Cambridge Chemistry Challenge Lower 6th

June 2012

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 back page of this booklet.

1. This question is about homeopathic solutions

The pseudo-science of homeopathy began over two hundred years ago, long before modern medicine. The main idea is that, against all scientific principles, medicines become increasingly potent the more they are diluted. Over the years, just about every well known poison has been used in certain homeopathic remedies, including arsenic, barium, mercury and even plutonium.

The arsenic compound usually used is an oxide, As_2O_3. In the remedies it is called by its Latin name *Arsenicum album* (white arsenic). The oxide is prepared industrially by roasting arsenic-containing ores such as arsenopyrite, FeAsS, in air. The other products formed are iron(III) oxide and sulfur dioxide.

(a) (i) What is the oxidation state of the arsenic in As_2O_3?

   (ii) Give an equation for the industrial production of As_2O_3 from FeAsS.

As_2O_3 is moderately soluble in water; one dm^3 of a saturated solution at 25 °C contains 20.6 g. When dissolved in water, the oxide reacts to form arsenous acid, H_3AsO_3.

(b) (i) Given that spectroscopy shows all the hydrogen atoms in H_3AsO_3 to be in the same environment, suggest a structure for the acid. What is the geometry around the arsenic atom?

   (ii) Give an equation for the formation of arsenous acid from As_2O_3.

   (iii) Calculate the concentration of the arsenous acid in $mol\ dm^{-3}$ in the saturated solution.

In homeopathy, a 'decimal-scale' is often used to specify the dilution of a given sample: D1 (sometimes labelled 1X) means the sample has been diluted 1 part in 10. D2 (or 2X) means the sample has been diluted 1 in 10, then 1 part of that solution has been further diluted 1 in 10 again to give a 1 in 100 dilution. A D6 (or 6X) solution has repeated this process six times to give a final dilution of 1 in 10^6.

   Arsenicum album is often sold as a D30 preparation. Let us assume that the initial stock solution before dilution was the saturated solution containing $20.6\ g\ dm^{-3}$ of As_2O_3.

(c) (i) Calculate the mass (in g) of As_2O_3 present in a 100 cm^3 glass of the D30 *Arsenicum album* remedy.

(ii) Given that 0.1 g of As_2O_3 is usually fatal, calculate the volume (in m^3) of the D30 solution that would be needed for a fatal dose of As_2O_3. Also express your answer as a fraction of the volume of the Earth (approximately 1.08×10^{12} km^3).

(iii) The preparations are usually sold in one ounce bottles (1 ounce = 28 cm^3). Calculate how many bottles of the D30 solution need to be bought in order, on average, to include one atom of arsenic.

Another 'remedy' is *Muriaticum acidum* which is actually diluted hydrochloric acid. This is available in various dilutions up to the extremely 'potent' D2000 preparation.

(d) Assuming the original stock solution before dilution was 1.0 mol dm^{-3}, what is the concentration of HCl in the following preparations?

    (i) D2   **(ii)** D4   **(iii)** D6   **(iv)** D8   **(v)** D10

The pH of a solution may be calculated using the following equation:

$$pH = -\log_{10} [H^+]$$

where $[H^+]$ is the **total** concentration of hydrogen ions in aqueous solution in mol dm^{-3}. Rearranging this equation allows us to calculate the total concentration of hydrogen ions from the pH of the solution:

$$[H^+] = 10^{-pH}$$

(e) (i) What is the pH of pure water at room temperature? Calculate $[H^+]$ for pure water.

(ii) Calculate the pH of the 1.0 mol dm^{-3} stock solution and the five dilutions from part **(d)**. Give your answers to one decimal place.

Whilst homeopathy deals with extremely dilute solutions, at the other extreme, high concentrations are limited by solubilities and, ultimately, the densities of materials.
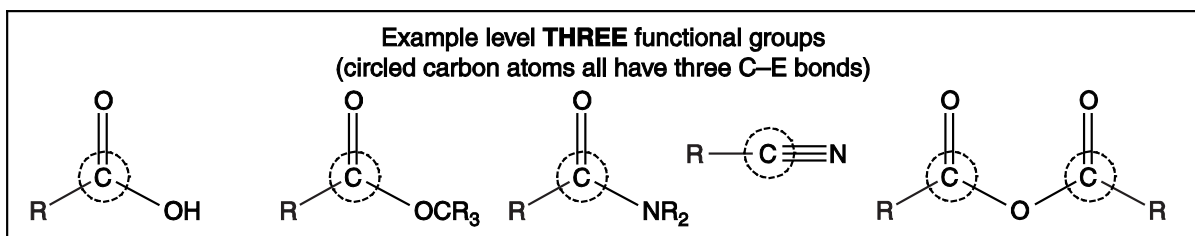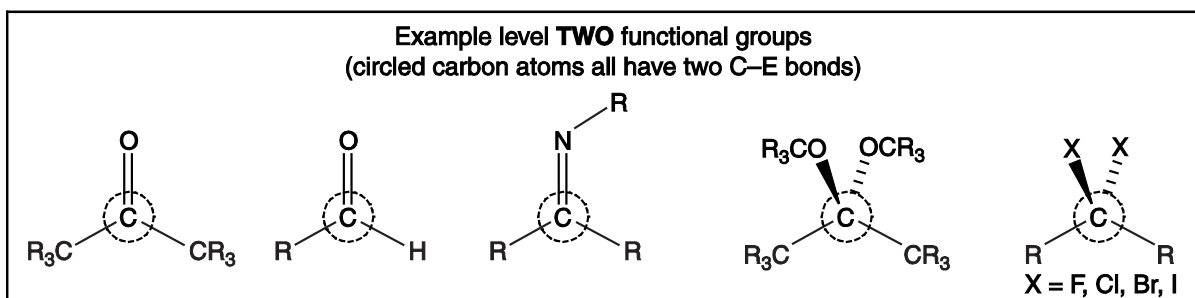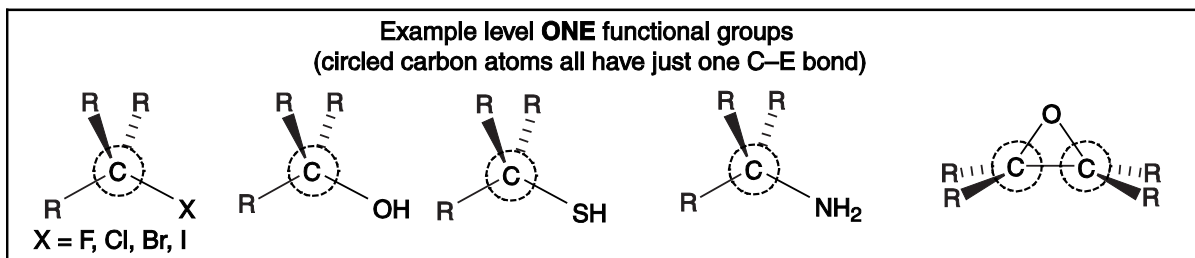
(f) Concentrated hydrochloric acid is sold as a 38% by mass solution with a density of 1.2 g cm^{-3}. Calculate the concentration of this solution in mol dm^{-3} and hence its pH.

(g) Given that the density of pure water is 1.0 kg dm^{-3}, calculate the concentration of pure water in mol dm^{-3}.

At high concentrations of acids, the above equations for pH are no longer valid. Not realising this, one popular science book has erroneously quoted the strongest acid (a boron-carbon cluster compound) as having a pH of −18.

(h) By considering the concentration of H^+ ions **only** (ignoring water and counter-ions), calculate the mass of one teaspoonful of this "pH minus 18" acid as predicted using the above equations. [Assume one teaspoonful is 5 cm^3.]

2. This question is about classifying simple organic reactions

One of the reasons organic chemists use skeletal formulae is to draw attention to the functional groups a molecule contains. These contain atoms other than carbon and hydrogen, so-called heteroatoms. Many different functional groups are possible, but it is often useful to keep track of the number of bonds that a given carbon atom has to electronegative atoms, the 'level' of a particular functional group. The electronegative elements include the halogens, oxygen, nitrogen and sulfur and will be represented by the symbol E; general alkyl groups are represented by an R. Some examples are shown below, but there are many other possibilities.

Example level ONE functional groups
(circled carbon atoms all have just one C–E bond)

X = F, Cl, Br, I

Example level TWO functional groups
(circled carbon atoms all have two C–E bonds)

X = F, Cl, Br, I

Example level THREE functional groups
(circled carbon atoms all have three C–E bonds)

Keeping track of the functional group level can be a useful way of understanding a large number of organic reactions.

> **In every one of the reactions in this question,**
> **no carbon-carbon bonds are broken or formed.**

During **oxidation** reactions, the functional group level will be found to increase as new C–E bonds are formed at the expense of C–H bonds.

During **reduction** reactions, the functional group level is found to decrease as new C–H bonds are formed at the expense of C–E bonds.

During **hydrolysis** reactions, the functional group level of every carbon remains the same, but the addition of water (*hydro*) may be used to split (*lyse*) functional groups, and / or replace some bonds to electronegative atoms with new bonds to oxygen. Different hydrolysis reactions may require different conditions with some only taking place at a significant rate with acid or alkali present.

(a) Each of the following ten reactions takes place with a single reagent. Classify each one as either an **oxidation**, a **reduction**, or a **hydrolysis** reaction. Simply tick the appropriate box for each in the answer booklet.

(i)

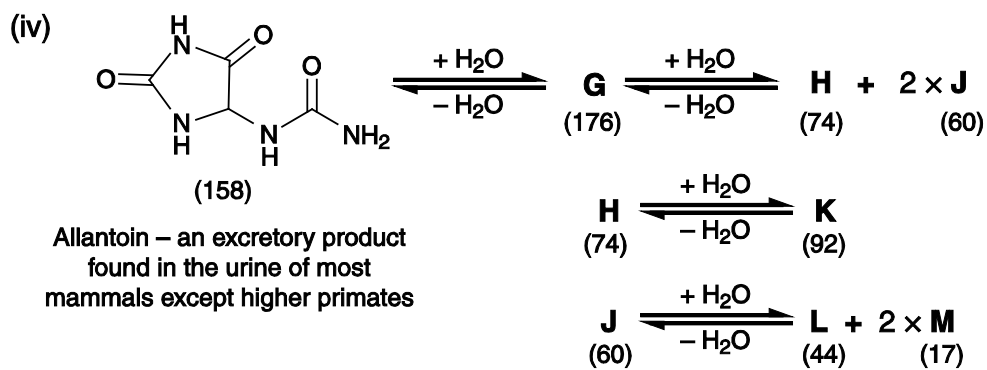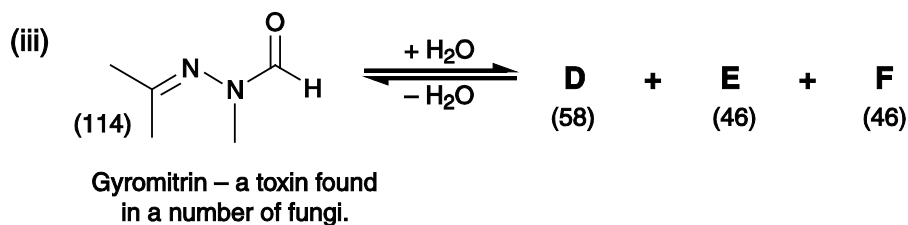(ii)

(iii)

(iv)

(v)

(vi)

(vii)

(viii) + C_2H_5OH

(ix)

(x)
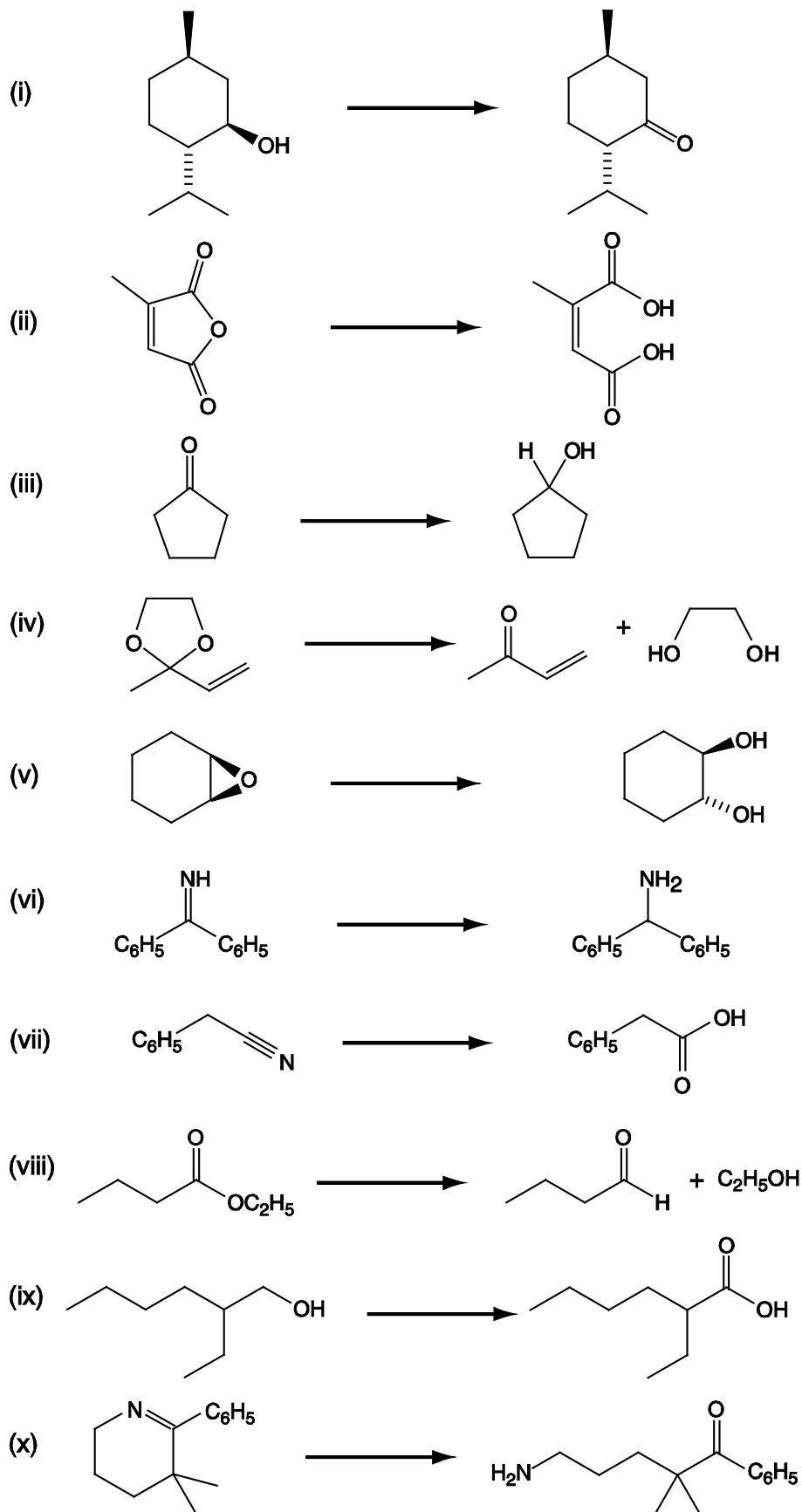
A honey bee

The fungus *Gyromitra esculenta*

(b) Each of the following natural products undergoes hydrolysis to give different products. Suggest structures for the products using their molecular masses (shown in brackets) to guide you.

(i)

$+ H_2O$ / $- H_2O$

A (46) **+** **B** (74)

(102)

An alarm pheromone in the honey bee

(ii)

(156)

$+ H_2O$ / $- H_2O$

C (174)

A sex pheromone of the olive fly.

(iii)

(114)

$+ H_2O$ / $- H_2O$

D (58) **+** **E** (46) **+** **F** (46)

Gyromitrin – a toxin found in a number of fungi.

(iv)

(158)

Allantoin – an excretory product found in the urine of most mammals except higher primates

$+ H_2O$ / $- H_2O$

G (176)

$+ H_2O$ / $- H_2O$

H (74) **+ 2 × J** (60)

H (74) $+ H_2O$ / $- H_2O$ **K** (92)

J (60) $+ H_2O$ / $- H_2O$ **L** (44) **+ 2 × M** (17)

6
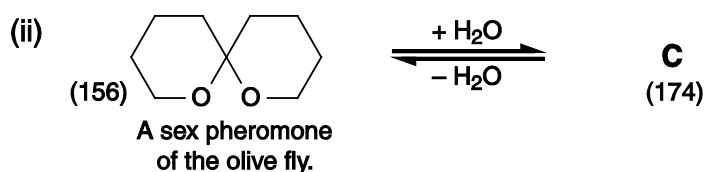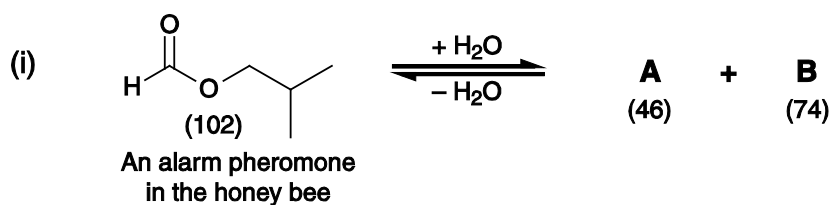
(c) The scheme below contains a number of mystery organic compounds **R–Z**. Draw the structures for the compounds **R–Z**.

Use the following hints to help you.

- All the compounds **R–Z** contain only carbon, hydrogen and oxygen.
- **Each carbon** atom in all of the molecules **R–Z** is **bonded to exactly one** other carbon atom.
- There are no C=C (double) or C≡C (triple) bonds in any of the compounds.
- It is usually more thermodynamically stable for a carbon to have a double bond to an oxygen atom than to have two single bonds to hydroxyl (OH) groups.

Periodic Table of the Elements

Key:

symbol
atomic number
mean atomic mass

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															

*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 $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$