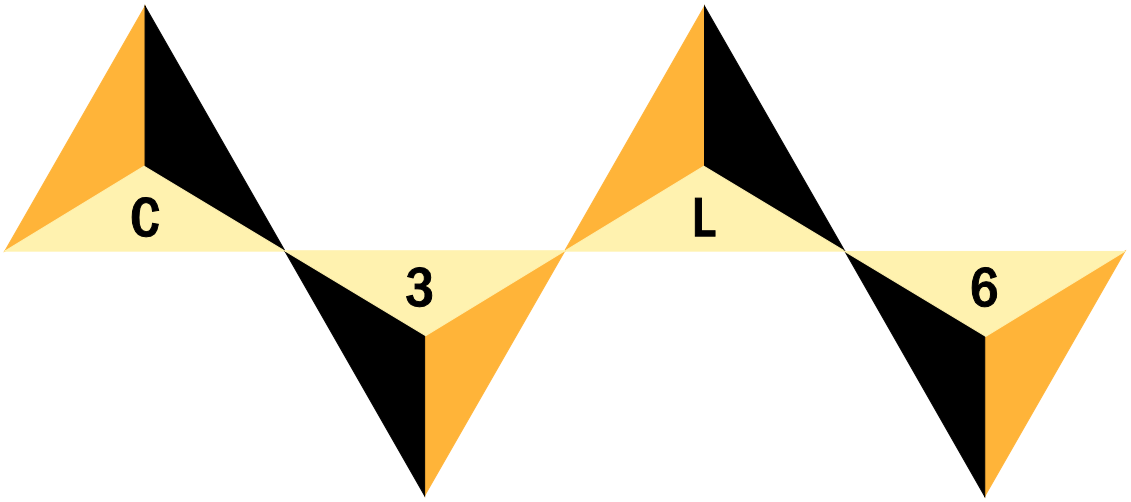


Cambridge Chemistry Challenge Lower 6th

June 2013

Some of the material in this booklet might be familiar to you, but other parts may be completely new. The questions are designed to be more challenging than those on typical AS papers, but you should still be able to attempt them. Use your scientific skills to work through the problems logically.

If you do become stuck on one part of a question, other parts might still be accessible, so do not give up. Good luck!

- The time allowed is 90 mins.
- Attempt all the questions.
- Write your answers in the answer booklet provided, giving only the essential steps in any calculations.
- Specify your answers to the appropriate number of significant figures and give the correct units.
- Please do not write in the right-hand margin.
- A periodic table and necessary constants are included on the next page.

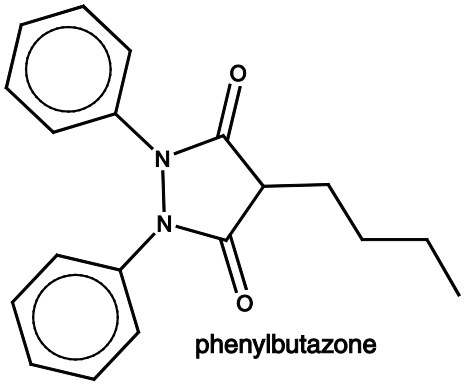
1																	18
H 1 1.008	2											13	14	15	16	17	**He** 2 4.003
Li 3 6.94	**Be** 4 9.01					**symbol** atomic number mean atomic mass						**B** 5 10.81	**C** 6 12.01	**N** 7 14.01	**O** 8 16.00	**F** 9 19.00	**Ne** 10 20.18
Na 11 22.99	**Mg** 12 24.31	3	4	5	6	7	8	9	10	11	12	**Al** 13 26.98	**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

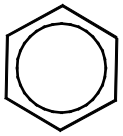
The Avogadro constant $N_A = 6.022 \times 10^{23}$ mol^{-1}

1. This question is about the recent horse-meat scandal

In the recent horse-meat "scandal", some foods were found to contain low levels of horse-meat, which was not declared on the list of ingredients. In addition, there was a worry that horse-meat from unregulated sources may be contaminated with the drug phenylbutazone, commonly called 'bute'.



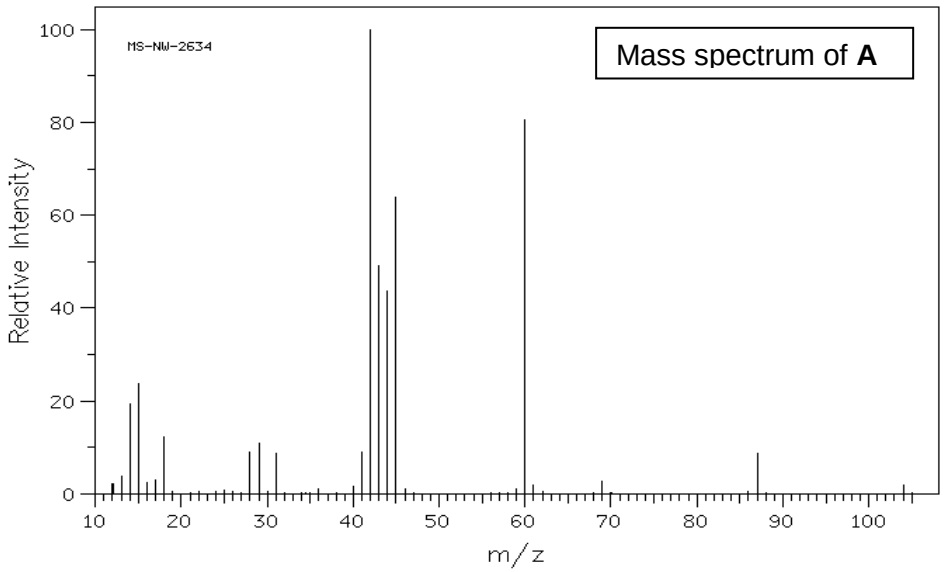
phenylbutazone

Note: in this question benzene, C_6H_6, is represented by 

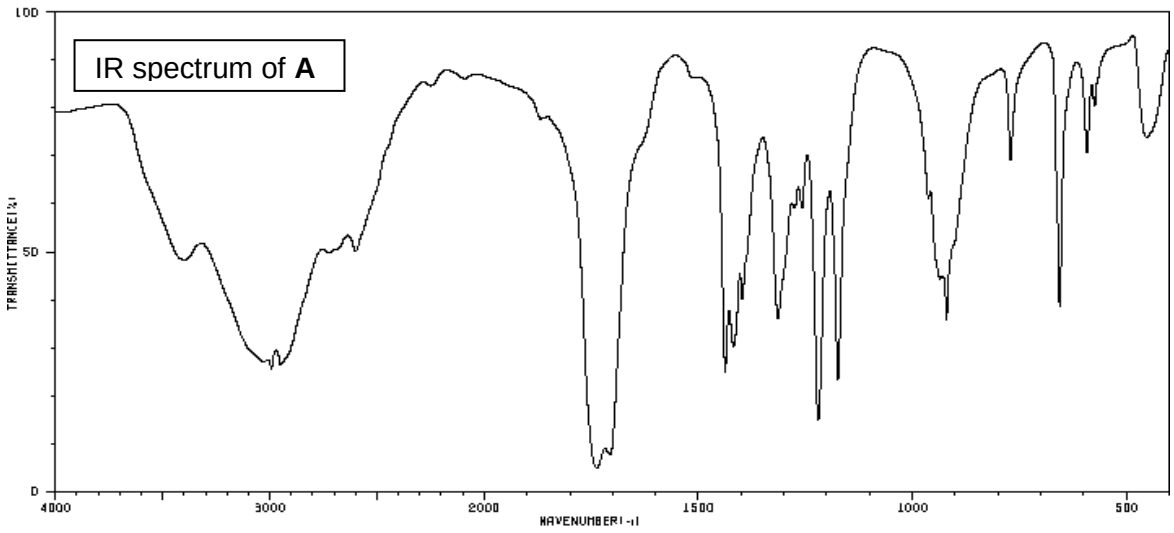
Synthesis and Analysis

Phenylbutazone may be synthesized starting from compound **A**. Data for compound **A** are given below.

Elemental composition of **A**: C 34.6%; H 3.85%; O 61.5%



(a) Give the empirical and molecular formulae of **A**.



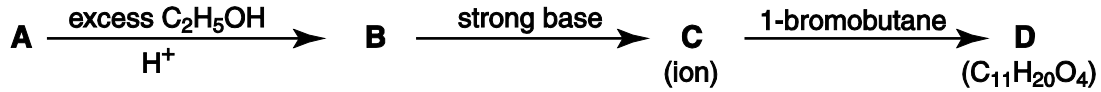
(b) Use the IR spectrum of **A** to suggest which functional group **A** contains.

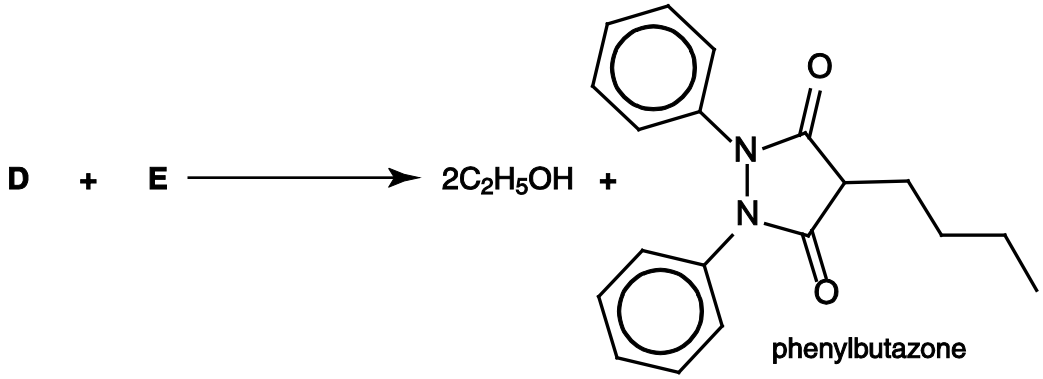
25.0 cm^3 of an aqueous solution containing 8.00 g dm^{-3} of **A** requires 19.2 cm^3 of 0.200 mol dm^{-3} NaOH(aq) for complete neutralisation.

(c) (i) Calculate the number of moles of NaOH needed to neutralise one mole of **A**.

(ii) Suggest a structure for **A** consistent with all the data given.

The synthesis of phenylbutazone from **A** is outlined below.





(d) Give the structure for **B**.

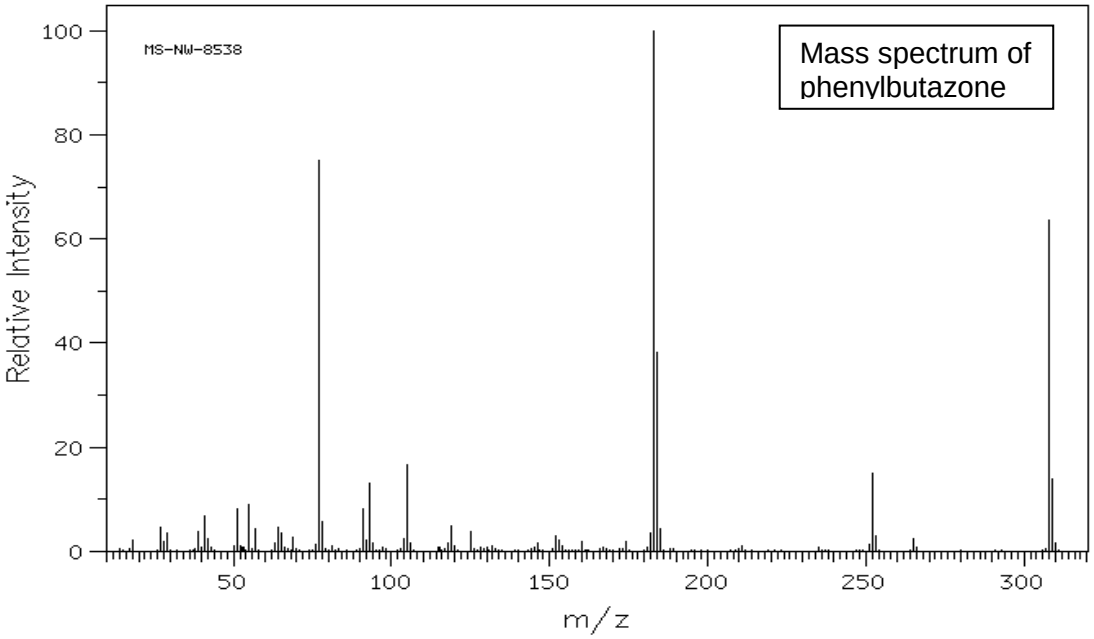
Hydrogens attached to carbon atoms which are adjacent to carbonyl groups can be removed by strong bases.

(e) Give the structure of the ion **C** and compound **D**.

One mole of **D** reacts with one mole of **E** to produce one mole of phenylbutazone and two moles of ethanol.

(f) Suggest a structure for compound **E**.

The mass spectrum of phenylbutazone is shown below.

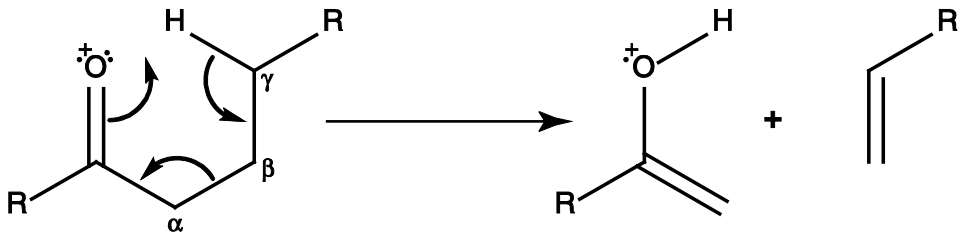


(g) Give the molecular formula for phenylbutazone.

(h) Which of the following could explain the peak at 309? Tick <u>all</u> possible explanations in the answer booklet.

(i) The M_r of phenylbutazone is 309.
(ii) The molecule fragments.
(iii) Naturally occurring carbon contains a small proportion of ^{13}C.
(iv) Naturally occurring hydrogen contains a large proportion of deuterium (^{2}H).
(v) One of the nitrogen atoms has been protonated.

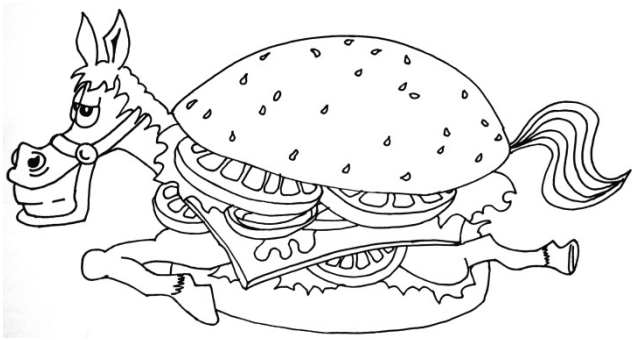
The peak at *m/z* 252 is interesting, as it gives evidence for a particular type of fragmentation of the molecular ion called a McLafferty rearrangement. This occurs in ketones that have a hydrogen atom that is attached to a carbon atom three carbons away from the carbonyl carbon (a so-called γ hydrogen):



(i) Draw the structure for the ion responsible for the peak at *m/z* 252 and also give the structure of the other fragment formed.

Phenylbutazone in Humans

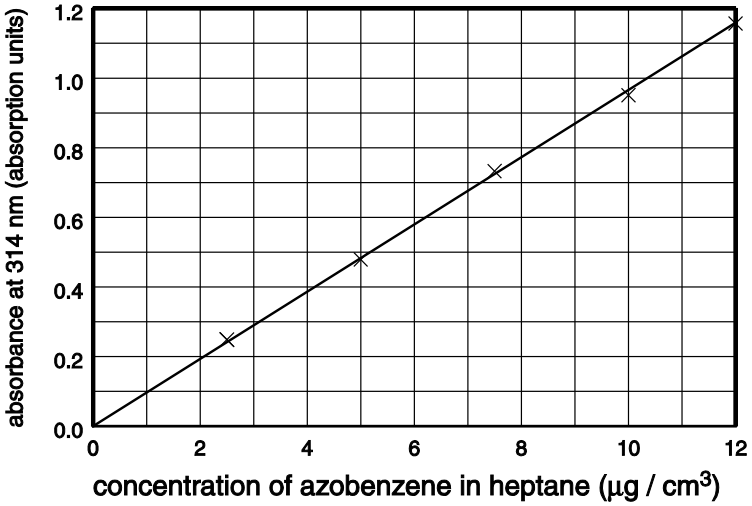
Phenylbutazone was originally approved for human use as a non-steroidal anti-inflammatory drug and is still used to control pain in horses. It was withdrawn from use in humans due to the side-effects experienced by a number of patients. In particular, at a therapeutic dose of 3.0 mg/kg of body mass, one in approximately thirty thousand patients developed aplastic anaemia.

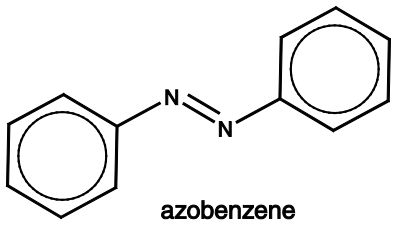


Phenylbutazone has been detected at a level of 4.0 parts-per-billion by mass in a horse-meat contaminated beef burger. (1 billion = 1×10^9)

(j) Calculate the number of 250 g burgers a 75 kg person would need to eat in order to consume the therapeutic dose of phenylbutazone.

There are a number of different ways of quantifying the amount of phenylbutazone present in a sample. One way of determining the concentration of phenylbutazone in the blood is to first extract the phenylbutazone from a blood sample and then oxidise it to azobenzene (shown below), at which point a simple spectrophotometric test can be used to determine the amount of azobenzene produced. The graph below shows the relationship between absorbance and the concentration of azobenzene.





azobenzene

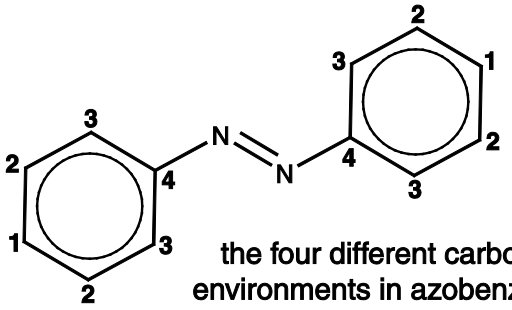
Patients were given a dose of 50 mg of phenylbutazone and after 6 hours a blood sample was taken to determine the level of phenylbutazone in the circulatory system. The phenylbutazone was first extracted from 10 cm^3 of blood and then oxidised to azobenzene. The azobenzene was extracted into 10 cm^3 of heptane and the absorbance of a 1.0 cm^3 sample of the resulting azobenzene/heptane solution was found to be 0.997.

(k) (i) Calculate the mass of azobenzene produced from the phenylbutazone present in the sample of blood.

(ii) Calculate the mass of phenylbutazone that was oxidized (assuming 100% conversion).

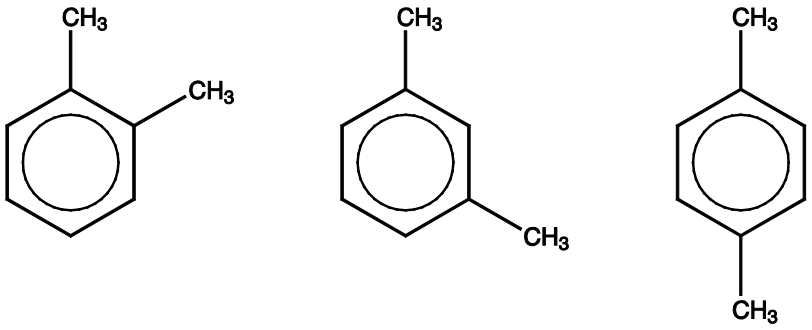
(iii) Calculate the concentration of phenylbutazone in the blood in mol dm^{-3}.

Carbon NMR is a technique used to give structural information about molecules in organic chemistry. The number of peaks in the spectrum corresponds to the number of different chemical environments of carbon atoms in a molecule. The total number of peaks in the spectrum of azobenzene is four since the symmetry and rapid rotations about single bonds mean that certain carbon atoms are equivalent. The carbon atoms in each different chemical environment are labelled below.



the four different carbon environments in azobenzene

Each isomer of dimethylbenzene has a different number of peaks in its carbon NMR spectrum.



1,2-dimethylbenzene 1,3-dimethylbenzene 1,4-dimethylbenzene

(l) Predict the number of peaks in the carbon NMR spectrum of each isomer of dimethylbenzene.

(m) Predict the number of peaks in the carbon NMR spectrum of phenylbutazone

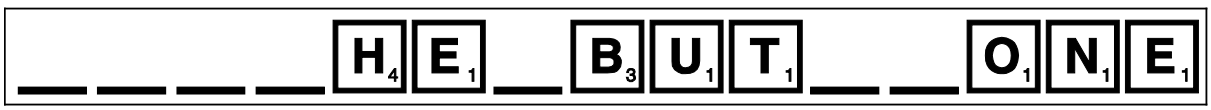
When phenylbutazone is metabolised in the human body, it is changed in the liver to a molecule that has a mass spectrum with a molecular ion at m/z 324.

(n) (i) Suggest what atom has been introduced into the molecule by this reaction in the liver.

(ii) This metabolite gives a carbon NMR spectrum with 15 peaks. Draw a structure for the metabolite consistent with this information.

Curiously, the name of this metabolite holds the title for the highest possible score for a single play in the game Scrabble (using American tournament rules).

(o) In light of your answer to part **(n)(i)**, suggest the name for this metabolite by filling in the missing blanks in your answer booklet. (Ignore the letter scores in the corner of each tile.)



2. This question is about the oldest water discovered on Earth

In May 2013, scientists announced the discovery of what is thought to be the oldest sample of water yet found on Earth. Trapped 2.4 km underground, the sample contained dissolved gases including carbon dioxide, hydrogen, methane, and the noble gases. The presence of hydrogen and methane was exciting since some bacteria are known to be able to use these to support life without photosynthesis. Analysis of the mixture of noble gases allowed the age of the sample to be determined.



The following standard enthalpy changes of formation at 298 K are given:

substance	$CO_2(aq)$	$H_2(aq)$	$CH_4(aq)$	$H_2O(l)$	$O_2(aq)$
$\Delta_f H°$/ kJ mol^{-1}	–121.0	–4.187	–89.10	–286.0	–11.72

Certain bacteria, such as *methanobacterium subterraneum*, found in underground samples of water, are capable of generating energy by forming methane from carbon dioxide and hydrogen according to the following overall equation:

$$CO_2(aq) + 4H_2(aq) \longrightarrow CH_4(aq) + 2H_2O(l)$$

(a) Calculate the standard enthalpy change at 298 K for hydrogenation of carbon dioxide (the reaction given above).

Another bacterium, *methylocuccus thermophiles*, utilizes energy obtained from the complete oxidation of methane.

(b) (i) Give the equation for the complete oxidation of methane in aqueous solution.

(ii) Calculate the standard enthalpy change for this reaction.

A number of isotopes of xenon were detected in the sample. One route for the formation of ^{129}Xe is from the decay of radioactive ^{129}I. The determination of iodine in the sample involved the oxidation of iodide to iodine using nitrate(III) ions, extraction of the iodine into hexane, reduction back to iodide with sulphate(IV), and then precipitation with silver nitrate before analysis by mass spectrometry. The oxidation of iodide to iodine with nitrate(III) ions evolves nitrogen gas.

(c) (i) Give the formulae for the nitrate(III) ion and the nitrate(V) ion.

(ii) Draw the structure of the nitrate(III) ion and the nitrate(V) ion and suggest the approximate bond angles in each.

(iii) Give the equation for the reaction between iodide and nitrate(III) ions in aqueous acid.

(iv) What sulfur containing ion will be formed when iodine reacts with sulfate(IV)?

(v) Give the equation for the reaction between sulfate(IV) and iodine in aqueous acid.

A number of methods were used to determine the age of the water, but the simplest is by looking at the quantity of ^{40}Ar formed from the decay of ^{40}K contained in the rock. In this, all the argon formed by the decay of the ^{40}K is assumed to remain dissolved in the water contained in the pores of the rock.

(d) Which of the follow may account for the production of ^{40}Ar from ^{40}K? Tick <u>all</u> possible explanations in the answer booklet.

(i) The ^{40}K emits an alpha particle.

(ii) A neutron in the ^{40}K decays into a proton, a positron (positive electron) and a neutrino.

(iii) A proton in the ^{40}K decays into a neutron, a positron (positive electron) and a neutrino.

(iv) A neutron in the ^{40}K decays into a proton, an electron, and a neutrino.

(v) A proton in the ^{40}K captures an electron, and decays into a neutron and a neutrino.

The rock has a density of 2.7 g cm^{-3} and is found to contain 2.0% by mass of potassium. Furthermore, 1.0% by volume of the rock is water-filled pores. The water from the rock was found to contain 0.0445 cm^3 of ^{40}Ar per cm^3 of water (measured at 0 °C).

(e) (i) Given that 1 mol of gas occupies a volume of 22.4 dm^3 at 0 °C, calculate the number of atoms of ^{40}Ar in 1 cm^3 of water.

(ii) What mass of rock contains this quantity of ^{40}Ar?

(iii) What is the mass of potassium in this quantity of rock?

(iv) Given that only 0.0117% of naturally occurring potassium is ^{40}K, determine the number of atoms of ^{40}K in the mass of rock from part **(ii)**.

The decay constant, λ, of ^{40}K is 5.54×10^{-10} per year. However, only a fraction (0.105) of the decay leads to the formation of ^{40}Ar, the rest leads to the production of ^{40}Ca.

The number of number of atoms of ^{40}Ar formed, $N_{40_{Ar}}$, over a time t years, is related to the number of atoms of ^{40}K remaining, N_{40_K}, by the following equation:

$$N_{40_{Ar}} = 0.105 \times N_{40_K} \times (e^{\lambda t} - 1)$$

(f) Use this equation and your answers to **(e)** to determine the age of the sample of water.

Acknowledgements

C3L6 would like to thank our sponsors:

University of Cambridge International Examinations

OCR

The Royal Society of Chemistry

Winton Capital Management

University of Cambridge Department of Chemistry

St Catharine's College, Cambridge

Question 1 was based on the papers:

Journal of Pharmaceutical Sciences, **63**, (1974) 1896-1901
"*Mass Spectral Analysis of Medicinal Pyrazolidinediones*" by R. Locock *et al*.

Journal of Pharmaceutical Sciences, **57**, (1968) 2053-2056
"*Ultraviolet spectrophotometric determination of phenylbutazone in biologic specimens* " by J. Wallace.

Spectra provided by SDBSWeb : http://sdbs.riodb.aist.go.jp
(National Institute of Advanced Industrial Science and Technology, May 2013)

Question 2 was based on the papers:

Nature, **497**, (16 May 2013) 357-360
"*Deep fracture fluids isolated in the crust since the Precambrian era*"
by G. Holland, C. J. Ballentine *et al*.

Thanks to Professor Ballentine for his help with this question.

FEMS Microbiology Reviews, **25**, (2001) 175-243
"*Energetics of overall metabolic reactions of thermophilic and hyper-thermophilic Archea and Bacteria*" by J. P. Amend and E. L. Shock

There are many excellent accounts of this work online – just search for "*oldest water on earth*"