43rd INTERNATIONAL CHEMISTRY OLYMPIAD

2011

UK Round One

STUDENT QUESTION BOOKLET

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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 in the right hand margin of the answer booklet.

Some questions may contain unfamiliar material. 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					**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		
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 a popular snack food.**

The ingredients of a 'salt and vinegar flavour baked corn snack' are listed as:

- maize
- vegetable oil
- flavouring
- salt

A small bag typically contains 22 g of the snack.

The snack was analysed as follows:

Calorimetry

A 2.0 g sample of the snack was burnt completely. The temperature of the water in the calorimeter rose by 20.9 ^{o}C. The calorimeter contained 500 g of water.

Titration

The crushed contents of a whole small bag of the snack were washed with distilled water to dissolve all of the salt. The resulting solution was made up to 250 cm^3 in a volumetric flask.

A 25.0 cm^3 portion of this solution was titrated against 0.100 mol dm^{-3} aqueous silver nitrate(V) using potassium chromate(VI) as the indicator.

8.20 cm^3 of aqueous silver nitrate(V) solution were required to reach the red-brown end point.

The specific heat capacity of water is 4.18 J K^{-1} g^{-1} 1kJ ≡ 0.239 dietary calories

a) Calculate the number of dietary calories in a typical small bag of the snack. [2]

b) Give the chemical formula for **(i)** silver nitrate(V) and **(ii)** potassium chromate(VI). [2]

c) Write an **ionic** equation for the titration reaction and calculate the mass of sodium chloride in a typical small bag of the snack. [3]

The 'sharp' taste of the snack comes from citric acid. The IUPAC recommended name for citric acid is 2-hydroxypropane-1,2,3-tricarboxylic acid.

d) Draw the skeletal structure for citric acid. [2]

A carbon atom bonded to four different groups is called a chiral centre or an asymmetric carbon atom.

e) How many chiral centres does a molecule of citric acid contain? [1]

2. This question is about calcium carbide.

Calcium carbide, CaC_2, also known as calcium acetylide, is produced in large quantities around the world, mostly in the Far East. Calcium carbide has been used in a variety of ways, including as a component in self-igniting maritime distress flares.

Use the following information about calcium carbide to help you answer questions **(a)**–**(g)** below.

- Calcium carbide is formed from the reaction between lime (calcium oxide) and coke (carbon) at about 2000 ^{o}C. The side-product of this reaction is a toxic gas, **A**, that is a reducing agent.
- The lime used in the production process commonly contains a small amount of calcium phosphate(V) as an impurity. In the reaction with coke, this impurity reacts to form compound **B** (a simple ionic compound of calcium and phosphorus) as well as gas **A**.
- Calcium carbide reacts with excess water to form a colourless, flammable gas, **C**. A white solid is also formed which is slightly soluble in water to give a colourless alkaline solution. Gas **C** is a hydrocarbon containing 92.3% carbon by mass. The relative molecular mass of **C** is shown to be 26.
- The addition of calcium carbide to water generates an unpleasant smell. It is now known that it is actually the reaction of water with compound **B** that produces this smell.

a) Draw a 'dot-cross' diagram of the carbide ion, C_2^{2-}. [2]

b) Which **two** well-known diatomic gases are *iso-electronic* (same number of electrons) with the carbide ion? [2]

c) Write a balanced equation for the formation of calcium carbide and gas **A** from lime and coke. [1]

d) Calculate **(i)** the empirical formula and **(ii)** the molecular formula of hydrocarbon **C**. [2]

e) Write a balanced equation for the reaction of calcium carbide with water. [1]

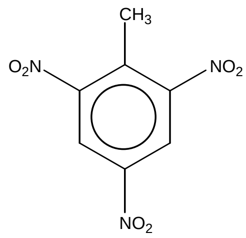
f) Write a balanced equation for the reaction between calcium phosphate(V) and coke to form gas **A** and compound **B**. [2]

g) Suggest the identity of the molecule responsible for the unpleasant odour that is produced when compound **B** reacts with water. [1]

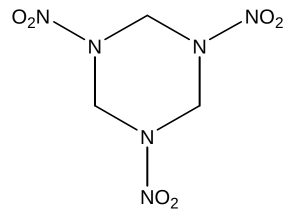
3. **This question is about explosives.**

Explosives are often associated with causing destruction and harm, but explosives have also played a major role in civil engineering for hundreds of years.

'Blasters' (explosives engineers) need a good understanding of geology and the science of explosives to be able to design explosions 'to order'.



TNT



RDX

Explosions occur when reactions proceed so that heat is generated more rapidly than it can be dispersed.

Some high explosives have the general formula $\mathbf{C_aH_bN_cO_d}$. The oxidiser (O) and the fuel (C, H) are present in the same molecule. Nitrogen atoms are present so that there is the highly exothermic production of hot N_2 gas.

a) Find an expression for ***d*** (in terms of ***a***, ***b*** and ***c***) that must be satisfied for an explosive $\mathbf{C_aH_bN_cO_d}$ to decompose to form CO_2, H_2O and N_2 only. [2]

The *oxygen balance* of an explosive is the mass of oxygen either in excess (i.e. the balance is positive) or in deficit (i.e. the balance is negative) of that required for **complete** oxidation of C and H.

The *oxygen balance* is expressed as a percentage of the molar mass of the explosive.

b) Write a general expression for the oxygen balance of $\mathbf{C_aH_bN_cO_d}$. [2]

c) Calculate the oxygen balance for **RDX**, whose structure is given above. [2]

When the explosive does not contain enough oxygen, there is incomplete oxidation of **C** and/or **H**. In the case of nitrated aromatic compounds, the reaction products are given by the following set of 'rules':

- carbon atoms react with the available oxygen to form CO
- N atoms combine to form N_2
- 1/3 of the CO produced is converted to $C + CO_2$
- 1/6 of the original CO produced reacts with any available H in the compound to form $C + H_2O$

d) Write the equation for the explosion of TNT. [2]

e) Calculate the mass of TNT that will explode to produce 1.0 dm^3 of gas at room temperature and pressure. [The molar volume of any gas = 24 dm^3 at RTP] [2]

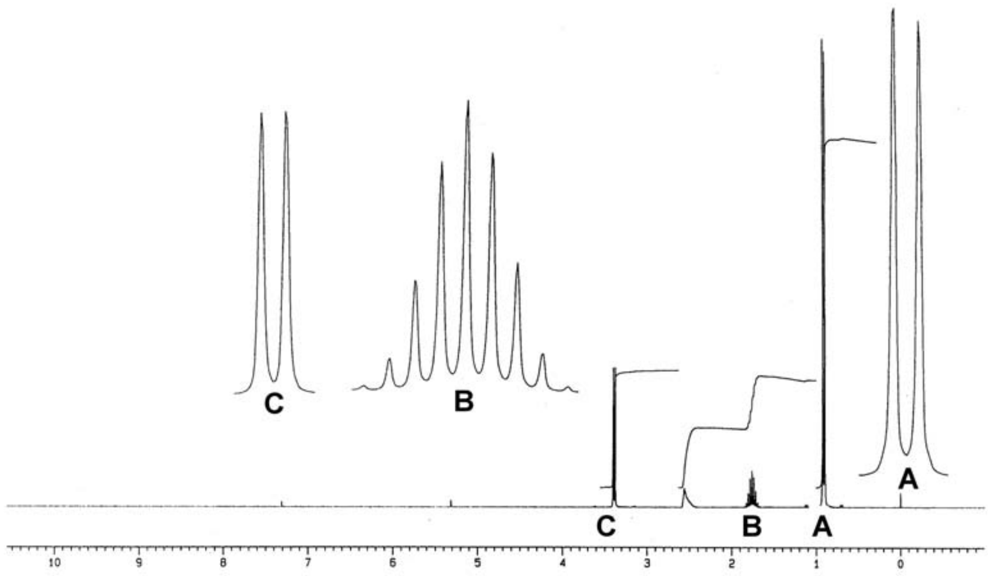
4. **This question is about solving a puzzle using spectroscopy.**

If required, use the information on the next page to help you answer this question.

Your task is to identify compounds **1-7** using the information given below.

In your answer booklet, you should draw the **skeletal** formula of each compound and give the systematic names of compounds **1- 4**. [13]

- Compounds **1-7** all have the same molecular formula, $\mathbf{C_4H_{10}O}$, but have different chemical, structural and spectroscopic properties.
- Compounds **5, 6,** and **7** have lower boiling points than compounds **1-4**.
- Compounds **1-4** have a broad absorption at 3300 cm^{-1} in their infra-red spectra.
- Compound **2** can exist as optical isomers.
- The ^{1}H NMR spectrum of compound **3** is shown below:



- The ^{1}H NMR spectra of compounds **4** and **5** each consist of two distinct signals.
- The ^{1}H NMR spectrum of compound **5** gives the following data:

Chemical Shift ppm	**Splitting pattern**	**Relative intensity**
1.21	triplet	3
3.47	quartet	2

- The ^{13}C NMR spectrum of compound **6** contains four distinct signals, whereas the ^{13}C NMR spectrum of compound **7** shows only three.

Information about NMR spectroscopy (for Q4).

NMR spectroscopy is a technique that reveals the number of different environments of certain nuclei in a molecule.

Thinking about the symmetry present in a molecule is important when interpreting NMR spectra.

Both carbon atoms (^{13}C) and hydrogen atoms (^{1}H) give NMR signals (i.e. are NMR-active nuclei).Each NMR-active nucleus in a different molecular environment will give rise to one signal with a characteristic *chemical shift* (measured in ppm).

The relative intensity of each signal in a spectrum is proportional to the number of nuclei in a particular molecular environment.

^{1}H NMR is complicated by *coupling*. If a hydrogen nucleus is within three bonds of another hydrogen nucleus *which is in a different molecular environment*, instead of appearing as a single peak, its signal is split into a number of peaks.

If a hydrogen nucleus couples to *n* other hydrogen nuclei, its signal will split into a total of (n+1) peaks.

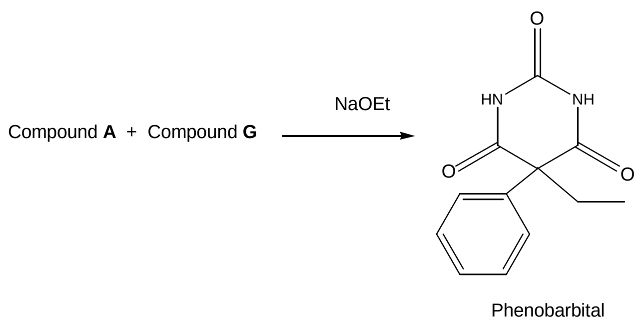
For example, the spectrum for compound **3** shown opposite, indicates that there are 4 different ^{1}H environments. The relative intensities of the peaks are 2:1:1:6.

The *splitting patterns* for peaks **A**, **B** and **C** are shown in larger scale.

5. **This question is about the synthesis of phenobarbital**

Barbiturates are derivatives of *barbituric acid* which act as central nervous system depressants. Barbiturates are used in the treatment of seizure disorders. One example of a barbiturate that has been used as an anti-convulsive for many years is phenobarbital.

Phenobarbital can be synthesised from two compounds, **A** and **G**:



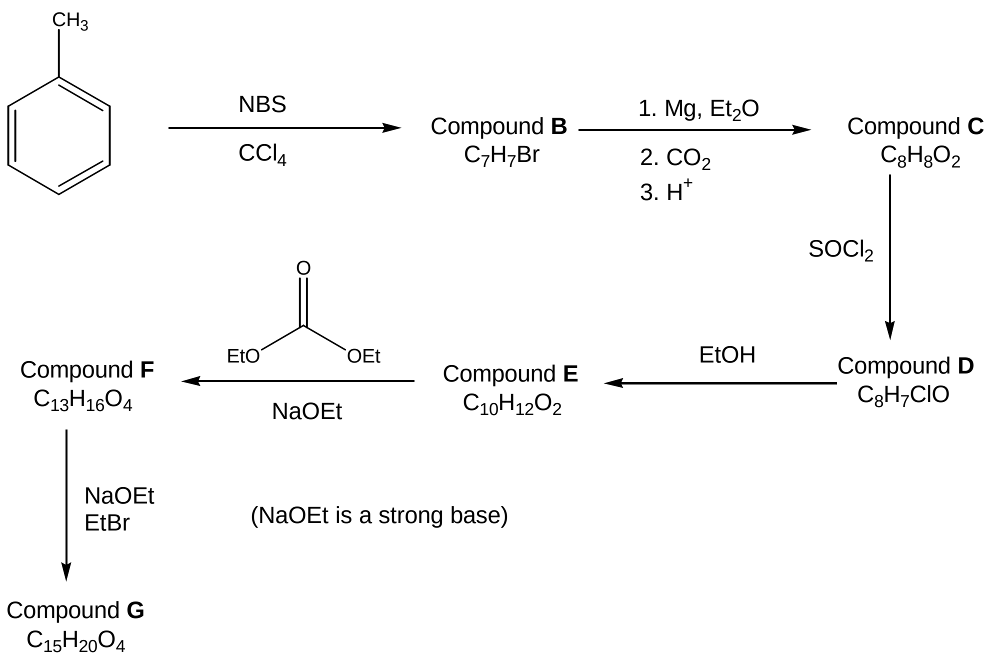
a) Compound **A** can be found as a metabolite in human urine.

Use the information below and in the introduction above to determine the molecular formula of compound **A**. Show clearly the important steps in your working. [4]

- Combustion of a 0.250g sample of compound **A** produces 0.178g of CO_2 and 0.146g of H_2O.
- A further 0.250g sample of compound **A**, when boiled with an excess of alkali, liberates all the nitrogen as ammonia, NH_3. The ammonia generated in this reaction is sufficient to neutralise 40.8cm^3 of 0.200 mol dm^{-3} aqueous hydrochloric acid.
- Mass spectrometry shows that compound **A** has a relative molecular mass of 60.

Compound **G** can be synthesised as follows:

[Note: NBS is *N*-bromosuccinimide - a source of bromine radicals and Et = ethyl]



b) In your answer booklet, draw the structural formulae of compounds **A** – **G**. [7]