

**38th INTERNATIONAL
CHEMISTRY OLYMPIAD**

2006

UK Round One

STUDENT QUESTION BOOKLET

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- **The time allowed is 2 hours.**
- **Attempt all 7 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.

| | | | | | | | | | | | | | | | | | | | | |
|---------------------------|---------------------------|--|---------------------------|---------------------------|--------------------------|--------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|------------------------|------------------------|--------------------------|
| H 1 1.008 | | | | | | | | | | | | | | | | | He 2 4.003 | | | |
| Li 3 6.94 | Be 4 9.01 | <table border="1"> <tr> <td>symbol</td> </tr> <tr> <td>atomic number</td> </tr> <tr> <td>mean atomic mass</td> </tr> </table> | | | | | | | | | | symbol | atomic number | mean atomic mass | B 5 10.81 | C 6 12.01 | N 7 14.01 | O 8 16.00 | F 9 19.00 | Ne 10 20.18 |
| symbol | | | | | | | | | | | | | | | | | | | | |
| atomic number | | | | | | | | | | | | | | | | | | | | |
| mean atomic mass | | | | | | | | | | | | | | | | | | | | |
| Na 11 22.99 | Mg 12 24.31 | | | | | | | | | | | Al 13 26.98 | Si 14 28.09 | P 15 30.97 | S 16 32.06 | Cl 17 35.45 | Ar 18 39.95 | | | |
| K 19 39.102 | Ca 20 40.08 | Sc 21 44.96 | Ti 22 47.90 | V 23 50.94 | Cr 24 52.00 | Mn 25 54.94 | Fe 26 55.85 | Co 27 58.93 | Ni 28 58.71 | Cu 29 63.55 | Zn 30 65.37 | Ga 31 69.72 | Ge 32 72.59 | As 33 74.92 | Se 34 78.96 | Br 35 79.904 | Kr 36 83.80 | | | |
| Rb 37 85.47 | Sr 38 87.62 | Y 39 88.91 | Zr 40 91.22 | Nb 41 92.91 | Mo 42 95.94 | Tc 43 | Ru 44 101.07 | Rh 45 102.91 | Pd 46 106.4 | Ag 47 107.87 | Cd 48 112.40 | In 49 114.82 | Sn 50 118.69 | Sb 51 121.75 | Te 52 127.60 | I 53 126.90 | Xe 54 131.30 | | | |
| Cs 55 132.91 | Ba 56 137.34 | La* 57 138.91 | Hf 72 178.49 | Ta 73 180.95 | W 74 183.85 | Re 75 186.2 | Os 76 190.2 | Ir 77 192.2 | Pt 78 195.09 | Au 79 196.97 | Hg 80 200.59 | Tl 81 204.37 | Pb 82 207.2 | Bi 83 208.98 | Po 84 | At 85 | Rn 86 | | | |
| Fr 87 | Ra 88 | Ac⁺ 89 | | | | | | | | | | | | | | | | | | |

| | | | | | | | | | | | | | | |
|---------------------|---------------------------|---------------------------|---------------------------|-----------------|--------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|
| *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 sherbet lemons

Sherbet lemons are sweets which consist of a flavoured sugar shell filled with sherbet.

The sherbet contains sodium hydrogencarbonate and tartaric acid (2,3-dihydroxybutanedioic acid).



- (a) Assuming all the sugar present is sucrose, $C_{12}H_{22}O_{11}$, write an equation for the complete combustion of the sugar.
- (b) The standard enthalpy change of combustion of sucrose is $-5644 \text{ kJ mol}^{-1}$. Calculate the energy released when one sweet containing 6.70 g of sucrose is completely burnt.
- (c) A man needs to consume about 2500 dietary calories per day. Given that $1 \text{ kJ} \equiv 0.239$ dietary calories, how many sweets must a man consume in order to meet his daily calorific requirement?

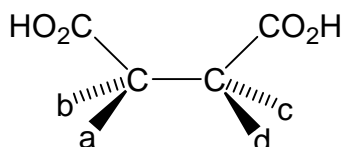
Sherbet produces a slight fizzing sensation in the mouth when the tartaric acid reacts with the sodium hydrogencarbonate to make carbon dioxide. In a laboratory experiment, one sherbet lemon sweet produced 6.00 cm^3 of carbon dioxide.

- (d) Calculate the minimum masses of tartaric acid and sodium hydrogencarbonate necessary to produce this volume of carbon dioxide.

[Assume 1 mol of any gas occupies 24.0 dm^3 at r.t.p.]

A carbon atom bonded to four different groups is called a chiral centre or an asymmetric carbon atom. A molecule which contains just one chiral centre exists as two stereoisomers (isomers containing the same groups attached to the same atoms). These stereoisomers are non-superimposable mirror images of each other called *enantiomers*. If a molecule contains more than one chiral centre, the number of stereoisomers increases and some of the stereoisomers may be superimposable on their mirror images.

- (e) By making the appropriate substitutions for **a**, **b**, **c**, and **d** in the structure shown below, draw all the different stereoisomers of tartaric acid, indicating clearly which (if any) are enantiomers.



- (f) Citric acid is used to flavour sherbet lemons. Its formula may be written $\text{HOOCCH}_2\text{C}(\text{OH})(\text{COOH})\text{CH}_2\text{COOH}$. How many asymmetric carbon atoms does this molecule contain?

2. This question is about the redox chemistry of vehicle pollution

The unwanted pollutants from the exhausts of vehicles include unburnt hydrocarbons (HCs), carbon monoxide and oxides of nitrogen, mainly NO and NO₂.

The first two pollutants arise if there is insufficient oxygen present to oxidise them fully. The oxides of nitrogen are formed in larger quantities if too much oxygen is present.



- (a) Write an equation for the complete combustion of petrol, assuming that the only hydrocarbon present is octane, C₈H₁₈.

Any unburnt hydrocarbons and carbon monoxide may be removed by being oxidised, either by oxygen or water. Platinum and / or palladium metal is used to catalyse these oxidation reactions.

- (b) Write an equation for the oxidation of CO by **i)** oxygen and **ii)** water.

The nitrogen oxides must be removed by being reduced to nitrogen gas. Any carbon monoxide present can accomplish this, as can any hydrogen gas present. These reduction reactions are catalysed by rhodium metal.

- (c) Write an equation for the reduction of NO by **i)** carbon monoxide and **ii)** hydrogen.

To help maintain a stable oxygen : fuel ratio, so-called 'oxygen-storage materials' are used. One commonly used is ceria which exists as an equilibrium mixture of cerium(III) and cerium(IV) oxides.

- (d) Write an equation for this equilibrium. (The symbol for cerium is Ce.)

The combustion of diesel is less efficient than that of petrol. Despite an excess of oxygen, unburnt hydrocarbons, CO and even solid carbon are produced. Whilst the first two pollutants may be removed as before in the catalytic converter, the carbon formed would simply block it up were it not removed. At the operating temperatures within the catalyst, very little of the carbon reacts with oxygen; it is, however, oxidised by nitrogen dioxide, NO₂, forming CO₂ and NO.

- (e) Write an equation for the reaction between carbon and NO₂.

In order to remove the oxides of nitrogen emitted from the catalyst, further reducing agent is added. One such reducing agent is ammonia, prepared by the decomposition of an aqueous solution of urea, H₂NCONH₂. The urea solution is known commercially as 'AdBlue'.



- (f) Draw the structure for urea indicating the approximate angles for the N–C–O and the H–N–H bonds.

- (g) Write an equation for the production of ammonia from urea and water.

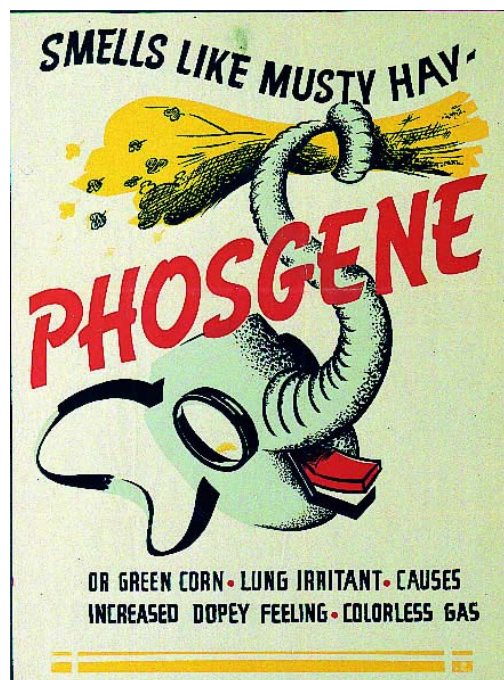
- (h) Write an equation for the reaction between ammonia and **i)** NO and **ii)** NO₂.

- (i) On your answers for parts **b**, **c**, **d**, **e** and **h** underline with a single line the atom(s) which undergo oxidation and underline with a double line those atom(s) which undergo reduction.

3. This question is about acyl chlorides and related functional groups

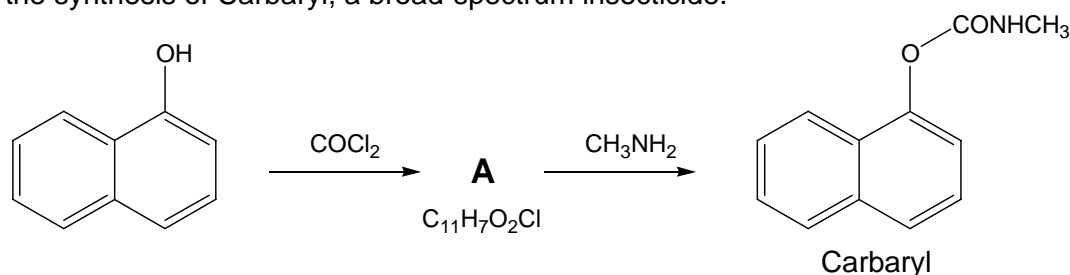
Acyl chlorides, RCOCl , are highly reactive compounds which rapidly react with water to give carboxylic acids, and with alcohols to give esters.

Other oxochlorides containing bonds to chlorine and double bonds to oxygen such as phosphoryl chloride (phosphorus trichloride oxide, POCl_3) and thionyl chloride (sulfur dichloride oxide, SOCl_2) react in an analogous fashion.



- (a) Write a balanced equation for the reaction between ethanoyl chloride and water.
- (b) Write a balanced equation for the reaction of propanoyl chloride with ethanol.

Phosgene (carbonyl chloride, COCl_2), which can be thought of as a diacyl chloride, reacts similarly with alcohols. It is often used in synthesis, despite its toxicity. It has been used in the synthesis of Carbaryl, a broad-spectrum insecticide.



- (c) Draw the structure for compound **A**.
- (d) Draw the structures of phosphoryl chloride and thionyl chloride, clearly indicating their shapes. What are the oxidation states of the phosphorus and the sulfur in these compounds?
- (e) Write an equation for the reaction between thionyl chloride and water.
- (f) Give the structure of the phosphate ester formed when 1 mole of POCl_3 reacts with i) 1 mole of methanol and ii) 2 moles of methanol.

1 mole of POCl_3 reacts with 3 moles of water to produce phosphoric acid, H_3PO_4 . When pure phosphoric acid is heated with POCl_3 another phosphorus-containing acid, **B**, is produced. The addition of aqueous silver nitrate to a solution of acid **B** produces a white precipitate which contains 71.3% by mass silver and 10.2% by mass phosphorus, the remainder being oxygen.

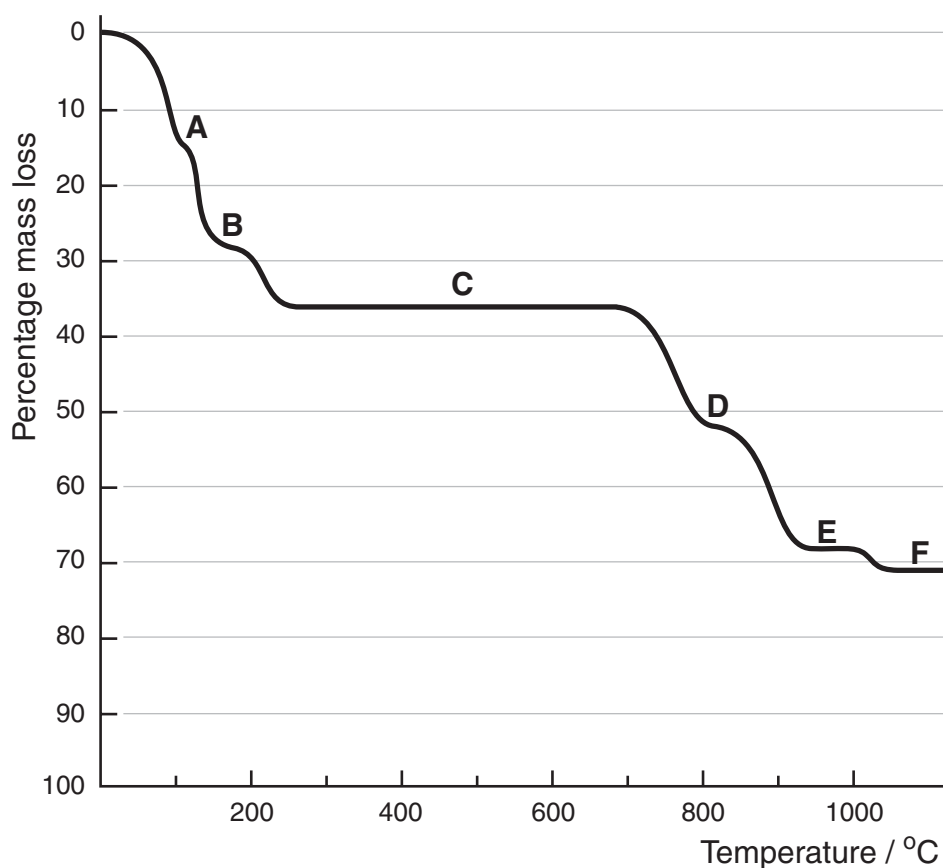
- (g) Suggest a structure for the acid **B** and write an equation for its formation from phosphoric acid and POCl_3 , given that the only other product is HCl .

4. This question is about the thermal decomposition of copper(II) sulfate

Thermogravimetry is an analytical technique which involves heating a substance and measuring the change in mass.

The graph below shows the change in mass as copper(II) sulfate pentahydrate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, is heated.

Decomposition takes place where the gradient is steepest leaving various decomposition products indicated by **A** to **F** in the diagram.

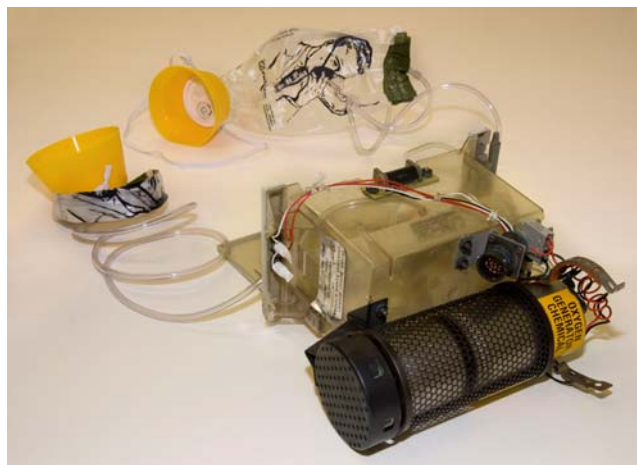


- (a) Using the data from the graph, suggest formulae for compounds **A**, **B**, and **C**.
- (b) On heating **E**, a redox reaction occurs to form **F**. Identify **E** and **F** and write an equation for this reaction.
- (c) Compound **D** is formed when exactly half of **C** has decomposed to form **E**. What is the empirical formula of **D**?

5. This question is about emergency oxygen supplies

Rather than carrying heavy high-pressure oxygen cylinders, most aeroplanes rely on chemically generated oxygen in the event of an emergency.

These generators are typically composed of a mixture of sodium chlorate(V), NaClO_3 , iron filings and barium peroxide, BaO_2 . Once initiated, the sodium chlorate(V) undergoes thermal decomposition producing oxygen gas. The iron combines with some of the oxygen to produce enough heat to sustain the reaction.

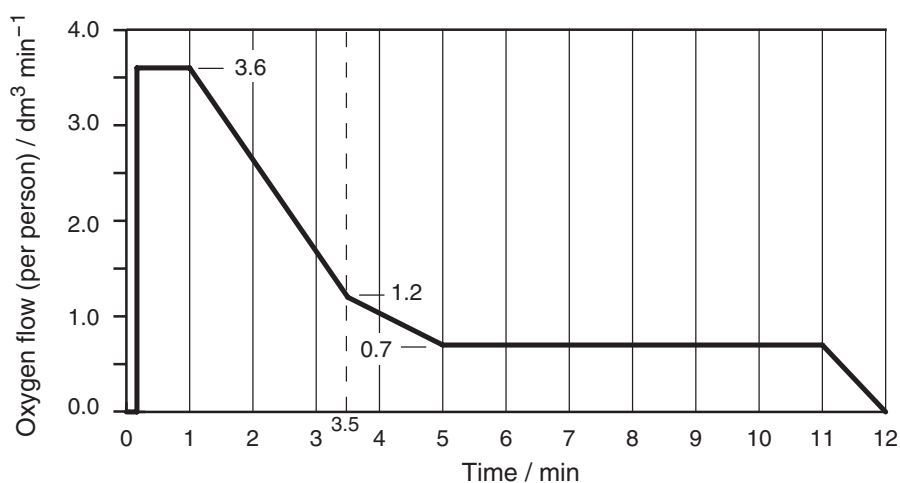


(a) Write a balanced equation for the decomposition of sodium chlorate(V).

The barium peroxide removes toxic side products which include chlorine and chloric(I) acid, HClO . Barium chloride and oxygen are common products in these two reactions.

(b) Write a balanced equation for the reaction between **i)** barium peroxide and chlorine and **ii)** barium peroxide and chloric(I) acid.

When a mask is deployed, the flow rate of oxygen gas is designed to change over time as the aeroplane falls to a safe altitude. Shown below is the manufacturer's specification for the flow rate from one such oxygen generator.



Ten seconds after being activated, the flow rate is at its maximum of $3.6 \text{ dm}^3 \text{ min}^{-1}$. This lasts for approximately 50 seconds before falling as shown in the graph.

- (c) Use the graph to estimate the total volume of oxygen produced by the generator.
- (d) Calculate the mass of sodium chlorate needed to produce 60 dm^3 of oxygen.
[Assume 1 mol of any gas occupies 24.0 dm^3 at r.t.p.]

A portable, self-contained closed-circuit breathing apparatus contains a chemical supply of oxygen similar to that in an aeroplane. It also contains a means to remove exhaled carbon dioxide. Very often potassium superoxide (KO_2) is used for this. KO_2 reacts with water, liberating further oxygen, and the by-product of this reaction absorbs the CO_2 .

- (e) Write down the oxidation state of the oxygen in **i)** CO_2 **ii)** BaO_2 and **iii)** KO_2 .
- (f) Give the equations for the reactions **i)** between potassium superoxide and water and **ii)** between the by-product and carbon dioxide.

6. This question is about the synthesis of Viagra™

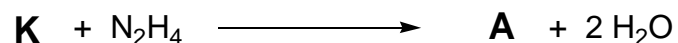
The reaction scheme shown opposite is based on the first synthesis of sildenafil. This is the active ingredient in Viagra, the drug used for the treatment of "male erectile dysfunction".

Note that the by-products are not necessarily indicated in this scheme.

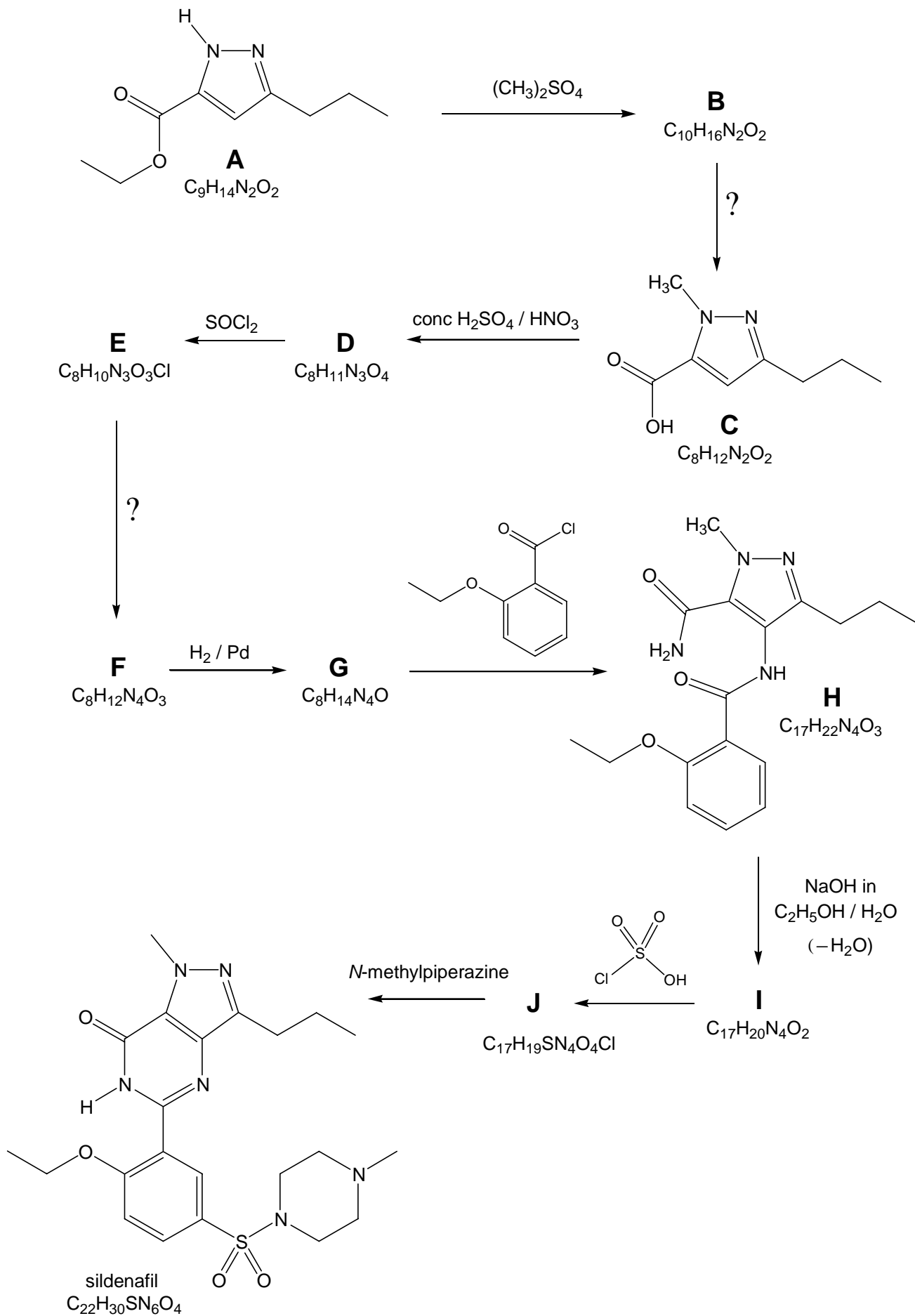


- (a) Draw structures for the intermediates **B**, **D**, **E**, **F**, **G**, **I**, and **J**.
- (b) i) Suggest suitable reagent(s) for the conversion of **B** to **C**.
- ii) Suggest a suitable reagent for the formation of **F** from **E**.
- (c) In the formation of **I** from **H**, the first step in the mechanism is a deprotonation by the sodium hydroxide solution. On the answer sheet, indicate clearly which hydrogen is removed by the base.
- (d) Deduce the structure for *N*-methylpiperazine, the reagent needed to convert **J** to sildenafil.

Compound **A** is actually prepared by the reaction between hydrazine, N_2H_4 , and reagent **K** according to the balanced equation below.



- (e) i) Draw the structure for hydrazine.
- ii) Suggest a structure for **K**.



7. This question is about the spectra of haloalkanes

Haloalkanes have been used as aerosol propellants and refrigerants but are now largely banned due to the damage they cause to the ozone layer. Halon 1211 was once commonly used in fire extinguishers (now only found in fighter jets) and 'Halothane' is an inhalational general anaesthetic.



Further examples of haloalkanes are given in the table below.

| | Common name | Structural formula |
|----------|-------------------------|--|
| A | CFC-113 | $\text{Cl}_2\text{FC}-\text{CClF}_2$ |
| B | CFC-113a | $\text{Cl}_3\text{C}-\text{CF}_3$ |
| C | HFC-134a | $\text{F}_3\text{C}-\text{CH}_2\text{F}$ |
| D | CFC-11 (Freon-11, R-11) | CCl_3F |
| E | CFC-12 (Freon-12, R-12) | CCl_2F_2 |
| F | CFC-13 | CClF_3 |
| G | Halon 1211 | CBrClF_2 |
| H | Methylene bromide | CH_2Br_2 |

Whilst naturally occurring carbon and fluorine exist as essentially the single isotopes ^{12}C and ^{19}F , chlorine consists of 75% ^{35}Cl and 25% ^{37}Cl ; bromine consists of 50% ^{79}Br and 50% ^{81}Br . The presence of chlorine and bromine atoms in molecules therefore leads to characteristic patterns for molecular ions in mass spectrometry. As an example, the mass spectrum of CFC-13 (**F**) includes peaks at $m/z = 104$ ($\text{CF}_3^{35}\text{Cl}^+$) and 106 ($\text{CF}_3^{37}\text{Cl}^+$) with intensity ratio 3:1.

- (a) Calculate the m/z values and relative intensities for the molecular ion peaks of CFC-12 (**E**).
- (b) Sketch the mass spectrum for the molecular ion peaks of Halon 1211 (**G**). Indicate the relative intensity of each peak and which ion(s) are responsible for them.

A sample of methylene bromide (**H**) was enriched with deuterium (^2H). On analysis it was found that half of the hydrogen content of the sample was deuterium. In the mass spectrum there are molecular ion peaks with m/z values of 172, 173, 174, 175, 176, 177 and 178.

- (c) Calculate the relative intensities of these molecular ion peaks.

NMR spectroscopy is a technique which reveals the number of different environments of certain nuclei in a molecule. NMR active nuclei such as ^1H , ^{13}C and ^{19}F are routinely studied. As an example, the two hydrogen atoms in methylene bromide (**H**) are equivalent and hence would give rise to a single peak in the ^1H NMR spectrum. The same is true for the hydrogens in HFC-134a (**C**).

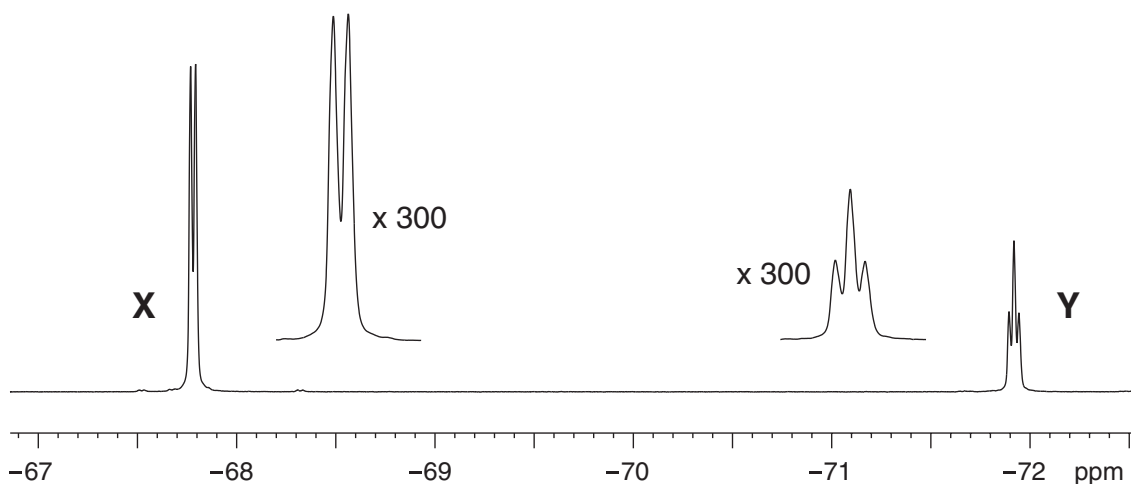
- (d) In your booklet, complete the table indicating the number of different fluorine environments for the each of the compounds **A-G**.
- (e) The anaesthetic *Halothane* has the formula $\text{C}_2\text{HBrClF}_3$ and shows one signal in its ^{19}F NMR spectrum. Draw the **two** possible three-dimensional structures for Halothane.

The intensity of a signal in a ^1H or ^{19}F NMR spectrum is proportional to the number of nuclei in that particular environment.

- (f) For each compound with more than one signal in its ^{19}F NMR spectrum, indicate in the appropriate column of the table the expected intensity ratio.

NMR spectra are complicated by coupling between nuclei. If an NMR-active nucleus is within three bonds of another similar nucleus *which is in a different chemical environment*, its signal will be split into a number of peaks instead of appearing as a single peak. If a nucleus couples to n NMR-active nuclei, its signal will split into a total of $(n+1)$ peaks.

- (g) The ^{19}F NMR spectrum of one of the haloalkanes from the table is shown below. In your answer booklet draw the structure of the haloalkane and indicate with an arrow which fluorines give rise the signals **X** and **Y**.



Acknowledgements

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The World War II poster of phosgene is reproduced courtesy of the National Museum of Health and Medicine, Armed Forces Institute of Pathology, Washington, D.C. Further chemistry-related posters may be found on their website:

www.nmhm.washingtondc.museum

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www.molecularproducts.co.uk

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www.marshallaerospace.com

The graph of the oxygen flow rate has been redrawn from a data sheet produced by the manufacturers Scott Aviation, a division of Scott Aviation Inc.

www.scottaviation.com

The synthesis of sildenafil is taken from:

“Sildenafil (VIAGRATM), a potent and selective inhibitor of type 5 cGMP phosphodiesterase with utility for the treatment of male erectile dysfunction”

Nicholas K. Terrett, Andrew S. Bell, David Brown and Peter Ellis

Bioorganic & Medicinal Chemistry Letters, 1996, Vol 6 p1819-24.

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