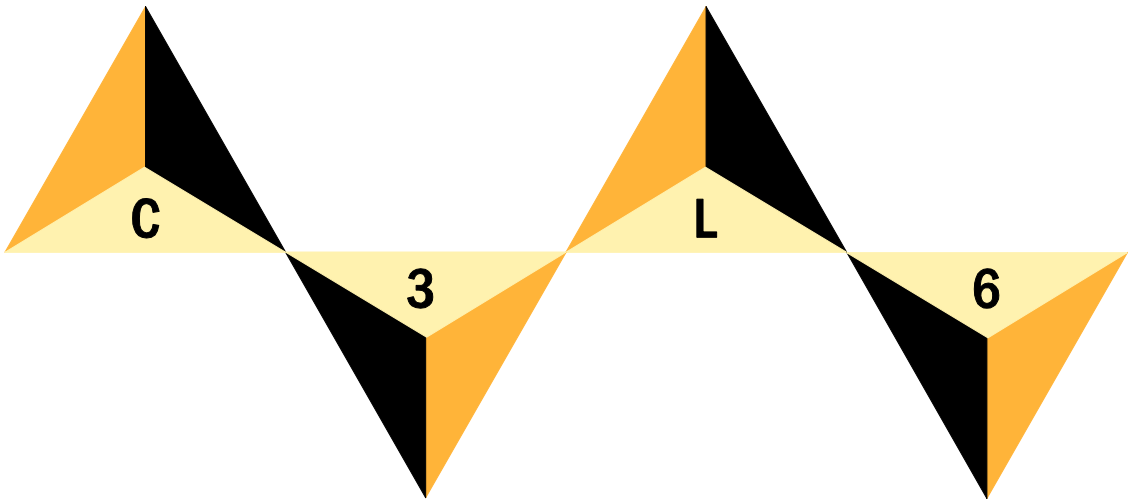


Cambridge Chemistry Challenge Lower 6th

December 2024

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 A-level 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 minutes under exam conditions.
- 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.

Period	1	2		3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
	s-block			d-block										p-block					
1	**H** 1 1.008																		**He** 2 4.003
2	**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
3	**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
4	**K** 19 39.10	**Ca** 20 40.08		**Sc** 21 44.96	**Ti** 22 47.87	**V** 23 50.94	**Cr** 24 52.00	**Mn** 25 54.94	**Fe** 26 55.85	**Co** 27 58.93	**Ni** 28 58.69	**Cu** 29 63.55	**Zn** 30 65.38	**Ga** 31 69.72	**Ge** 32 72.63	**As** 33 74.92	**Se** 34 78.97	**Br** 35 79.90	**Kr** 36 83.80
5	**Rb** 37 85.47	**Sr** 38 87.62		**Y** 39 88.91	**Zr** 40 91.22	**Nb** 41 92.91	**Mo** 42 95.95	**Tc** 43	**Ru** 44 101.07	**Rh** 45 102.91	**Pd** 46 106.42	**Ag** 47 107.87	**Cd** 48 112.41	**In** 49 114.82	**Sn** 50 118.71	**Sb** 51 121.76	**Te** 52 127.60	**I** 53 126.90	**Xe** 54 131.29
6	**Cs** 55 132.91	**Ba** 56 137.34	*	**Lu** 71 174.97	**Hf** 72 178.49	**Ta** 73 180.95	**W** 74 183.84	**Re** 75 186.21	**Os** 76 190.23	**Ir** 77 192.22	**Pt** 78 195.08	**Au** 79 196.97	**Hg** 80 200.59	**Tl** 81 204.38	**Pb** 82 207.2	**Bi** 83 208.98	**Po** 84	**At** 85	**Rn** 86
7	**Fr** 87	**Ra** 88	+	**Lr** 103	**Rf** 104	**Db** 105	**Sg** 106	**Bh** 107	**Hs** 108	**Mt** 109	**Ds** 110	**Rg** 111	**Cn** 112	**Nh** 113	**Fl** 114	**Mc** 115	**Lv** 116	**Ts** 117	**Og** 118

Group Number

Symbol
atomic number
mean atomic mass

f-block

Lanthanoids:	*	**La** 57 138.91	**Ce** 58 140.12	**Pr** 59 140.91	**Nd** 60 144.24	**Pm** 61	**Sm** 62 150.36	**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** 70 173.05
Actinoids:	+	**Ac** 89	**Th** 90 232.04	**Pa** 91 231.04	**U** 92 238.03	**Np** 93	**Pu** 94	**Am** 95	**Cm** 96	**Bk** 97	**Cf** 98	**Es** 99	**Fm** 100	**Md** 101	**No** 102

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

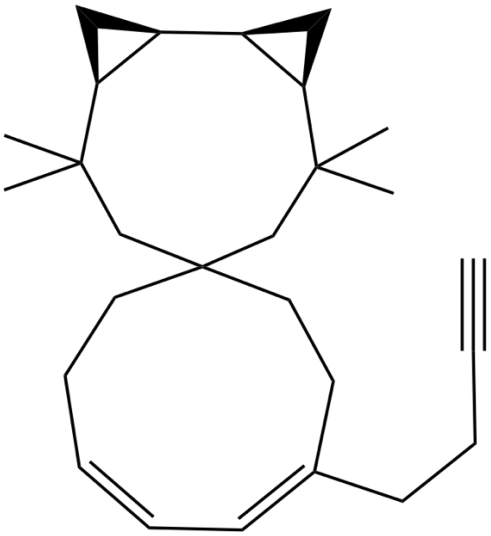
1. This question is about using Double Bond Equivalents

When presented with the formula for an organic compound, it is useful to work out the so-called 'degree of unsaturation' or number of Double Bond Equivalents (DBE). This tells us how many rings or π-bonds the structure must contain which helps when thinking of possible structures.

The DBE are based on comparing the actual molecular formula to the theoretical formula if the structure were saturated—having no rings and containing only σ bonds (with all atoms having their standard valence).

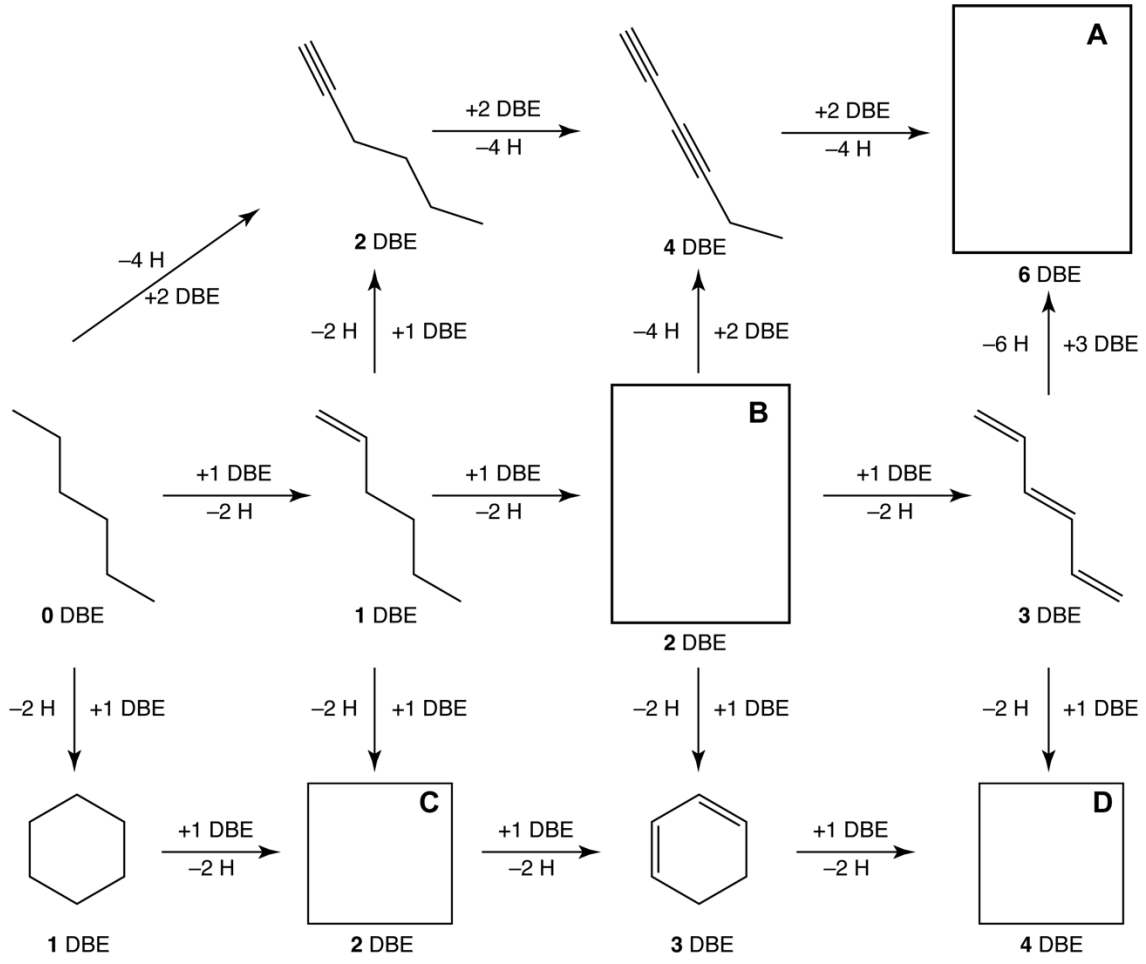
Double bond equivalents arise because each time a double bond or a ring is formed, there are two fewer hydrogens present in the compound relative to it having no double bond or ring, as shown in the diagram below. A double bond or a ring each count as 1 DBE; a triple bond counts as 2 DBE.

'felyne'



A new alkyne proposed by C3L6; still-to-be synthesised!

(a) (i) Complete the diagram below by filling in the missing structures **A**–**D** in your answer booklet.



(a) (ii) How many DBE are there in the structure of felyne?

(b) The general formula for a non-cyclic alkane is C_nH_{2n+2}. Give the general formulae for the following:

(i) an alkene or cycloalkane

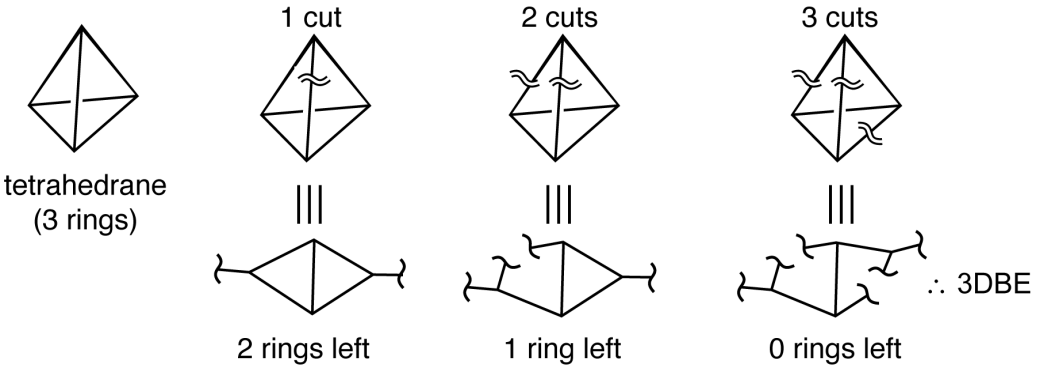
(ii) A di-alkyne (a hydrocarbon containing two C≡C triple bonds)

(iii) a cycloalkene

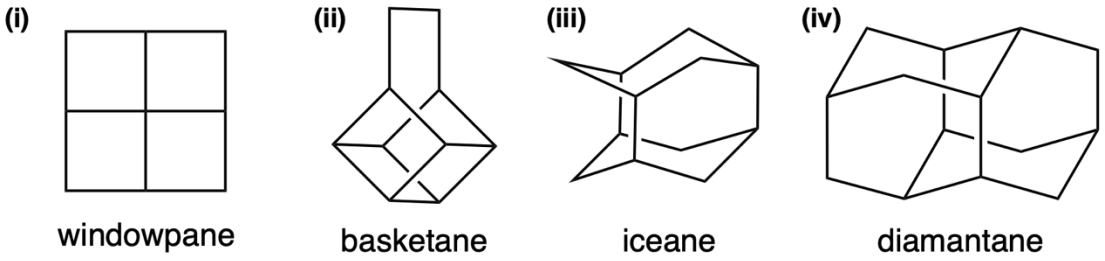
(iv) a hydrocarbon containing n carbons with x DBE.

(c) Give an expression for the number of DBE in the hydrocarbon with formula C_nH_y in terms of n and y.

When trying to count the number of DBE in structures with multiple rings, the number of rings may be determined by counting the minimum number of cuts through bonds needed to be made in order to leave the structure ring-free. This is illustrated with the structure tetrahedrane below.



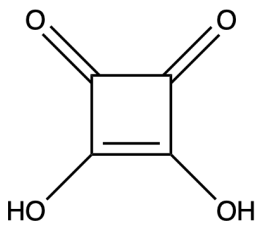
(d) How many DBE are present in each of the following structures?



The concept of double bond equivalents can also be applied for rings and double bonds formed to heteroatoms, for example, with oxygen atoms. To work out the number of DBE for a formula containing carbon, hydrogen and oxygen only, we can simply ignore the oxygen as if it were not there. Any DBE a structure contains could be accounted for as a C=O double bond as well as a C=C double bond, or with rings which may or may not include an oxygen atom. For example, $C_4H_{10}O_2$ has the same number of DBE as C_4H_{10} (zero DBE), whereas $C_4H_8O_2$ has the same number of DBE as C_4H_8 (1 DBE).

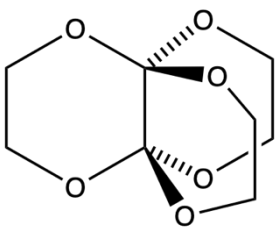
(e) How many DBE in each of these structures? Write down their chemical formulae.

(i)



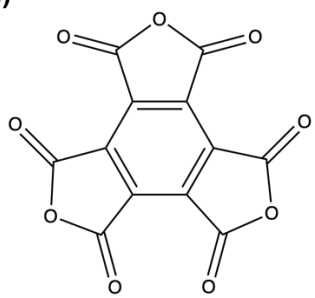
squaric acid

(ii)



a hexaoxapropellane

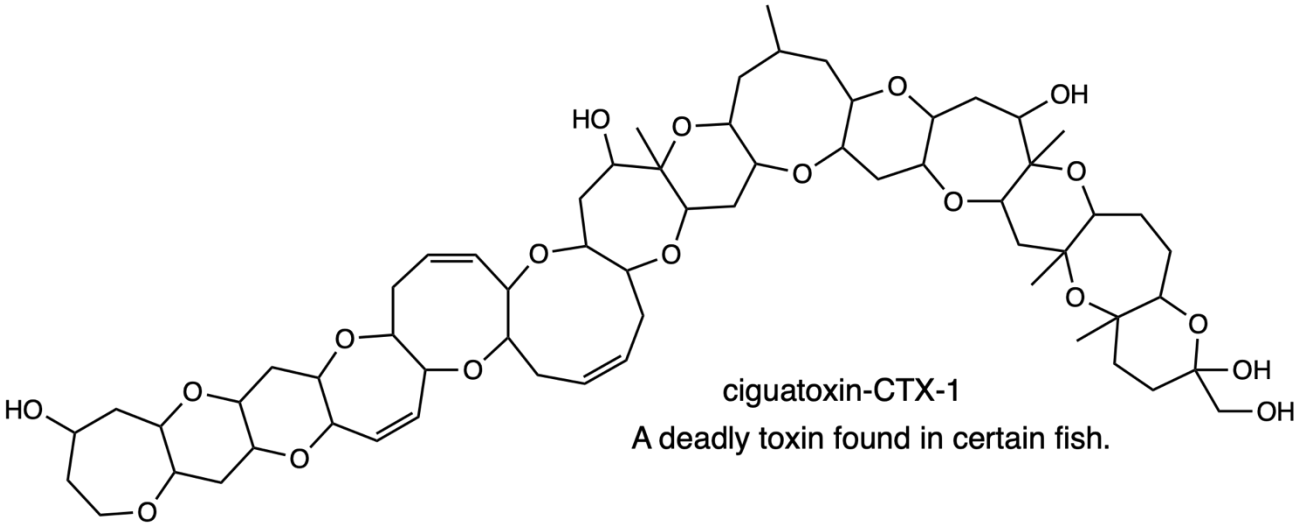
(iii)



mellitic anhydride

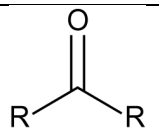
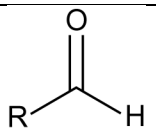
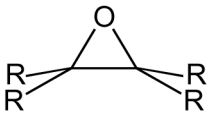
(f) (i) How many DBE in the structure ciguatoxin-CTX-1, shown below?

(ii) Given the molecule contains 62 carbon atoms, calculate the formula of ciguatoxin-CTX-1. (Don't try counting the hydrogens – there are too many!)

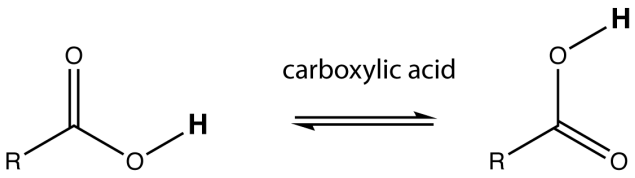


ciguatoxin-CTX-1
A deadly toxin found in certain fish.

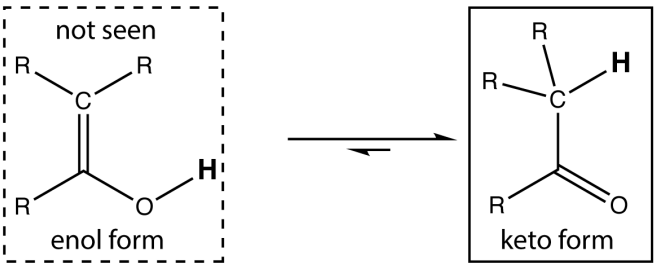
For a compound with known formula, once the number of DBE are known, analytical techniques such as NMR spectroscopy can be used to account for the DBE. For compounds with just one oxygen atom, only the following functional groups are possible:

Functional Group	Alcohol	Ketone	Aldehyde	Ether (chain or cyclic)		Epoxide (3-membered ring cyclic ether)
	R—OH			R—O—R		
				chain	cyclic	
Number of DBE	0	1	1	0	1	1

The arrangement where an –OH group is directly attached to a CC π bond is called an 'enol'. You may be aware how the acidic proton in a carboxylic acid group could swap between the two oxygen atoms. A similar proton swap can occur from the –OH of the enol onto the CC π bond, but the new arrangement, the so-called 'keto-form' containing a CO π bond is considerably more stable and so is usually the only form seen.

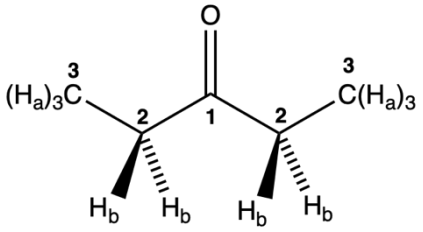
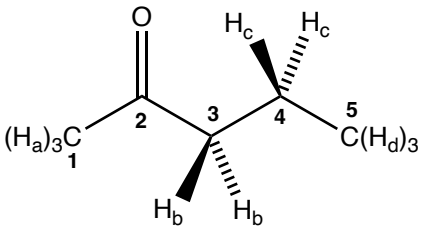
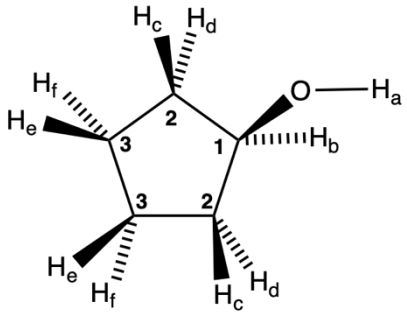
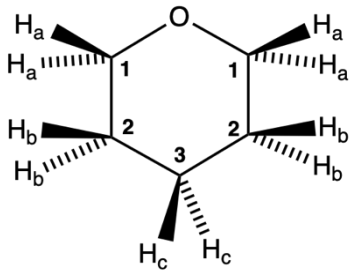
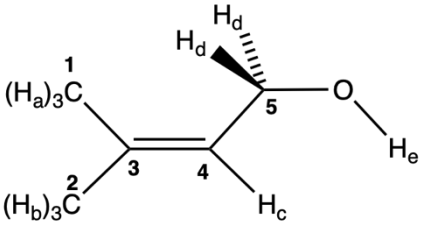


the proton can easily swap between the oxygens



the keto form is usually much more stable than the enol form

NMR (nuclear magnetic resonance) is routinely used to determine structures. At the simplest level, the technique reveals how many unique environments of hydrogen and carbon there are in a structure. Atoms may be in the same environment if the structure contains mirror planes of symmetry or rotational symmetry axes. Some isomers of $C_5H_{10}O$ are shown below in which the unique hydrogen environments are labelled H_a, H_b, H_c, etc and the unique carbon environments are labelled **1**, **2**, **3**, etc.

compound	Useful symmetry	Number of unique hydrogen environments	Number of unique carbon environments
	2 mirror planes 1 rotational axis	2	3
	1 mirror plane	4	5
	1 mirror plane	6	3
	2 mirror planes 1 rotational axis	3	3
	1 mirror plane	5	5

(g) (i) Suggest two additional structures with formula $C_5H_{10}O$ that also have only 2 unique hydrogen environments.

(ii) How many unique carbon environments are there in the structure of 'felyne' [see intro]?

The remainder of the question looks at the isomers with formula C_3H_4O (2 DBE). Some of these are stable compounds, others are not.

(h) (i) There are THREE enol structures, **E**, **F**, & **G**, with formula C_3H_4O which form three different keto-forms, **H**, **I** & **J**. The number of unique hydrogen environments in each keto form is given in the table below. Give the structures for isomers **E** – **J**.

enol form	keto form	number of unique hydrogen environments in keto form
E	**H**	1
F	**I**	4
G	**J**	2

(ii) **K** & **L** are the only isomers of C_3H_4O that contain an –OH group but are not enols. **K** has three unique carbon environments whereas **L** has two. Give the structures of **K** and **L**.

(iii) **M** is the only isomer of C_3H_4O that has no π bonds. Give the structure of **M** and state how many unique environments of hydrogen it contains.

(iv) **N**, **O**, **P**, **Q** are isomers of C_3H_4O that contain an ether / epoxide oxygen. The number of unique hydrogen environments each contains is given in the table below. Hydrogenation of the π bond in **O** and **P** would give the same compound, **R**. Give the structures of isomers **N** – **Q**, and for compound **R**.

isomer	number of unique hydrogen environments in isomer
N	2
O	2
P	3
Q	3

2. This question is about homeopathic solutions

Homeopathy is a type of alternative pseudo-medicine that uses extremely high dilutions of often toxic substances in the hope that some therapeutic effect will be seen in a patient. Amongst the many poisonous substances used in the homeopathic treatment of disease, one is based upon the element mercury. The homeopathic medicine is called *Mercurius Solubilis*, or *Merc Sol*. The precise chemical composition of *Merc Sol* is unclear from the scientific literature, but the homeopathic literature suggests that it was first prepared by the German doctor, Samuel Hahnemann. It is said that Hahnemann took mercury metal, dissolved it in nitric acid and then added ammonia solution until a precipitate was formed. This precipitate was then re-dissolved in water to form *Merc Sol*.



To prepare *Merc Sol*, mercury is reacted with nitric acid, but the products depend upon the concentration of the nitric acid. Dilute nitric acid forms mercury(I) nitrate, but more concentrated acid and longer reaction times lead to the formation of mercury(II) nitrate. In neither case is hydrogen gas formed. Instead the mercury is oxidised by the nitric acid, leading to the formation of nitrogen(II) oxide, NO. Mercury(I) salts do not contain discrete Hg^{+} ions, but are generally found to contain the Hg_2^{2+} ion.

(a) **(i)** Draw a dot-and-cross diagram for nitric(V) acid.

(ii) Write a balanced equation for the reaction of mercury with **dilute** nitric acid.

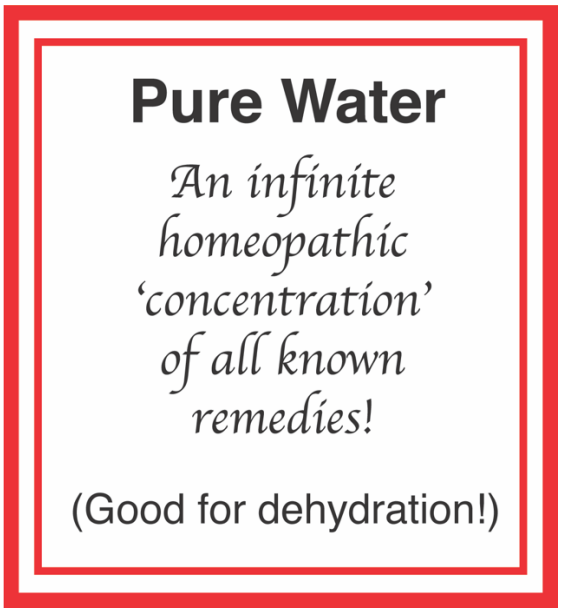
(iii) Write a balanced equation for the reaction of mercury with **concentrated** nitric acid.

(iv) The NO gas formed instantly reacts with the oxygen in the air to give a brown gas. Give an equation for this reaction.

The solution of mercury in nitric acid is then treated with ammonia to produce a precipitate. Careful reading of the chemical literature suggests solutions of mercury(I) and mercury(II) nitrate with aqueous ammonia form neutral compounds in which the mercury(I) or (II) ions are bound to both a nitrate ion and (probably covalently) to an amide ion, NH_2^{-}.

(b) Give the formula of both Hg(I) and Hg(II) compounds that are formed with aqueous ammonia.

It is easy to buy solutions of *Merc Sol*, which may cause some alarm as mercury salts are known to be extremely toxic to most organisms. However, the solutions that may be purchased are very dilute. Hahnemann used a logarithmic dilution scale, which is called the "centesimal" scale. This involves the dilution by a factor of 100. A *2C* dilution dilutes the original stock twice, each by a factor of 100, so a *2C* dilution is diluted 10,000 times. The solution of *Merc Sol* easily available that theoretically contains the highest concentration of mercury is a *30C* dilution. However, some of the homeopathic literature uses a *6C* dilution in their investigations. It is said that a *6C* dilution contains 8.21×10^{-16} mg mL^{-1} of mercury ions, Hg^{2+}.



For these calculation, assume the original mercury compound used to make the homeopathic remedies is just mercury(II) nitrate.

(c) **(i)** Calculate the concentration (in mol dm^{-3}) of the original stock solution.

(ii) Calculate the concentration (in mol dm^{-3}) of the *30C* solution.

(iii) What is the mass (in g) of mercury(II) nitrate in typical bottle containing 28 mL of 'most potent' *200C* solution?

Mercury(II) nitrate is very toxic and doses as small as 0.5 g have been reported as fatal for humans.

(d) **(i)** Calculate the mass of Hg^{2+} contained in 0.5 g of mercury(II) nitrate.

(ii) Calculate the volume (in litres) of the 'dangerously concentrated' *6C* dilution that would need to be consumed to ingest a toxic dose.

(iii) Express your answer to **(d)(ii)** as a fraction of the volume of the Water Cube National Aquatics Centre swimming pool in Beijing (approximately 2.5 million litres when used for the Beijing Olympics in 2008).

Another 'remedy' is *Nitricum Acidum* which is actually diluted nitric acid. This is available in various dilutions up to the extremely 'potent' *1M* preparation. A *1M* dilution is not 1 mol dm^{-3}; a homeopathic *1M* dilution is equivalent to a crazy *1000C*.

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

(i) *2C* **(ii)** *3C* **(iii)** *4C* **(iv)** *1M*.

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:

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

(f) (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 of nitric acid. Give your answer to one decimal place.

(iii) Calculate the pH of the four dilutions from part **(e)**. 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. Concentrated nitric acid is sold as a 68% by mass solution with a density of 1.41 g cm^{-3}.

(g) (i) Calculate the concentration of concentrated nitric acid in mol dm^{-3}.

(ii) Use the equations above to calculate the theoretical pH of a concentrated nitric acid of strength 12 mol dm^{-3}.

(iii) 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, and confusing pH with pK_a, many sites on the internet quote the strongest acid (fluoroantimonic acid) as having a pH of –31.3.

(h) By considering the concentration of H^+ ions **only** (ignoring water and counter-ions), calculate the mass of one teaspoonful of this "pH minus 31.3" acid as predicted using the above equations. [Assume one teaspoonful is 5 cm^3.]