GENERAL CERTIFICATE OF EDUCATION

Chemistry

Advanced Extension Award
6821

Specimen Paper and Mark Scheme

Qualification Available: Summer 2002

Special Features

- Designed to extend and stimulate the study of Advanced level Chemistry.
- Free standing: does not require candidates to be entered for a particular Advanced level.
- Designed to be independent of individual Advanced level specifications.

General Certificate of Education
Specimen Assessment Material
Advanced Extension Award

CHEMISTRY
Specimen Paper

In addition to this paper you will require:
- a calculator;
- a 12 page answer book.

Time allowed: 3 hours

Instructions
- Use blue or black ink or ball-point pen.
- Write the Paper reference 6821 on the front cover of your answer book.
- Answer **all** questions in the answer book.
- All working must be shown.
- Do all rough work in the answer book. Cross through any work you do not want marked.

Information
- The maximum mark for this paper is 160.
- Mark allocations are shown in brackets.
- You are expected to use a calculator where appropriate.
- A Periodic Table is provided on page 2 of this paper.
- Quality of Written Communication will be assessed in your answer to Section C. You will be assessed on your ability to use an appropriate form and style of writing, to organise relevant information clearly and coherently, and to use specialist vocabulary where appropriate.

Advice
- You are advised to spend about 30 minutes on **Section A**, 2 hours on **Section B** and 30 minutes on **Section C**.

Paper reference: 6821

This **Periodic Table** *may be useful in answering some of the questions in the examination.*

Periodic Table

Group / Period	1	2											3	4	5	6	7	0
1	1.0 H 1																	4.0 He 2
2	6.9 Li 3	9.0 Be 4											10.8 B 5	12.0 C 6	14.0 N 7	16.0 O 8	19.0 F 9	20.2 Ne 10
3	23.0 Na 11	24.3 Mg 12											27.0 Al 13	28.1 Si 14	31.0 P 15	32.1 S 16	35.5 Cl 17	39.9 Ar 18
4	39.1 K 19	40.1 Ca 20	45.0 Sc 21	47.9 Ti 22	50.9 V 23	52.0 Cr 24	54.9 Mn 25	55.8 Fe 26	58.9 Co 27	58.7 Ni 28	63.5 Cu 29	65.4 Zn 30	69.7 Ga 31	72.6 Ge 32	74.9 As 33	79.0 Se 34	79.9 Br 35	83.8 Kr 36
5	85.5 Rb 37	87.6 Sr 38	88.9 Y 39	91.2 Zr 40	92.9 Nb 41	95.9 Mo 42	(98) Tc 43	101.1 Ru 44	102.9 Rh 45	106.4 Pd 46	107.9 Ag 47	112.4 Cd 48	114.8 In 49	118.7 Sn 50	121.8 Sb 51	127.6 Te 52	126.9 I 53	131.3 Xe 54
6	132.9 Cs 55	137.3 Ba 56	* 57 - 71	178.5 Hf 72	180.9 Ta 73	183.9 W 74	186.2 Re 75	190.2 Os 76	192.2 Ir 77	195.1 Pt 78	197.0 Au 79	200.6 Hg 80	204.4 Tl 81	207.2 Pb 82	209.0 Bi 83	(209) Po 84	(210) At 85	(222) Rn 86
7	(223) Fr 87	226.0 Ra 88	** 89 - 103															

Key

Relative Atomic Mass → AA

E ← Element

Atomic Number → ZZ

Insert elements * 57 - 71 | Insert elements ** 89 - 103

(Note - in some elements the most abundant isotope is shown)

*	138.9 La 57	140.1 Ce 58	140.9 Pr 59	144.2 Nd 60	(145) Pm 61	150.4 Sm 62	152.0 Eu 63	157.3 Gd 64	158.9 Tb 65	162.5 Dy 66	164.9 Ho 67	167.3 Er 68	168.9 Tm 69	173.0 Yb 70	175.0 Lu 71
**	227.0 Ac 89	232.0 Th 90	231.0 Pa 91	238.0 U 92	237.0 Np 93	(244) Pu 94	(243) Am 95	(247) Cm 96	(247) Bk 97	(251) Cf 98	(252) Es 99	(257) Fm 100	(258) Md 101	(259) No 102	(260) Lr 103

SECTION A

You are advised to spend about 30 minutes on this section.

This section carries 16 marks.

---

1 Your answer to this question should be based on the passage on pages 4-5. You are advised to read the questions, then read the passage, and then answer the questions.

Note that you are not expected merely to quote from the passage, but rather to select appropriate information and where necessary to explain and evaluate it.

(a) Explain in terms of molecular structure and chemical interactions the changes in colour and texture which occur during the boiling of vegetables. *(10 marks)*

(b) There are some similarities and some differences in the chemistry that explains the changes in colour and texture which occur during the cooking of red meat compared with the boiling of vegetables. Discuss these similarities and differences. *(6 marks)*

The Boiling of Vegetables

The colour of green vegetables is due to chlorophyll. This has a complex cyclic structure represented in **Figure 1** which can best be regarded as a ring containing 4 nitrogen atoms arranged around a central Mg^{2+} ion. The ring has two COOH groups which are esterified; one with methanol and the other with phytol ($C_{20}H_{39}OH$); this is the reason why chlorophyll is insoluble in water.

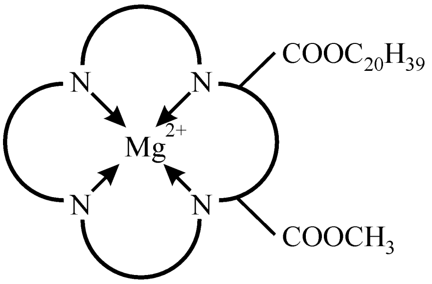


Figure 1

When placed in acid solution, e.g. pH 3, the Mg^{2+} is removed irreversibly to give a brown-green product known as pheophytin. It is, therefore, important to maintain a relatively high pH when green vegetables are processed or boiled. This may be achieved by adding $NaHCO_3$. Although the loss of Mg^{2+} is irreversible, other metal ions can insert into the structure in its place. A good example is Cu^{2+} which gives rise to a vivid blue-green colour with pheophytin. If the pH is too high, e.g. pH 10, there is a tendency for the phytyl ester to be hydrolysed and for the chlorophyll to become soluble in water, but this is much less important than the effect of low pH on colour.

One intercellular polysaccharide in plants is known as pectin; one of its functions is to hold the cells together. This substance is mainly a polymer of α-1,4-linked galacturonic acid with some of the acid groups esterified with methanol; the structure of a part of this molecule is shown in **Figure 2**.

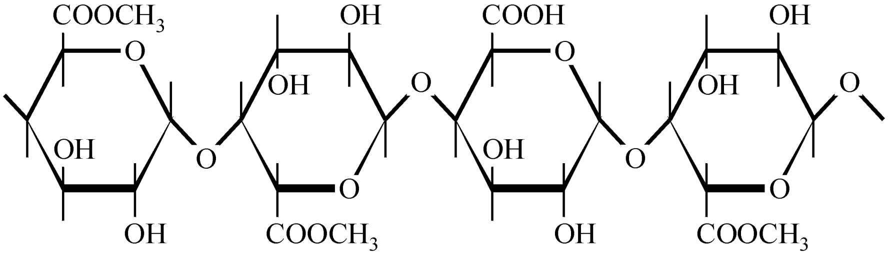


Figure 2

Pectin is insoluble in water but boiling, particularly in alkaline solution, causes hydrolysis of the methyl ester and the molecules become soluble. The salt of pectinic acid is formed. This is one reason why the texture of vegetables softens on boiling. The pH at which green vegetables are boiled is a compromise between the effects of low pH on colour and high pH on texture.

The addition of Ca^{2+} or Mg^{2+} has a marked effect on the texture of vegetables. At the pH at which vegetables are boiled, the COOH groups of pectinic acid are ionised (i.e. they are present as COO^- groups). The metal cations can form bridges (see **Figure 3**) between the COO^- groups on adjacent polymer chains to form a cross-linked polymer.

Hydrogen bonds also contribute to give a large 3-dimensional structure with water molecules trapped between the polymer chains. This type of structure is known as a gel and it can contain as much as 99.5% by mass of water. It is common to add Ca^{2+} in the canning of vegetables, e.g. carrots, to improve their texture. Hardness in water can provide a significant benefit in this respect.

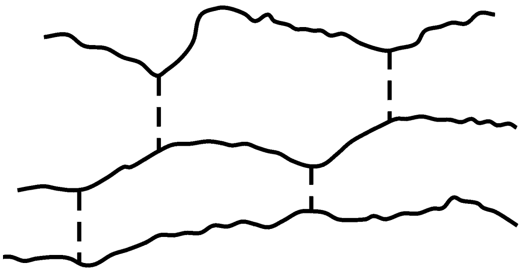
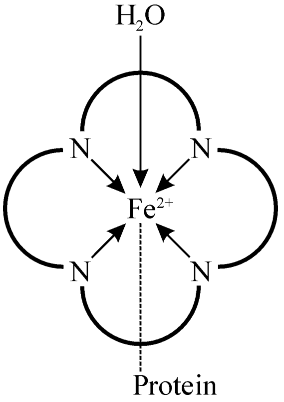


Figure 3

The Cooking of Meat

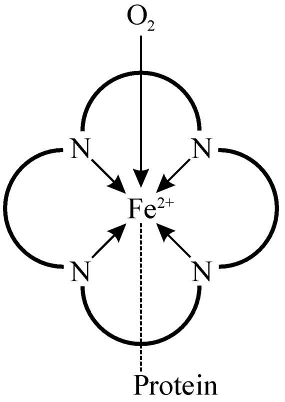
The colour of meat is due to the haem group of the protein myoglobin (**Figure 4**). The structures of chlorophyll and haem are closely related but with important differences. In haem, the central metal ion is Fe^{2+} and the two COOH groups are free, i.e. not esterified. The Fe^{2+} forms coordinate bonds to the four nitrogen atoms of the ring structure. In myoglobin, the haem group is embedded in the protein structure and one of the remaining positions for coordination to Fe^{2+} is taken by an amino acid residue of the protein. The other position is occupied normally by water or oxygen. Van der Waals interactions hold the haem in place on the protein molecule.

The reaction of myoglobin with oxygen leads to oxymyoglobin in which the ligand H_2O is replaced by O_2 with a corresponding change in colour from purple to red. The iron remains as Fe^{2+}. The colour of the surface of 'red' meat is due to oxymyoglobin (**Figure 5**) but, on cutting the meat, a purple colour is visible below the surface where there is no oxygen. The oxidation of Fe^{2+} to Fe^{3+} gives a product (**Figure 6**) which is brown. In living systems and in fresh meat there is an efficient mechanism to reduce any Fe^{3+} in myoglobin to Fe^{2+}. This is less effective in meat which has been stored. The best condition for the oxidation of Fe^{2+} in myoglobin is when meat is heated to a temperature greater than 80 °C, i.e. when the protein becomes denatured.



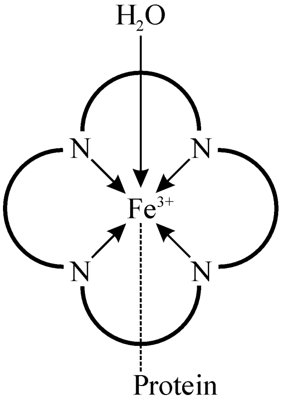
myoglobin - purple

Figure 4



oxymyoglobin - red

Figure 5



metmyoglobin - brown

Figure 6

Meat consists of connective tissue protein (collagen) alongside functional protein fibres which cause muscle to contract when in living animals. The heating of such tissue above 40 °C initially causes the fibres to shrink as a result of protein denaturation; during the early part of cooking the meat becomes tougher and water is lost. On the other hand prolonged heating above 80 °C in the presence of water causes the hydrolysis of the collagen to gelatin which is soluble, allowing the muscle fibres to separate. The texture of meat which has been subjected to prolonged wet heat tends to be more "granular" than that of meat which has been fried rapidly.

SECTION B

Answer all three questions in this section.

You are advised to spend about 40 minutes on each question.

Each question carries 40 marks.

---

2 Fluorine is the most reactive of all non-metals. This question is about the chemistry of fluorine and fluorides.

(a) The table below contains some mean bond enthalpy data.

Bond	**F—F**	**C—F**	**H—F**	**Cl—Cl**	**C—Cl**	**H—Cl**	**C—H**
Mean bond enthalpy /kJ mol^{-1}	158	484	562	242	338	431	412

Use these data to show that the reaction between methane and fluorine is much more exothermic than that between methane and chlorine. Suggest why fluorine reacts much faster with methane than does chlorine. *(6 marks)*

(b) Hydrofluoric acid, HF, is a weak acid with an acid dissociation constant, K_a, equal to 5.6×10^{-4} mol dm^{-3}. Salts of weak acids, such as hydrofluoric acid, form alkaline solutions when dissolved in water. The following equation represents one of the processes which occur when a salt of HF dissolves in water.

$$F^-(aq) + H_2O(l) \rightleftharpoons HF(aq) + OH^-(aq)$$

(i) Write an expression for the equilibrium constant, K, for this reaction and explain why the expression for K is usually written without including a term for the concentration of water. *(3 marks)*

(ii) Use expressions for the acid dissociation constant of HF (K_a) and the ionic product of water (K_w) together with your expression for K from part (b)(i) to derive an expression for K in terms of K_a and K_w. Hence calculate the pH of a 1.0 mol dm^{-3} solution of sodium fluoride.

$$K_w = 1 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$$ *(13 marks)*

(iii)
$$HF(aq) \rightarrow H^+(aq) + F^-(aq) \qquad \Delta H^\ominus = -13 \text{ kJ mol}^{-1}$$
$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l) \qquad \Delta H^\ominus = -57 \text{ kJ mol}^{-1}$$

Use these enthalpy values and Hess's Law to calculate a value of $\Delta H^\ominus$ for the forward reaction in the following equilibrium.

$$F^-(aq) + H_2O(l) \rightleftharpoons HF(aq) + OH^-(aq)$$

Hence predict and explain the effect of an increase in temperature on the pH of aqueous sodium fluoride. *(7 marks)*

(iv) Calculate the pH of a solution made by mixing 100 cm^3 of 1.0 mol dm^{-3} aqueous hydrogen fluoride with 30 cm^3 of 1.0 mol dm^{-3} sodium hydroxide. Explain why the pH remains unchanged when the final solution is diluted with water. Explain how the pH of the solution would be influenced, if at all, by addition of calcium chloride. Calcium chloride is soluble in water but calcium fluoride is sparingly soluble. *(11 marks)*

TURN OVER FOR THE NEXT QUESTION

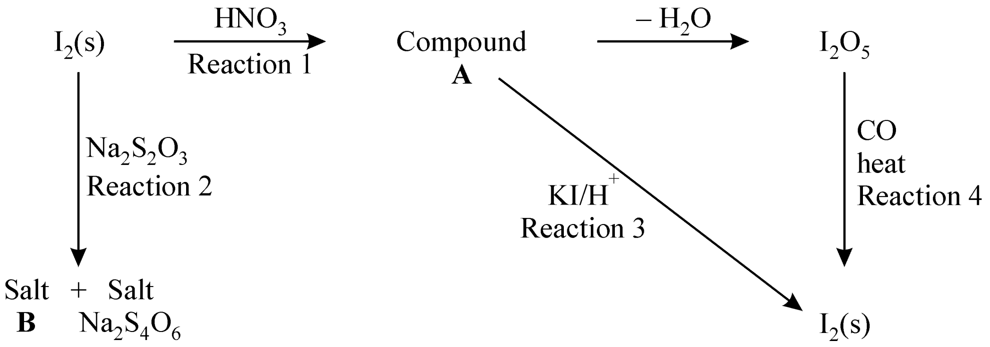
3 (a) Suggest an explanation for the following observations and write equations for the reactions occurring.

(i) When left in air, pure aluminium forms a protective coating. This coating can be removed by treatment with either hydrochloric acid or sodium hydroxide solutions. When placed in either hydrochloric acid or sodium hydroxide solutions, initially there is no observable reaction but, after a few minutes, a colourless gas is evolved. *(10 marks)*

(ii) When aluminium foil is placed in aqueous mercury(II) chloride, a shiny layer forms on the surface of the aluminium. When the aluminium is removed, washed with water and left to stand in the air, it becomes hot and white powder rapidly forms on its surface. *(5 marks)*

(b) Concentrated nitric acid is an oxidising agent.

Consider the following reaction scheme and answer the questions below.



(i) Identify compound **A** and salt **B**. *(2 marks)*

(ii) Write a half equation for the reduction of concentrated nitric acid to NO_2 and write equations for Reactions 1 to 4. *(8 marks)*

(c) When boron trichloride (BCl_3) and iodine monochloride (ICl) react, a single product is formed. This product, compound **C**, contains one anion and one cation. The cation acts as an electrophile in the preparation of iodobenzene from benzene. Suggest a formula for compound **C**. Draw the shape of the anion in compound **C** and explain its bonding. *(5 marks)*

(d) (i) Four compounds each contain a different octahedral Co(III) complex. All four compounds have the general empirical formula $[CoCl_x(NH_3)_y]Cl_z$. Two of the complexes have the same formula but have the ligands arranged differently in space and so are isomers of each other.

Treatment of an aqueous solution of each compound with $AgNO_3(aq)$ will give a white precipitate of AgCl. The table below contains details of the colours of each complex and of the number of moles of $AgNO_3$ which would react with 1.0 mol of each compound.

Number of complex	**1**	**2**	**3**	**4**
Colour of solid complex	golden brown	purple	green	violet
Amount of $AgNO_3$ required per mole of compound / mol	3.0	2.0	1.0	1.0

Suggest the structures of the four complexes. Explain your reasoning. Draw the octahedral structures of the two isomers. *(5 marks)*

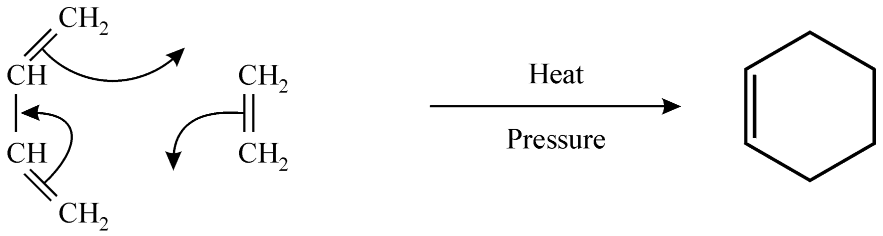
(ii) The ligand, 1,2-diaminoethane ($H_2NCH_2CH_2NH_2$), can be represented as 'en'.

The ion Co^{3+} reacts with 'en' to give $[Co(en)_3]^{3+}$, which is an octahedral complex ion. The complex can exist in two different forms, which are mirror images of each other.

Identify the feature of 'en' that enables it to form two co-ordinate bonds with a transition metal ion. Explain why only three molecules of 1,2-diaminoethane are required to form $[Co(en)_3]^{3+}$.

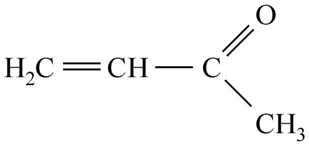
Draw a diagram of $[Co(en)_3]^{3+}$ which clearly shows the three-dimensional structure of the complex ion. Draw a second diagram to show the structure of its mirror image. *(5 marks)*

4 (a) The Diels-Alder reaction between a diene and a compound containing a carbon-carbon double bond is a versatile method for constructing six membered rings. For example:



buta-1,3-diene

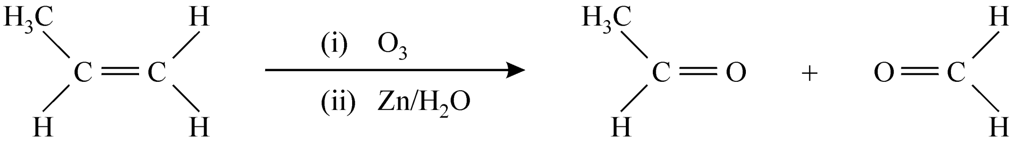
Deduce all of the possible products, including stereoisomers, of Diels-Alder reactions in each of the following:

(i) buta-1,3-diene with 

$H_2C{=}CH{-}C(=O)CH_3$

(ii) buta-1,3-diene with $CH_3CH{=}CHCH_3$ *(6 marks)*

(b) Reductive ozonolysis (illustrated below) can be used to help to prove the structure of alkenes, since it yields aldehydes and ketones, which can be identified readily.



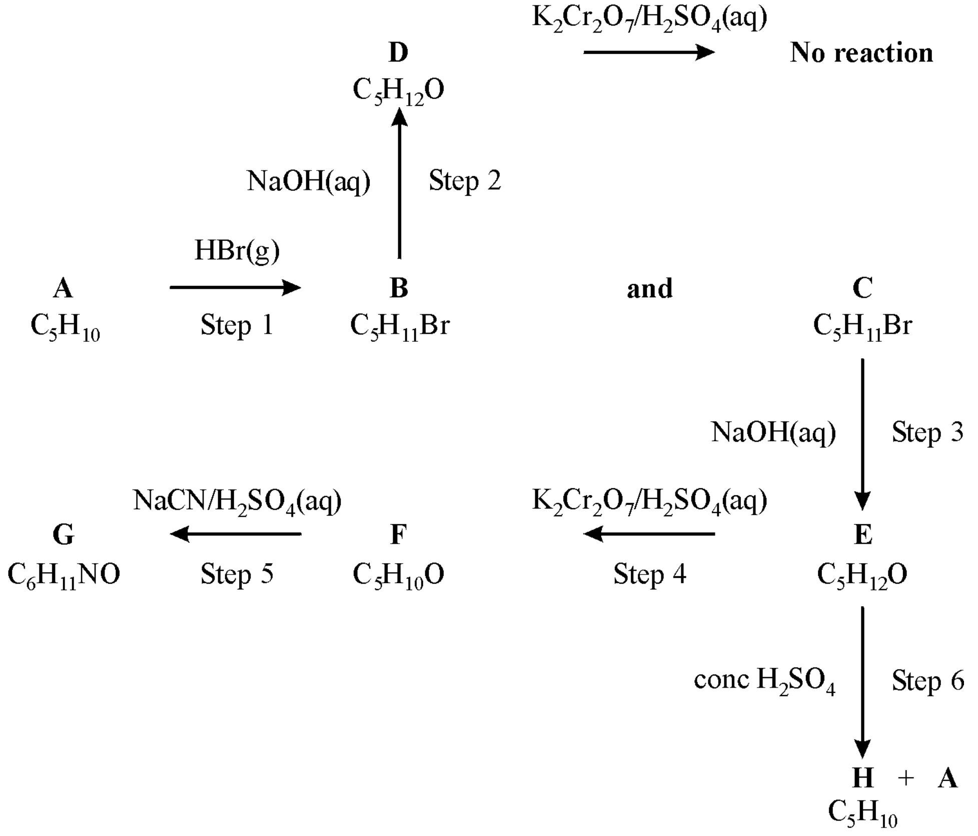
Predict the products of reductive ozonolysis of:

(i) 2,3-dimethylbut-2-ene

(ii) 2-methylbut-1-ene

(iii) buta-1,3-diene *(6 marks)*

(c) Consider the following sequence of reactions for compounds **A** to **H**.



(i) Identify compounds **A** to **H** and name the types of reaction in Steps 1 to 6. *(14 marks)*

(ii) Compound **C** exists as two isomers. Draw the isomers, name the type of isomerism and state the feature of the molecule which is responsible for this type of isomerism. Identify any other of the compounds, **A** to **H**, able to show this type of isomerism. *(6 marks)*

(d) (i) A hydrocarbon **X** has a relative molecular mass of 72. Chlorination of **X** gives a mixture containing only one monochloride and only two dichlorides. What are the structures of **X** and the three chlorination products? *(5 marks)*

(ii) A pure sample of one of the dichlorides was isolated. When the sample was examined by mass spectrometry, it was shown that the molecules in the sample did not all have the same relative molecular mass.

Describe and explain the appearance of the mass spectrum in the molecular ion region. You should assume that chlorine has isotopes ^{35}Cl and ^{37}Cl, and that the abundance ratio is 3:1. *(3 marks)*

SECTION C

Answer **either** Question 5(a) **or** Question 5(b).

You are advised to spend about 30 minutes on this section.

This section carries 24 marks.

5 Either

(a) Discuss the importance of the reactions of water.

Illustrate your answer by reference to a series of examples from both inorganic and organic chemistry.

Or

(b) Discuss the important part that catalysts play in modifying the way that chemical reactions proceed.

Illustrate your answer by reference to a series of examples from both inorganic and organic chemistry.

(24 marks)

END OF QUESTIONS

CHEMISTRY
ADVANCED EXTENSION AWARD
SPECIMEN MARK SCHEME

SECTION A

Question 1

(a) **Colour**

plants contain chlorophyll, which is green and contains an Mg^{2+} ion	1	
the Mg^{2+} ion is surrounded by a complex ring structure		
including four groups with N atoms which act as ligands	1	
boiling in low pH conditions causes loss of Mg^{2+} from chlorophyll	1	
the product, pheophytin, is brown-green	1	

Texture

plant cells partly held together by pectin	1	
pectin is partially esterfied polygalacturonic acid	1	
ester is a methyl ester	1	
boiling leads to hydrolysis of the ester	1	
pectin becomes much more soluble after hydrolysis	1	
loss of pectin through increased solubility allows cells to		
separate and texture softens	1	
if Ca^{2+} or Mg^{2+} is added during cooking, the metal ions		
cross-link hydrolysed pectin chains	1	**max**
a gel forms and texture becomes more firm	1	**10**

(b) **Similarities**

haem which causes red colour in meat and chlorophyll which causes green		
colour in plants have chemically similar structure	1	
both have metal ion surrounded by complex ring structure,		
with 4 N atoms in ring acting as ligands	1	

Differences

metal ion in haem is Fe^{3+} whereas in chlorophyll it is Mg^{2+}	1	
COOH groups on ring are not esterified in haem	1	
change of colour due to different mechanisms in red meat colour change is		
due to oxidation reactions	1	
change in texture due to different mechanisms		
in red meat denaturing of protein fibres initially causes toughening		
further cooking causes hydrolysis of connective proteins and meat becomes	1	
‘granular’		**max**
	1	**6**

Total
16

SECTION B

Question 2

(a) consider $CH_4 + F_2 \rightarrow CH_3F + HF$ 1

$\Delta H = \Sigma$ bonds broken − Σ bonds formed 1
$= 412 + 158 - (484 + 562) = 476 \text{ kJ mol}^{-1}$ 1

for Cl_2, $\Delta H = 412 + 242 - (338 + 431) = -115 \text{ kJ mol}^{-1}$ 1

first steps in reaction is $F\text{–}F \rightarrow 2F$ 1

much lower energy for F_2 because bond is weaker 1 **6**

(b) (i)

$$K = \frac{[HF][OH^-]}{[F^-]} \quad \text{(equation 1)}$$ 1

$[H_2O]$ very large 1
effectively constant 1 **3**

(ii) $HF \rightleftharpoons H^+ + F^-$ 1

$$K_a = \frac{[H^+][F^-]}{[HF]}$$ 1

$$\text{therefore } [F^-] = \frac{K_a[HF]}{[H^+]} \quad \text{(equation 2)}$$ 1

$H_2O \rightleftharpoons H^+ + OH^-$ 1
$K_w = [H^+]\,[OH^-]$ (equation 3) 1

$$K = \frac{[HF][OH^-] \times [H^+]}{K_a[HF]} \quad \text{using equation 2 to substitute for } [F^-] \text{ in equation 1}$$

$$= \frac{K_w}{K_a} \quad \text{using equation 3}$$ 1

$$= \frac{10^{-14}}{5.6 \times 10^{-4}} = 1.786 \times 10^{-11} \text{ mol dm}^{-3}$$ 1

in NaF, $[HF] = [OH^-]$ 1

$$\therefore K = \frac{[OH^-]^2}{[F^-]} = 1.786 \times 10^{-11}$$ 1

$$\therefore [OH^-] = \sqrt{1.786 \times 10^{-11}} = 4.2 \times 10^{-6}$$ 1

$$[H^+] = \frac{K_w}{[OH^-]} = \frac{10^{-14}}{4.2 \times 10^{-6}}$$ 1

$$= 2.37 \times 10^{-9}$$ 1

pH = 8.6 1 **13**

(iii) $F^- + H_2O \rightarrow HF + OH^-$

$+57\downarrow \qquad\qquad \uparrow+13$ 1

$F^- + H^+ + OH^-$

$\Delta H^\ominus = +57 + 13$ 1

$= 70\ \text{kJ mol}^{-1}$ 1

$\therefore$ if T increases, equilibrium → right 1

to try and lower T (or by Le Chatelier's principle) 1

$\therefore [OH^-]$ increases 1

$\therefore$ pH increases 1 **7**

(iv) $HF \rightleftharpoons H^+ + F^-$ 1

$$K_a = \frac{[H^+][F^-]}{[HF]}$$

$$[H^+] = K_a \frac{[HF]}{[F^-]}$$ 1

moles F^- = moles NaOH $= \frac{30}{1000} \times 1 = 0.03$ 1

moles HF $\approx \frac{100}{1000} \times 1 - 0.03 = 0.07$ 1

$\therefore [H^+] = 5.6 \times 10^{-4} \times \frac{0.07}{0.03} = 1.3 \times 10^{-3}$ 1

pH = 2.9 1

if solution is diluted, ratio $\frac{[HF]}{[F^-]}$ remains unchanged 1

$\therefore [H^+]$ is unchanged $\therefore$pH unchanged 1

(increased ionisation of HF negligible)

on addition $CaCl_2$, F^- ions removed as insoluble CaF_2 1

$\therefore$ equilibrium $HF \rightleftharpoons H^+ + F^-$ moves completely to right 1

$[H^+]$ increases, pH decreases 1 **11**

Total
40

Question 3

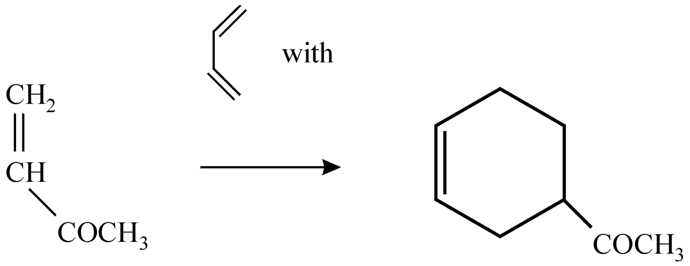
(a)	(i)	protective layer is Al_2O_3	1	
		$4Al + 3O_2 \rightarrow 2Al_2O_3$	1	
		initial reaction of oxide layer with the acid to give aluminium chloride	1	
		$Al_2O_3 + 6HCl \rightarrow 2AlCl_3 + 3H_2O$	1	
		then metal reacts with the acid and hydrogen gas is evolved	1	
		$2Al + 6HCl \rightarrow 2AlCl_3 + 3H_2$	1	
		initial reaction of oxide layer with the alkali to give aluminate	1	
		$Al_2O_3 + 6OH^- + 3H_2O \rightarrow 2[Al(OH)_6]^{3-}$	1	
		then metal reacts with the alkali, aluminate and hydrogen gas are evolved	1	
		$2Al + 6OH^- + 6H_2O \rightarrow 2[Al(OH)_6]^{3-} + 3H_2$	1	**10**
	(ii)	shiny surface is mercury or displacement reaction occurred	1	
		$3HgCl_2 + 2Al \rightarrow 2AlCl_3 + 3Hg$	1	
		mercury prevents the formation of Al_2O_3	1	
		once mercury washed off, aluminium reacts with air to give oxide	1	
		aluminium highly reactive so reaction very exothermic	1	**5**
(b)	(i)	**A** = iodic(V) acid or HIO_3	1	
		B = sodium iodide or NaI	1	**2**
	(ii)	$NO_3^- + 2H^+ + e^- \rightarrow NO_2 + H_2O$		
		for reduced species (NO_2)	1	
		for overall equation correct	1	
		$1 = I_2 + 10HNO_3 \rightarrow 2HIO_3 + 10NO_2 + 4H_2O$ (species + balance)	2	
		$2 = I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$	1	
		$3 = HIO_3 + 5I^- + 5H^+ \rightarrow 3I_2 + 3H_2O$ (species + balance)	2	
		$4 = I_2O_5 + 5CO \rightarrow I_2 + 5CO_2$	1	**8**
(c)		**C** = $IBCl_4$	1	
		shape tetrahedral	1	
		three covalent bonds from the original molecule	1	
		one dative bond	1	
		formed by donation of lone pair from Cl^-	1	**5**
(d)	(i)	complex **1** - $3Cl^-$ ions outside $\therefore$ $[Co(NH_3)_6]^{3+}$	1	
		complex **2** - $2Cl^-$ ions outside $\therefore$ $[Co(NH_3)_5Cl]^{2+}$	1	
		complexes **3** and **4** - one Cl^- ion outside complex $\therefore$ $[Co(NH_3)_4Cl_2]^+$	1	
		diagram of complex **3** clearly showing octahedral shape	1	
		diagram of complex **4** shown as cis/trans isomer of complex **3**	1	**5**
	(ii)	each 'en' molecule has 2 N atoms	1	
		each of these N atoms has a lone pair able to form a coordinate bond	1	
		3 'en' can make 3 × 2 bonds; octahedral complex uses 6 bonds with ligands	1	
		first isomer clearly drawn	1	
		second isomer clearly a mirror image of first	1	**5**

Total
40

Question 4

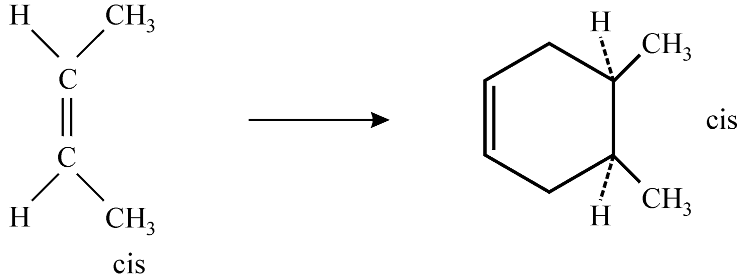
(a) Diels Alder

(i)

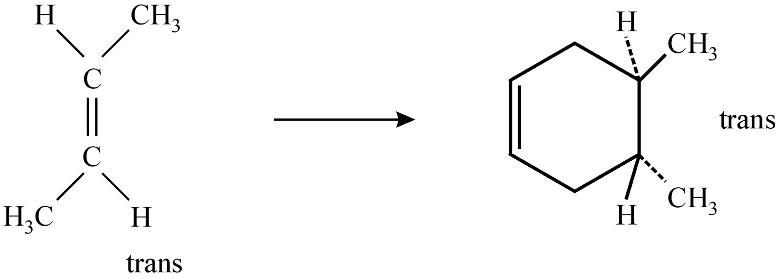


2

(ii)



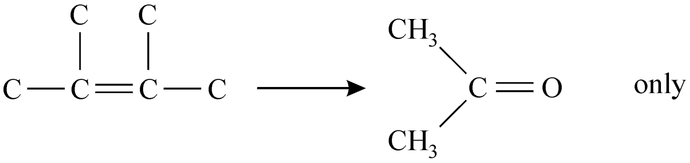
2



2 **6**

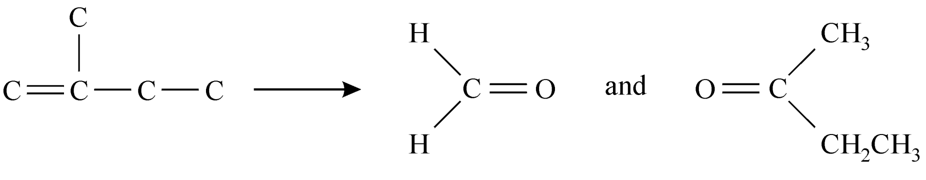
(b) reductive ozonolysis

(i)



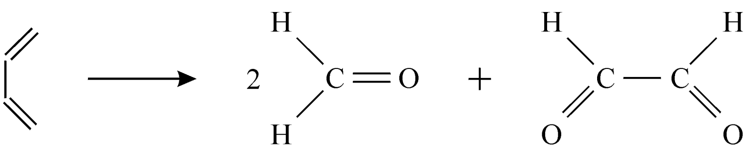
1

(ii)



2

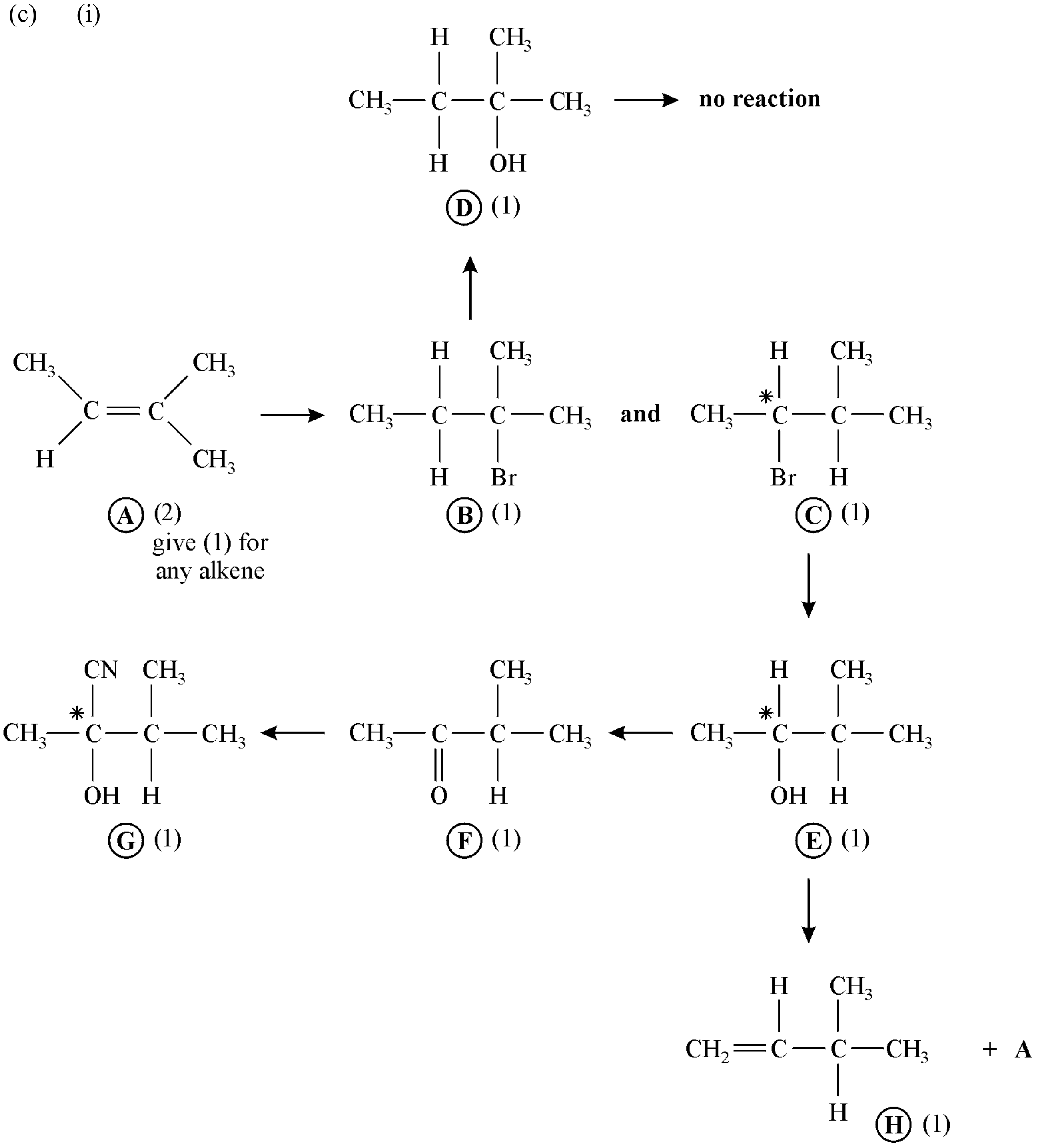
(iii)



3 **6**

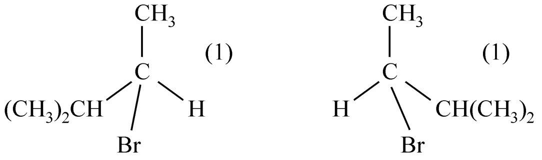
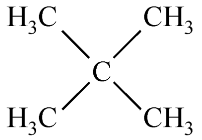
one mark for each product, one mark for 2 moles of methanal

(c) (i)



* = asymmetric carbon
D has no reaction with acidified dichromate so is 3° alcohol
E must be 2° alcohol since reaction with acidified dichromate gives ketone

step 1 electrophilic addition	1	
steps 2 + 3 nucleophilic substitution	1	
step 4 oxidation	1	
step 5 nucleophilic addition	1	
step 6 elimination / dehydration	1	**14**

	(ii)	 (1) (1)	2	
		optical (stereo) substitution	1	
		asymmetric carbon atom / chiral	1	
		compound **E**	1	
		compound **G**	1	**6**
(d)	(i)	Mr = 72 one mono chloride ∴ all H are equivalent	1	
		 (1) ⟶ $C(CH_3)_3(CH_2Cl)$ (1)		
		dichlorides are $C(CH_3)_3\ CHCl_2$	1	
		and $C(CH_3)_2(CH_2Cl)_2$	1	**5**
	(ii)	Mr = 140 / 142 / 144	1	
		ratio 9 : 6 : 1	1	
		reason for ratio	1	**3**
				Total **40**

SECTION C

Question 5

Candidates answer either (a) or (b). The marking points which follow are not exhaustive. There are many other valid points which in an operational examination would gain credit.

(a) **inorganic**

metal ions hydrate in water $M^{n+}(g) + (aq) \rightarrow M^{n+}(aq)$	1	
anions are also hydrated in aqueous solution	1	
ΔH_{hyd} values are negative / hydration of metal ions is exothermic	1	
if M^{n+} has a low charge density, it will be weakly polarising	1	
attractions are ion-dipole	1	
if M^{n+} has a high charge density, it will be strongly polarising	1	
attractions are co-ordinate bonds	1	
high charge density leads to reactions in which hydrolysis occurs	1	
this results in acidity by the reaction of water removing a proton	1	
oxides of some Group 5 elements are hydrolysed when they react with water	1	
e.g. P_4O_{10}	1	
some Group 5 chlorides are hydrolysed by reaction with water	1	**max**
e.g. PCl_3	1	**15**

organic

carbon to carbon double bonds can be hydrated	1	
in the presence of an acid catalyst	1	
the double bond behaves as a source of electron density / nucleophile	1	
carboxylic acid derivatives are susceptible to hydrolysis	1	
by nucleophilic attack involving donation of a pair of electrons	1	
e.g. $RCOCl + H_2O \rightarrow RCOOH + HCl$	1	
Grignard reagents are hydrolysed by water	1	
so have to be used in anhydrous conditions	1	
haloalkanes can be hydrolysed by water	1	
proteins can be hydrolysed	1	
hydrolysis involves addition followed by elimination	1	**max 15**

marks for written communication

give a mark out of 4 for the quality of the candidate's written communication

the factors that should influence the award of the mark include:

- the breadth and balance of the examples chosen
- the overall structure of the essay (organisation, avoidance of repetition)
- the correct use of chemical terms
- the appropriate use of equations, mechanisms, diagrams **max 4**

Total 24

(b) **general points:**

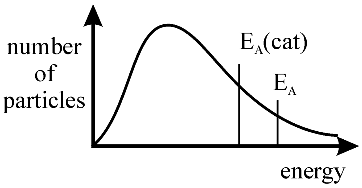
reactions proceed by a series of collisions 1

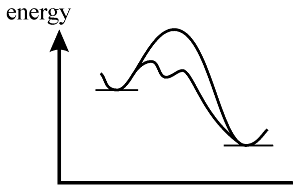
for a collision to be successful it must be sufficiently energetic / have the minimum activation energy 1

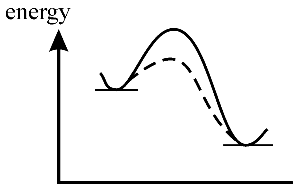
a catalyst is a substance which changes the rate of a chemical reaction but is itself unchanged at the end of the reaction 1

catalysts enable alternative routes / mechanisms of lower activation energy 1

allow 1 mark for each relevant and correct diagram e.g.:







catalysts can be classified as homogeneous – same state 1
or heterogeneous – different state 1

heterogeneous - overall process involving

- adsorption or reference to active sites 1
- weaken / make / break bonds **or**
  better orientation **or**
  increase concentration 1
- desorption 1 **max 10**

do **not** give credit for diffusion of gas to and from the surface

inorganic examples:	1	
Fe^{2+} / Fe^{3+}(aq) catalysis of $S_2O_8^{2-}$ / I^- reaction		
more rapid using catalyst (ions of opposite charge reacting)	1	
balanced equation	1	
evidence of intermediate mechanistic steps	1	
V_2O_5 in Contact process	1	**max 6**
balanced equation	1	
organic examples:	1	
dehydration of ethanol with concentrated strong acid catalyst		
more rapid using catalyst (easier loss of H_2O)	1	
balanced equation	1	
evidence of intermediate mechanistic steps	1	
hydrogenation of C=C in ethene, oils	1	
balanced equation	1	
enzymes act like catalysts in biological systems	1	
specific example of enzyme	1	**max 6**
specific example of industrial use of enzyme	1	

marks for written communication

give a mark out of 4 for the quality of the candidate's written communication

the factors that should influence the award of the mark include:

- the breadth and balance of the examples chosen
- the overall structure of the essay (organisation, avoidance of repetition)
- the correct use of chemical terms
- the appropriate use of equations, mechanisms, diagrams

max 4

Total 24