ROYAL SOCIETY OF CHEMISTRY

INEOS

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# 46<sup>th</sup> INTERNATIONAL

# CHEMISTRY OLYMPIAD

# 2014

# UK Round One

## STUDENT QUESTION BOOKLET

### ✳ ✳ ✳ ✳ ✳

■ **The time allowed is 2 hours.**

■ **Attempt all 5 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.**

■ **The marks available for each question are shown below; this may be helpful when dividing your time between questions.**

| Question | 1 | 2 | 3 | 4 | 5 | Total |
|---|---|---|---|---|---|---|
| Marks Available | 9 | 9 | 13 | 18 | 16 | **65** |

**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.**

Periodic Table

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 |
|---|---|---|---|---|---|---|---|---|----|----|----|----|----|----|----|----|----|
| **H** 1 1.008 | | | | | | | | | | | | | | | | | **He** 2 4.003 |
| **Li** 3 6.94 | **Be** 4 9.01 | | | | | | | | | | | **B** 5 10.81 | **C** 6 12.01 | **N** 7 14.01 | **O** 8 16.00 | **F** 9 19.00 | **Ne** 10 20.18 |
| **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 | | | | | | | | | | | | | | | |

Legend:
symbol
atomic number
mean atomic mass

| **\*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 |

$N_A = 6.02 \times 10^{23}\ \text{mol}^{-1}$     $1\ \text{nm} = 1 \times 10^{-9}\ \text{m}$     $0\ °\text{C} = 273\ \text{K}$

**1. This question is about controlling phosphate levels**

Although phosphorus compounds are essential in our diet, too much phosphate ion, $PO_4^{3-}$, in our blood can be harmful. One treatment for high phosphate levels uses a drug called Fosrenol®, the active ingredient of which is lanthanum carbonate.

Once the chewed tablet is swallowed, the carbonate first reacts with the hydrochloric acid present in the stomach. Then the lanthanum ions react with any phosphate ions present to give a precipitate of lanthanum phosphate. Lanthanum phosphate is essentially completely insoluble in water.

All lanthanum compounds in this question contain lanthanum in the +3 oxidation state.

**(a)** **(i)** Give an equation for the reaction between lanthanum carbonate and hydrochloric acid.

**(ii)** Give an ionic equation for the formation of lanthanum phosphate.

Lanthanum carbonate may be prepared by simply mixing aqueous solutions of lanthanum nitrate and sodium carbonate.

**(b)** Write a balanced equation for this reaction.

The lanthanum carbonate precipitated by the previous reaction is usually the octahydrate. The first sample of pure anhydrous lanthanum carbonate was prepared by dissolving lanthanum oxide in aqueous trichloroethanoic acid to form lanthanum trichloroethanoate. Heating this solution for six hours gave the desired carbonate, trichloromethane, and carbon dioxide.

**(c)** **(i)** Draw the displayed formula for trichloroethanoic acid.

**(ii)** Give the equation for the reaction between lanthanum oxide and trichloroethanoic acid.

**(iii)** Give the equation for the formation of lanthanum carbonate.

The lanthanum carbonate contained in the Fosrenol® tablets is prepared by mixing aqueous solutions of lanthanum chloride and ammonium hydrogencarbonate. During this reaction, carbon dioxide gas is given off.

**(d)** Give an equation for this reaction.

Fosrenol® is sold in different sizes of tablet, "1000 mg", "750 mg", and "500 mg". The number refers to the mass of lanthanum ions contained in the tablet.

**(e)** **(i)** Calculate the mass of lathanum carbonate dihydrate contained in the 1000 mg tablet.

**(ii)** Calculate the mass of phosphate ion removed after taking a single 1000 mg tablet of Fosrenol®.

## 2. This question is about a sodium street lamp

Many of our streets are lit by the extremely energy efficient low-pressure sodium discharge lamps. The light appears mainly yellow, but a spectroscope reveals a number of colours present, each with a particular frequency. Careful analysis of the spectrum enables us to determine the first ionization energy of sodium.

The so-called 'ground state' of an atom is where all the electrons are in their lowest possible energy levels.

**(a)** Give the complete electronic configuration for the ground state of sodium in terms of the relevant s and p sub-shells.

The 'valence-shell electron' is the electron easiest to remove from a neutral sodium atom.

**(b)** What is the valence-shell electron of sodium?

The familiar yellow colour of a sodium flame is actually due to an excited electron in a sodium atom essentially falling from a 3p orbital to the 3s. The wavelength for this transition is 589.8 nm.

The energy, $E$, (in joules) corresponding to light of wavelength $\lambda$ (m) is given by the equation:

$$E = \frac{hc}{\lambda}$$

where    $h$ is Planck's constant = $6.626 \times 10^{-34}$ J s

$c$ is the speed of light = $2.998 \times 10^{8}$ m s$^{-1}$.

**(c)**        Calculate the energy for the 3p to 3s transition in:

**(i)**   J (atom$^{-1}$)

**(ii)**   kJ mol$^{-1}$.

The atomic emission spectrum of sodium includes a series of lines which all fall on a straight line when (1 / wavelength) is plotted against (1 / $n^2$), where $n$ is the integer shown in the following table.

| Wavelength / nm | 466.6 | 498.0 | 568.1 | 818.1 |
|---|---|---|---|---|
| $n$ | 6 | 5 | 4 | 3 |
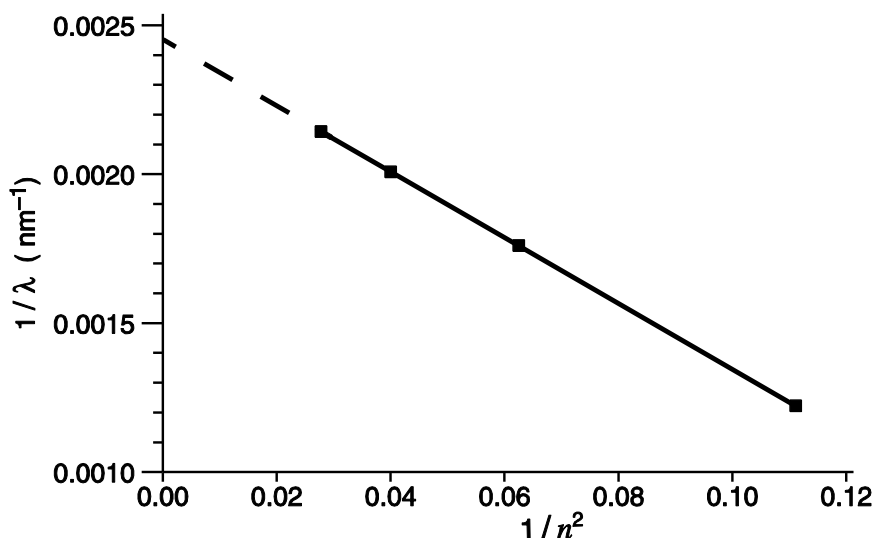


The origin of the linear relationship is due to fact that the (1 / $n^2$) is proportional to the ionization energy ($I.E.$) of an excited sodium atom after the valence electron has been promoted to the $n$d shell:

$$I.E.\,(n\mathrm{d}) = k \times \frac{1}{n^2}$$

where $k$ is an arbitrary constant, and $n$ is the principal quantum number, e.g. $n$ =1 for the 1s shell; 2 for the 2s and 2p shell; 3 for the 3s, 3p and 3d shell and so on.

[Note for the graph, $n$ cannot be one or two since there is no 1d or 2d shell.]

**(d)** What does this ionization energy of the excited $n$d electron tend to as the electron is removed from successively higher d shells? Circle one of the following answers in the answer booklet.

**one**          **zero**          **infinity**          **the constant $k$**

Each of the atomic emission lines included in the table and graph are due to transitions where the valence electron drops from an excited d shell to the 3p shell in the neutral sodium atom.

**(e)** Give an expression for the energy change of these transitions in terms of $I.E.$($n$d), and $I.E.$(3p) (the ionization energy of the excited sodium atom after the valence electron has been promoted to the 3p).

**(f)** **(i)** Use the graph to determine $I.E.$(3p) in J (atom$^{-1}$).

   **(ii)** What is the ionization energy of the ground state of sodium in kJ mol$^{-1}$?

### 3. This question is about spot cream

The drug tazarotene (sold under the trade names of Zorac® or Tazorac®) can be prescribed as a cream that can be applied to the skin to help to treat acne and certain other skin conditions. It is commonly sold as a 0.05% cream by mass.
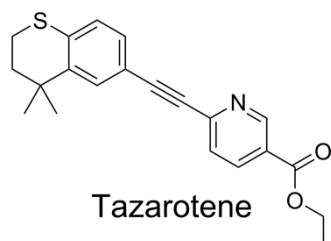


Tazarotene

**(a)** The molar mass of tazarotene is 351.46 g mol$^{-1}$. Assuming that tazarotene cream has a density of 0.90 g cm$^{-3}$, calculate the concentration of tazarotene in the cream in mol dm$^{-3}$.
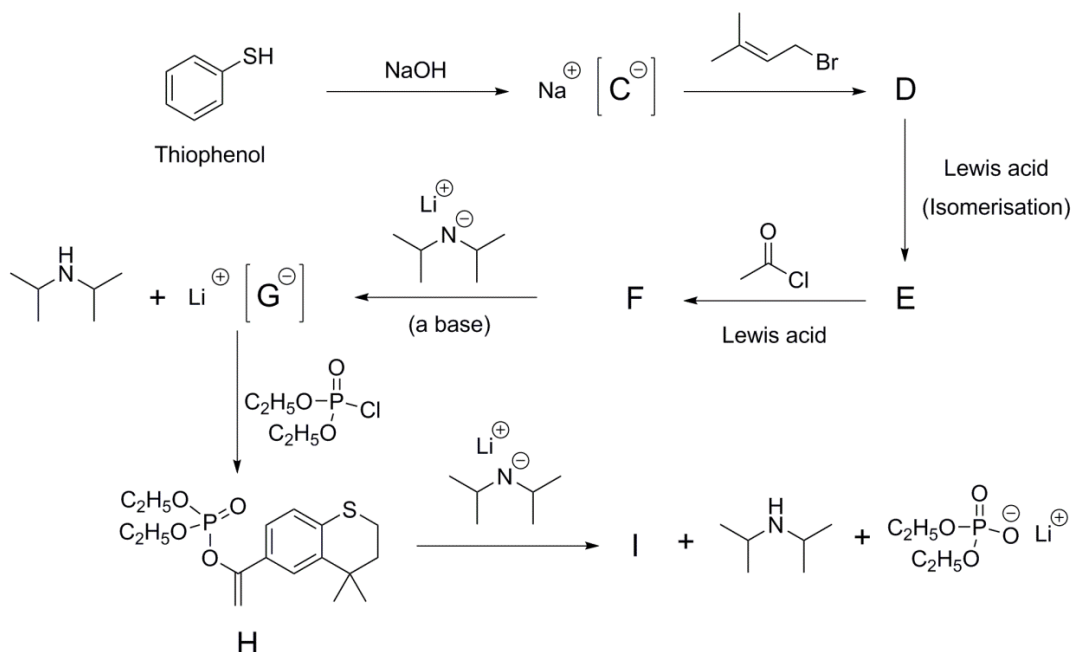
The synthesis of tazarotene is shown below. Not all of the reaction by-products are shown.

The synthesis begins with the conversion of 2-chloro-5-methylpyridine to Ester **B**.



2-Chloro-5-methylpyridine
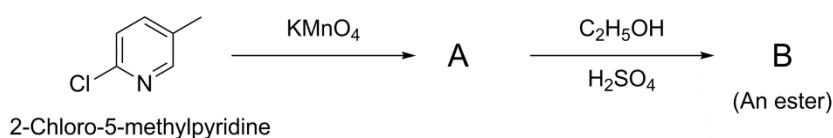
**(b)** Draw the structure of Compound **A** and Ester **B**.

The second part of the synthesis begins with thiophenol, which is converted into Compound **I** by a number of steps.



**(c)** Draw the structures of Compounds **D**, **E**, **F** and **I**, and anions **C**$^-$ and **G**$^-$.

**(d)** How would you classify the reaction of Compound **H** into Compound **I**?

Circle one of the following answers in the answer booklet.
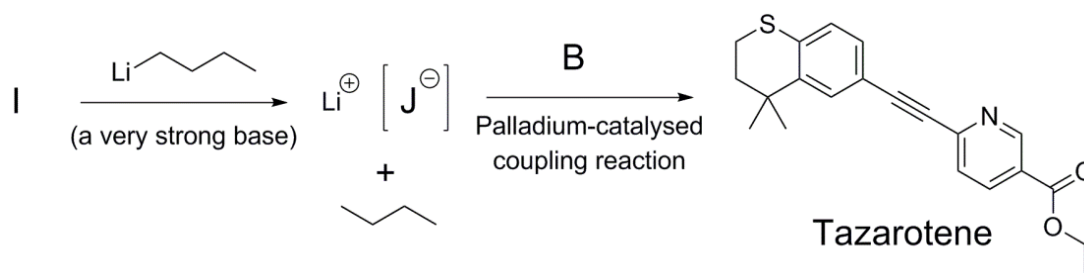
**Oxidation**       **Reduction**       **Addition**       **Elimination**       **Substitution**

Finally, Compound **I** is treated with a very strong base to form anion **J**.

Anion **J** can be reacted with Compound **B** to form tazarotene.



**(e)** Suggest a structure for Anion **J**.

**(f)** How many signals would you expect to see in the $^{13}C$ NMR spectrum of tazarotene?

Tazarotene is actually a pro-drug, meaning it is metabolised to its active form when inside the body.

The active form has a molar mass of 323.41 g mol$^{-1}$ and two fewer signals in its $^{13}C$ NMR spectrum than tazarotene.

**(g)** Suggest a structure for the active form of the drug.

## 4. This question is about bombardier beetles

Bombardier beetles get their name from the defence mechanism that they have when attacked, whereby they shoot a hot chemical spray at their attackers. In their abdomen they have two separate chambers, one containing an aqueous solution of hydrogen peroxide and the other an aqueous solution of an organic compound, denoted here as **A**.

When the beetle is attacked, fluid from both chambers is squirted into a mixing chamber which contains enzymes. One of these enzymes, *catalase*, catalyses the breakdown of hydrogen peroxide into oxygen and water.

**(a)** **(i)** Write a balanced equation for this reaction.

**(ii)** How would you classify this reaction? Circle one of the following answers in the answer booklet.

**Oxidation          Reduction          Disproportionation          Hydrolysis          Dehydration**

Some of the intermediates produced during the breakdown of hydrogen peroxide react with the organic compound, **A**, to give a product **B**. The overall equation for the reaction can be considered as the result of **A** reacting with all of the oxygen produced by the equation in part **(a)(i)** as in the equation below.

$$\textbf{A} + \tfrac{1}{2}O_2 \rightarrow \textbf{B} + H_2O$$
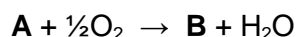
**(b)** Write an overall equation for the reaction of hydrogen peroxide with **A** to form **B**.

The temperature of the mixture ejected from bombardier beetles has been measured to reach the boiling point of water, considerably hotter than the beetle's body temperature, which matches the surroundings (20 °C).

**(c)** **(i)** Calculate the amount of energy needed to heat 1 $dm^3$ of this mixture by this amount. Assume the specific heat capacity of the mixture is the same as that of pure water, 4.18 $J\ g^{-1}\ K^{-1}$ and that the density of the mixture is the same as that of pure water, 1.00 $g\ cm^{-3}$.

**(ii)** Assuming equal volumes of the two solutions are mixed, what is the minimum concentration of the hydrogen peroxide solution in the beetle's hydrogen peroxide chamber?

The standard enthalpy change for the overall reaction (your answer to part (b)) per mole of **A** is −203 $kJ\ mol^{-1}$.

Compound **A** is a 1,2,4-trisubstituted benzene, shown on the right, where there are substituents present at the positions labelled with an X.
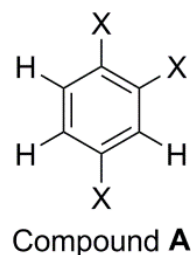


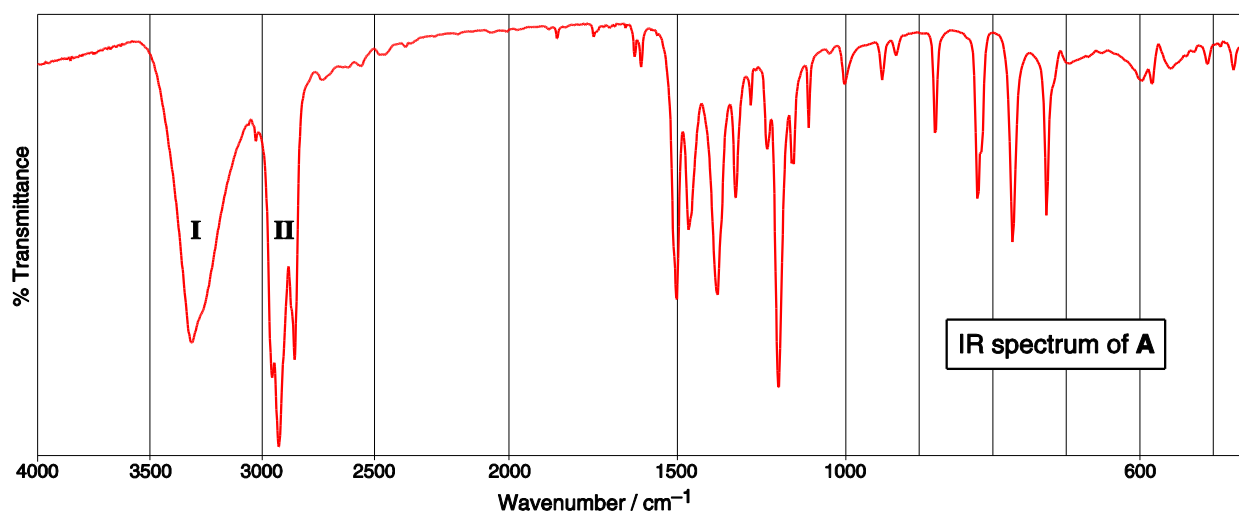Compound **A**

**(d)** How many possible structures are there of this 1,2,4-trisubstituted benzene when:

    **(i)** All of the X substituents are different from each other?

    **(ii)** Two of the X substituents are identical?

Combustion analysis of Compound **A** indicates that it contains only carbon, hydrogen and oxygen.

In compound **A**, stretching in some of the bonds contained in the X substituents contributes to characteristic peaks in the IR spectrum of this compound (shown below).

These characteristic peaks are marked **I** and **II** on the spectrum.

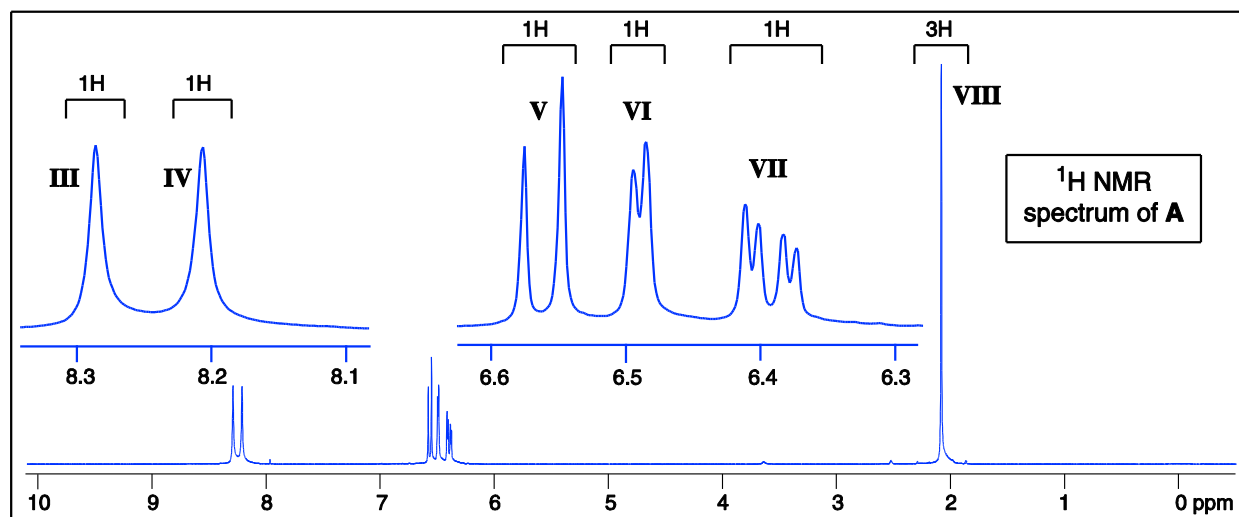**(e)** Suggest which bond stretches are responsible for **I** and **II**.



IR spectrum of **A**

9

In compound **A**, two of the three X substituents are the same (i.e. the substituents are $X_a$, $X_a$ and $X_b$).

The $^{13}C$ NMR spectrum of compound **A** contains seven signals.

The $^1H$ NMR spectrum of compound **A** is shown below.

Peaks III and IV in the $^1H$ NMR spectrum disappear on addition of $D_2O$ to the sample.

**1H NMR spectrum of A**

Peaks labelled (left to right):
III (1H), IV (1H) near 8.3–8.2 ppm; V (1H), VI (1H) near 6.6–6.5; VII (1H) near 6.4; VIII (3H) near 2 ppm.
x-axis: 10 9 8 7 6 5 4 3 2 1 0 ppm; expansions at 8.3 8.2 8.1 and 6.6 6.5 6.4 6.3

**(f)** **(i)** Suggest an identity for the two identical substituents ($X_a$ and $X_a$).

**(ii)** Suggest an identity for the other substituent ($X_b$).

The protons on the benzene ring in compound **A** ($H_1$, $H_2$ and $H_3$) can be assigned by analysis of their coupling constants in the $^1H$ NMR spectrum.

The splitting that is observed in the spectrum due to coupling between two non-equivalent benzene ring protons in a 1,2-relationship to each other, is considerably larger than the splitting observed due to coupling between two non-equivalent benzene ring protons in a 1,3-relationship.

The splitting due to coupling between two non-equivalent benzene ring protons in a 1,4-relationship is generally too small to be observed.

(Structure shown: benzene ring with substituents X at positions, and protons $H_1$, $H_2$, $H_3$.)
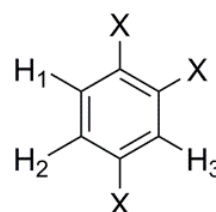
**(g)** Assign one of the signals **III**-**VIII** in the $^1H$ NMR spectrum of **A** to each of the protons $H_1$, $H_2$ and $H_3$.

Bombardier beetles also use a simpler organic compound, **C** for the same purpose.

Compound **C** is a relative of compound **A** where one of the X substituents is replaced by a hydrogen atom, making a disubstituted benzene.

The $^1H$ NMR spectrum of compound **C** only contains two signals.

**(h)** Suggest a structure for compound **C** and hence also a structure for compound **A**.

Compound **C** is oxidised to **D** in the same way that compound **A** is oxidised to **B**.

The $^1H$ NMR spectrum of compound **D** only contains one signal.

**(i)** Suggest a structure for compound **B** and a structure for compound **D**.

## 5. This question is about fire and ice

Water is able to form a range of cage structures called clathrates which can contain many small molecules; a common example is methane hydrate $(CH_4)_x(H_2O)_y$. Methane hydrates potentially offer a valuable supply of methane to satisfy our demand for natural gas. Large reserves of methane hydrates have been found at the bottom of Lake Baikal in Russia.

**(a)** Write the balanced equation for the combustion of methane in excess oxygen.

A 100 g sample of methane hydrate, in the form known as clathrate structure II, $(CH_4)_x(H_2O)_y$ was burnt in excess oxygen in a sealed container. After the reaction had completed and the products had cooled, 116.92 g of water was recovered from the container, and the gas, when shaken with excess limewater, gave 84.73 g of $CaCO_3$.

**(b)** **(i)** Determine the empirical formula of the methane hydrate in structure II. The molar mass of $CaCO_3$ is 100.09 g mol$^{-1}$.

   **(ii)** The molar mass of the hydrate was 2835.18 g mol$^{-1}$. Determine the molecular formula of the methane hydrate in structure II.

**(c)** $6.67 \times 10^{11}$ kg of methane is estimated to be at the bottom of Lake Baikal. Determine the volume the gas would occupy if it were to escape the lake during the winter, at $-19.0$ °C.

   Use the ideal gas equation $pV = nRT$ where $p$ is the pressure in Pascal, $V$ is the volume in m$^3$, $T$ is the temperature in Kelvin and $R$ is 8.31 J K$^{-1}$ mol$^{-1}$. [1 atm = $1.0 \times 10^5$ Pa]

The methane hydrate at the bottom of Lake Baikal is found as clathrate structure I having the formula $(CH_4)_8(H_2O)_{46}$ and a molar mass of 957.07 g mol$^{-1}$.

**(d)** **(i)** Determine the percentage by mass of methane within the methane hydrate.

   **(ii)** Using your answer to part **(d)(i)** to determine the mass of methane hydrate found at the bottom of Lake Baikal.

   **(iii)** The density of methane hydrate crystals is 0.95 g cm$^{-3}$. Calculate the volume of methane hydrate crystals at the bottom of Lake Baikal.
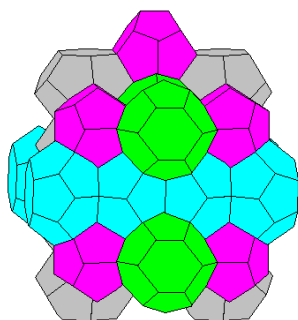


**Clathrate structure I**
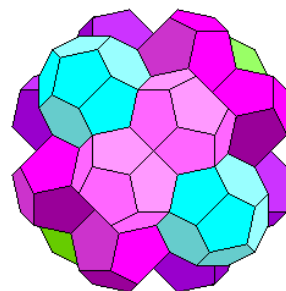


**Clathrate structure II**

The smallest repeating unit of methane hydrate that contains all the symmetry of the crystal is known as the unit cell. The unit cell for methane hydrate is a cube that entirely contains 8 methane molecules and 46 waters.

**(e)** **(i)** What is the mass of a single unit cell?

**(ii)** Using the density of methane hydrate (0.95 g cm$^{-3}$) calculate the length of an edge of the cubic unit cell.

Although the methane and water molecules are not spheres, we can treat them as spheres, and an effective spherical radius can be estimated for them: 0.14 nm for water and 0.21 nm for methane.

The formula for the volume of a sphere, $V$, is given below.

$$V = \frac{4}{3}\pi r^3$$

**(iii)** Determine the volume of methane and the volume of water within a unit cell.

**(iv)** Work out the percentage of space in the crystal that is occupied with molecules.

When $(CH_4)_8(H_2O)_{46}$ is burnt in excess oxygen at 298 K, the enthalpy change of combustion is −6690.4 kJ mol$^{-1}$.

**(f)** Use the data below to determine the enthalpy change when methane hydrate is formed from methane and water at 298 K.

Standard enthalpy changes of formation at 298 K in kJ mol$^{-1}$:

$CH_4$: −74.8,  $H_2O$: −285.8,  $CO_2$: −393.5
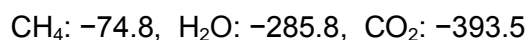
# Acknowledgements & References

**References for questions**

**Q1**
**Process for the preparation of lanthanum carbonate dehydrate**
P. R. Muddasani *et al.*, United States Patent US 2012/0058200

**The Rare Earth Metals and their Compounds. XII. Carbonates *of* Lanthanum, Neodymium and Samarium**
M. L. Salutsky and L. L. Quill, *J. Am. Chem. Soc.*, **72**, 3306-7, 1950.

**Q2**
Images from Department of Chemistry, University of Cambridge

**Q3**
**Contemporary Drug Synthesis**
J.-J. Li *et al.*, *Wiley-Blackwell*, 2004

The image is from © Shutterstock.

**Q4**
**A Biomimetic Study of the Explosive Discharge of the Bombardier Beetle**
N. Beheshti & A. C. McIntosh, *Int. Journal of Design & Nature*, **1**, 1-9, 2006.

**Chemical Defence of a Primitive Australian Bombardier Beetle (Carabidae): *Mystropomus regularis***
T. Eisner *et al.*, *Chemoecology*, **2**, 29-34, 1991.

Photograph from Patrick Coin (Wikipedia)

The ^{1}H NMR spectrum and IR spectrum were adapted from those available from Sigma Aldrich.

**Q5**
Image of burning methane hydrate from:
*http://energy.gov/articles/new-methane-hydrate-research-investing-our-energy-future*

Images of crystal structures from Steve Dutch at the University of Wisconsin–Green Bay:
*http://www.uwgb.edu/dutchs/Petrology/Clathrate-1.HTM*
*http://www.uwgb.edu/dutchs/Petrology/Clathrate-2.HTM*

Further details about clathrate structures can be found at:
*http://www.lsbu.ac.uk/water/clathrat2.html*