal, i.e. the thickness of one layer is one third of the distance **A** to **C**.

- (g) The great golden *Dome of the Rock* in Jerusalem is a hemisphere of diameter 21 m. The late King Hussein of Jordan donated 80 kg of gold to cover the outside of the dome.
- i) Given that the surface area of a sphere is $4\pi r^2$, calculate the average thickness in cm of the gold on the dome.
 - ii) Hence calculate the average number of layers of gold atoms covering the surface of the dome.

Acknowledgements & References

References for questions

- Q1 *Formal Synthesis of Ambrox and 9-epiambrox*
M. Cortés, V. Armstrong, M. E. Reyes, J. López and E. Madariaga
Synthetic Communications 26(10) 1996
- Q5 *A General Oxidative Cyclisation of 1,5-Dienes*
T. J. Donohoe and S. Butterworth
Angewandte Chemie Int Ed. Engl. 2003, 42, 948-951.
- Q6 Picture of the Dome of the Rock from flickr
www.flickr.com/photos/battyward/2050268080

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