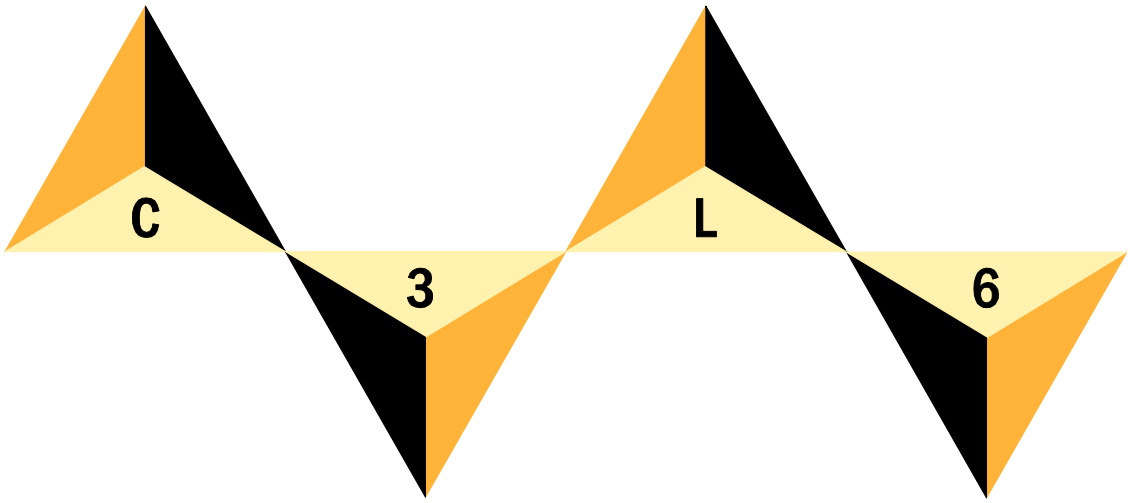


Cambridge Chemistry Challenge Lower 6th

June 2022

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.

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

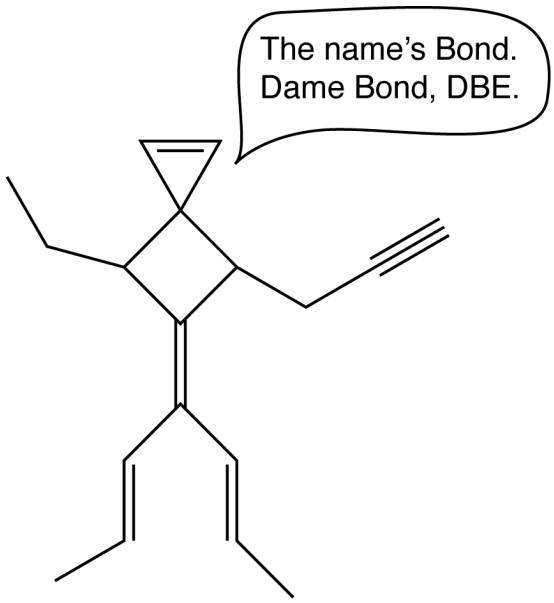
The Avogadro constant $N_A = 6.022 \times 10^{23}$ mol^{-1}

1. This question is about 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.

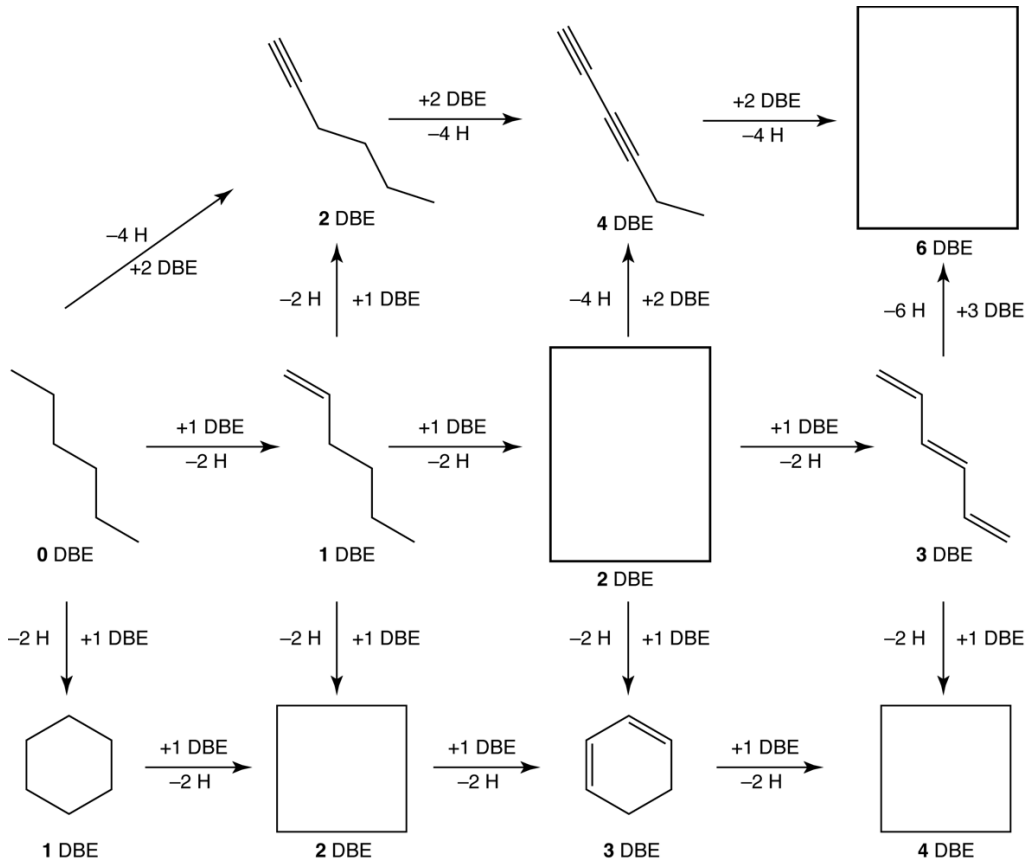
The DBE are based on comparing the actual molecular formula to the theoretical formula if the structure were saturated—having no rings and containing only σ bonds (with all atoms having their standard valence).

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.



Dame Bond, DBE, shown above, is a younger, more athletic version of the now-retired character from a 2016 Chemistry Olympiad Paper.

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



(a) (ii) How many DBE does Dame Bond have? Circle the correct answer in your answer booklet.

004 005 006 007 008 009

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

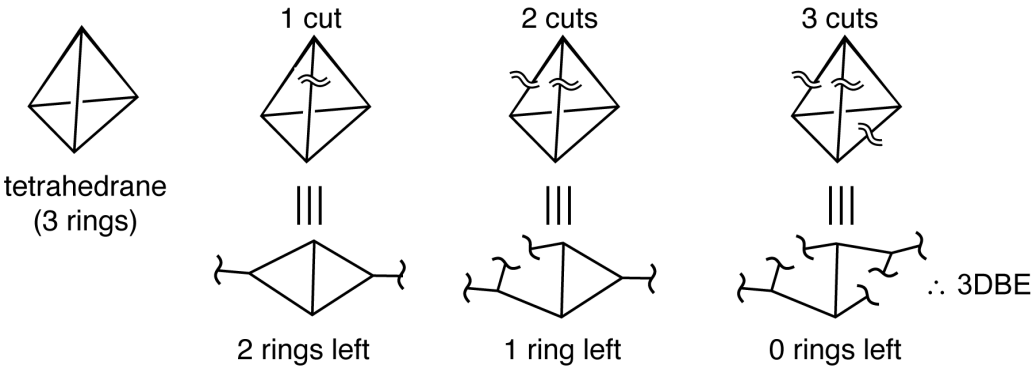
(i) an alkene or cycloalkane **(ii)** an alkyne (a hydrocarbon containing a C≡C triple bond)

(iii) a cycloalkene **(iv)** a tri-alkyne

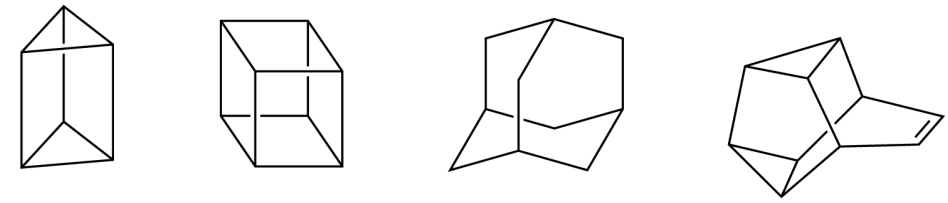
(v) a hydrocarbon containing n carbons with x DBE.

(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.

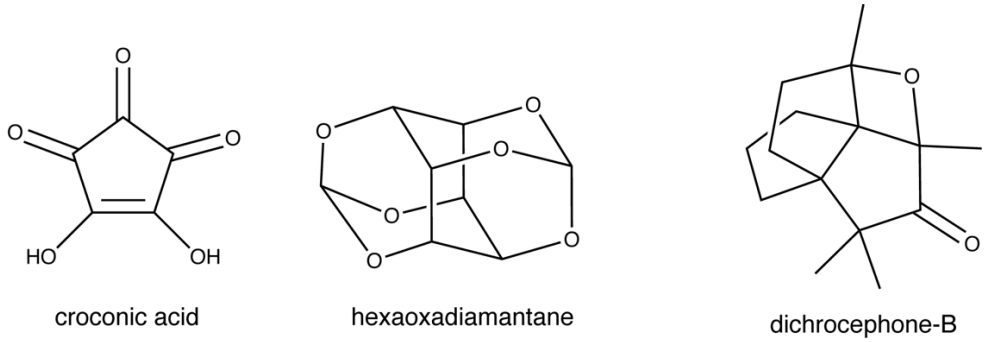


(d) How many DBE are present in each of the following structures?



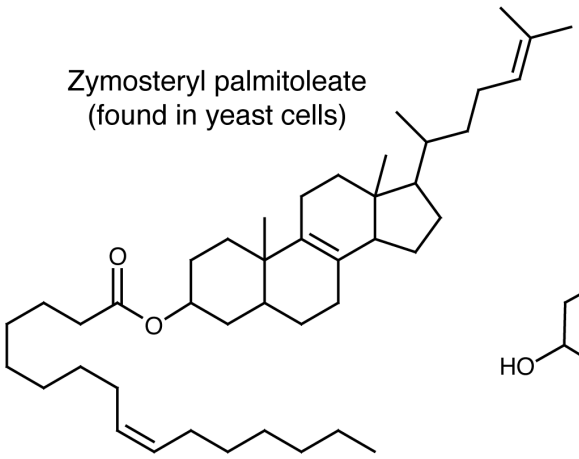
The concept of double bond equivalents can also be applied for rings and double bonds formed to heteroatoms, for example, with oxygen atoms. To work out the number of DBE for a formula containing carbon, hydrogen and oxygen only, we can simply ignore the oxygen as if it were not there. Any DBE a structure 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.



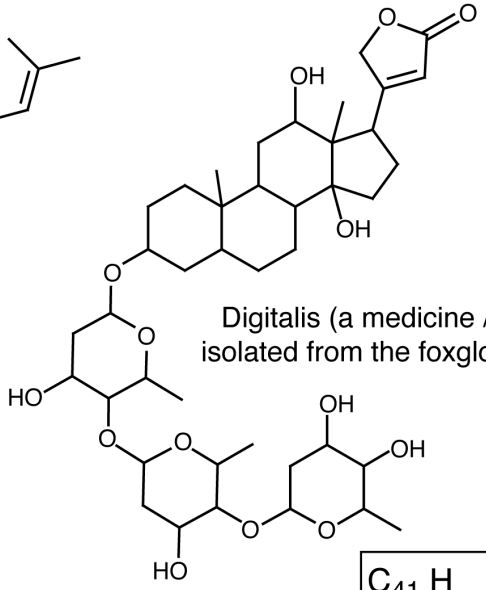
(f) Count the number of DBE in each of these structures. Use the number of DBE and the given number of carbon atoms each contains to work out the number of hydrogen atoms and hence their formulae. Write your answer in your answer booklet.
(Don't try counting the hydrogens – there are too many!)

Zymosteryl palmitoleate
(found in yeast cells)

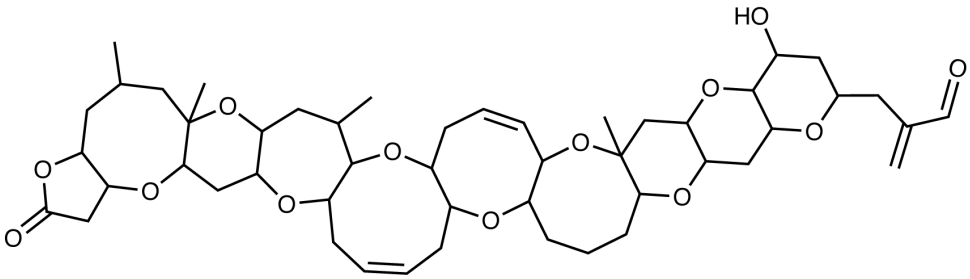


C_{43} H__ O__

Digitalis (a medicine / poison isolated from the foxglove plant)



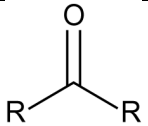
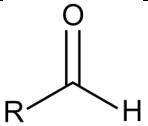
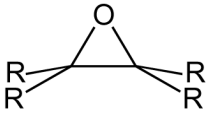
C_{41} H__ O__



Brevetoxin-A
(a potent neurotoxin from red algae)

C_{49} H__ O__

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

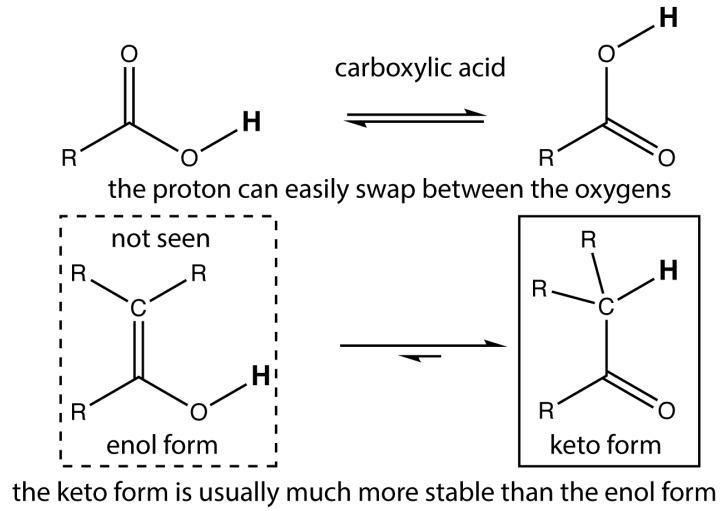
Functional Group	Alcohol	Ketone	Aldehyde	Ether (chain or cyclic)		Epoxide (3-membered ring cyclic ether)
	R—OH			R—O—R		
				chain	cyclic	
Number of DBE	0	1	1	0	1	1

The table below shows the possible combinations of rings, double bonds and triple bonds, alcohols and ethers possible to produce a compound with DBE = 0 and DBE = 1 when there is a single oxygen in the molecule.

DBE	Rings	C≡C	C=C	C=O	Alcohols	Ethers
0					**1**	
						1
1	**1**				**1**	
	1					**1**
			1		**1**	
			1			**1**
				1		

(g) In your answer booklet, continue the table for the possible combinations for **2** DBE.

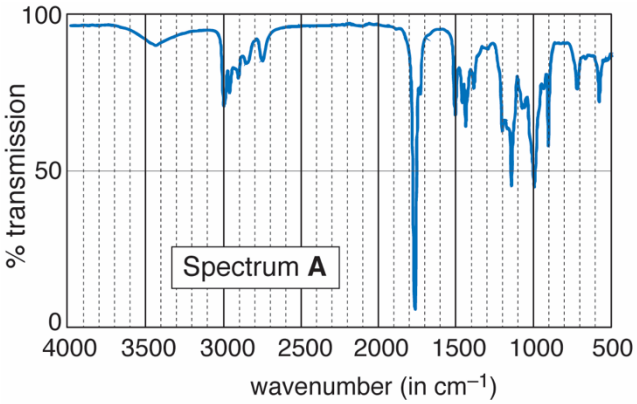
In the next part of the question, we will look at isomers with the formula C_3H_6O (1DBE). A number of structural isomers are possible, but one arrangement does not give any stable compounds; this is where an –OH group is directly attached to a C=C bond to form a so-called 'enol'. You may be aware how 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 C=C double bond, but the new arrangement is much more stable. Consequently, only the keto forms (ketones or aldehydes) may be isolated, not the enol form.

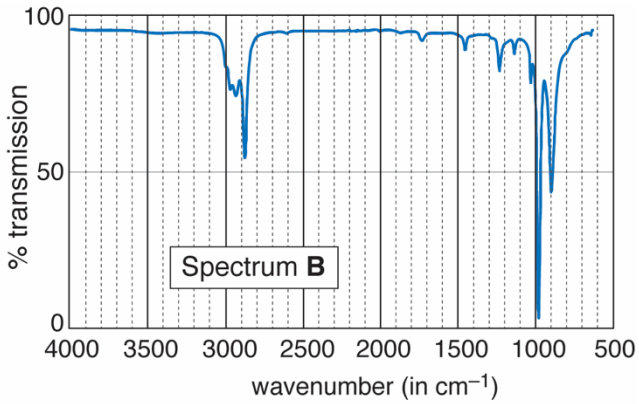


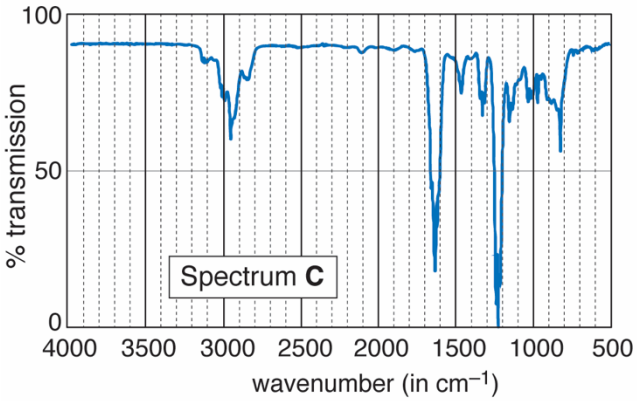
(h) Draw the structures of THREE enol isomers of C_3H_6O and for each one, draw the structure of the preferred keto form.

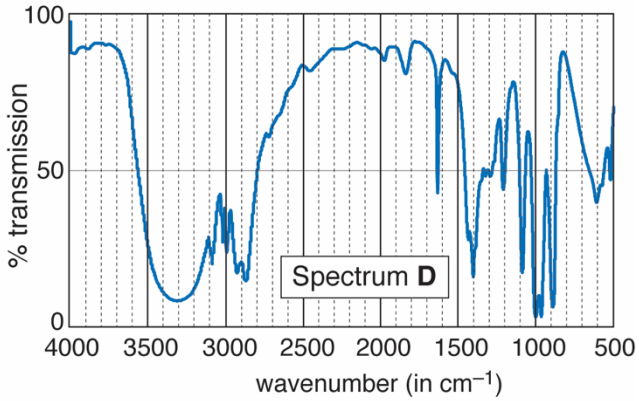
The IR spectra of some of the stable isomers of C_3H_6O are shown below, together with some data.

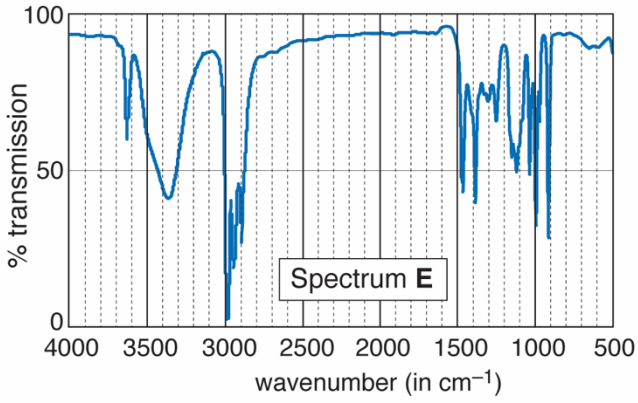
Useful data and tips for interpreting IR spectra.					
C–H	O–H (alcohol)	C≡C	C=C	C=O	C–O
a number of peaks ~ 3000 cm^{-1}.	broad peak 3200-3400 cm^{-1}	2100-2250 cm^{-1}	1600-1700 cm^{-1}	1700-1800 cm^{-1}	(below 1500 cm^{-1})
As usual, the spectra have been recorded as *transmission* spectra, i.e. the vertical axis shows the percentage of light that is transmitted through the sample; a *strong absorption* corresponds to a *small* transmission. Only consider peaks with a strong absorption (less than 50% transmission). The regions in the spectra below 1500 cm^{-1} corresponds to more complicated vibrations of the molecule and may be ignored.					











(i) Give the structure(s) that could possibly correspond to each of the spectra. (Where it is not possible to distinguish between two possible structures, give both structures.)

2. This question is about aluminium, anti-perspirants, and honeystone.

Aluminium is a chemically interesting metal. Compounds of aluminium have been formed and detected throughout the observable universe, from industrial units where aluminium is extracted or recycled, to the red giant carbon star CW Leonis, which is 400 light years from Earth.



IMAGE: ESA/Hubble, NASA, Toshiya Ueta (University of Denver), Hyosun Kim (KASI)

The chemistry of aluminium, as a group 13 element, is dominated by a single oxidation state.

(a) (i) Complete the electron configuration of an aluminium atom:
$1s^2 2s^2$…….

(ii) The aluminium atom can lose or gain electrons to complete its outer shell. How many electrons do you expect aluminium to a) lose, and b) gain to complete its outer shell?

Aluminium(III) chloride has a complex chemistry which is affected by temperature and solvent. Solid, anhydrous aluminium(III) chloride at room temperature has a relative formula mass (M_r) of 133.33. This compound is often considered to be ionic in the solid state, with the crystal structure showing each aluminium ion surrounded by six chloride ions.

(b) What is the empirical formula of aluminium(III) chloride under these conditions?

However, it is relatively easy to change the structure of, and the bonding in, aluminium(III) chloride. Solid aluminium(III) chloride sublimes at atmospheric pressure and at a temperature of 180.2 °C. The gas that is formed contains molecules that have an M_r of 266.66. If this gas is further heated to 1100 °C, it forms molecules that have an M_r of 133.33.

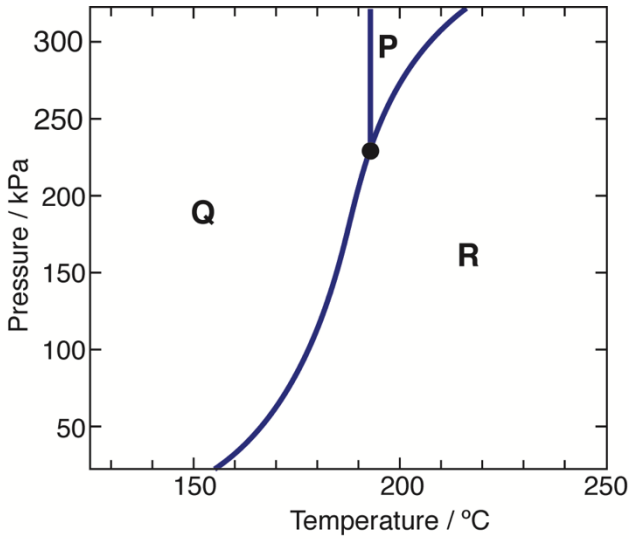
(c) (i) Draw a dot and cross diagram to show the covalent bonds in the molecule that has an M_r of 133.33.

(ii) What is the angle between any two Al–Cl bonds?

(iii) The aluminium centre in this molecule is described as electron deficient. This means that the aluminium can accept a lone pair of electrons from a donor atom to complete its outer shell. With this in mind, draw a structure for the molecule of M_r 266.66 in which each aluminium centre has a complete outer shell of electrons.

The figure on the right shows a phase diagram for aluminium(III) chloride. This shows the conditions of pressure and temperature at which the different phases (solid, liquid, and gas) are stable – these define the regions **P**, **Q**, and **R** (in random order).

Atmospheric pressure is 101.3 kPa.



(d) (i) Which of the regions **P**, **Q**, and **R** correspond to which of the three phases solid, liquid and gas?

(ii) What is the minimum temperature and pressure for liquid aluminium(III) chloride to be stable?

(iii) What is unique about the combination of pressure and temperature indicated by the solid black circle?

(iv) Under the conditions in (d)(ii), the liquid formed does not conduct electricity. What is the most likely structure of the species in the liquid state? Tick one of the following options in your answer booklet:

a) a mixture of aluminium and chloride ions
b) a molecule of M_r 133.33
c) a molecule of M_r 266.66.

If 0.500 g of gaseous aluminium(III) chloride (**A**) is reacted with 0.202 g of liquid aluminium at 1200 °C, a new, gaseous compound of aluminium (**B**) is formed as the only product. This reaction is endothermic and the enthalpy change observed on this scale is 1.532 kJ.

Compound **B** has been detected by measuring the spectrum of light in the millimetre range, coming from the atmosphere of a distant star in the constellation Leo. The molecular formula of **B** is the same as its empirical formula.

(e) (i) Give a balanced equation for this reaction forming compound **B**.

(ii) Given that the aluminium atom is not electron deficient in compound **B**, draw a dot and cross diagram that illustrates the bonding in this molecule.

(iii) Calculate the average aluminium–chlorine bond energy in compounds **A** and **B**, given the following data:

$\Delta_f H^o$ (compound **A**(g)) = –584.6 kJ mol^{-1}
$\Delta_f H^o$ (Al(l)) = +10.56 kJ mol^{-1}; $\Delta_f H^o$ (Al(g)) = +330 kJ mol^{-1}
Cl–Cl bond dissociation energy = +242.6 kJ mol^{-1}.

Aluminium(III) chloride also exists as a hydrated ionic salt, whose formula is $AlCl_3 \bullet 6H_2O$. When this solid is heated, it decomposes forming a new solid and liberating two gases. 2 moles of the solid produce 16 moles of product, one of which turns blue litmus paper red.

(f) Give a balanced equation for this decomposition reaction.

If aluminium(III) chloride hexahydrate is added to an excess of water, it can form a number of aluminium-containing ions in which aluminium ions are surrounded by water molecules and/or hydroxide ions. The general formula of these ions can be written as $[Al(H_2O)_x (OH)_y]^{(3-y)+}$. Which ion is present is dependant upon the pH of the solution.

(g) For the following values of x and y, give the formula of the ions and choose a value of pH (either 3, 9 or 12) at which the ion will be the most stable:

x = 6, y = 0; x = 4, y = 2; x = 0, y = 4

Aluminium also forms a series of solid, basic chlorides, whose formula may be represented as $Al_2(OH)_{6-x}Cl_x$. Some of these may occur as rare minerals; artificial samples are the active ingredient in many anti-perspirant products. 1.000 g of one of these compounds is dissolved in dilute aqueous nitric acid to give 250.0 cm^3 of solution. The dissolving process releases the chloride ions into the solution. 25.0 cm^3 of this solution was titrated against aqueous silver nitrate (0.0500 mol dm^{-3}). 20.75 cm^3 of the silver nitrate solution was required to precipitate all of the chloride ions as AgCl.

(h) Calculate the formula of the basic aluminium chloride being analysed.

Another mineral, variously known as honeystone or mellite, is interesting because it is a rare example of a mineral formed between an inorganic cation, in this case Al(III), and an organic anion. When heated at various temperatures in a vacuum, the hydrated mineral first undergoes dehydration at 200 °C, followed by decomposition at temperatures up to 600 °C. The analysis of the decomposition products allows us to calculate a formula for the organic anion. The details of these analyses are given below.

- When 100 mg of the mineral is heated at 200 °C, it loses 41.1% of its mass as water vapour.
- When the resulting anhydrous solid is heated to 600 °C, it produces 26.5 mg of carbon dioxide, 4.1 mg of carbon monoxide and leaves 28.3 mg of a residue which contains 55.13% aluminium(III) oxide and 44.87 % carbon.

(j) (i) Using these data, and assuming that there are a whole number of water molecules associated with the aluminium compound in the mineral, calculate a formula for mellite, expressing your answer in the form $Al_aC_bO_c \bullet dH_2O$; a,b,c and d are whole numbers.

(ii) Given there is one multiple-charged anion for every two aluminium ions, give the formula of the anion in mellite.

(iii) When fully protonated, the anion gives mellitic acid. Given that the structure has a benzene ring in it, suggest a structure for this acid.

(iv) When heated, mellitic acid can be completely dehydrated to give mellitic anhydride. Draw the structure for this anhydride and give its formula. How many DBE does it contain?

Acknowledgements

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