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Centre Number

Candidate Number

ADVANCED
General Certificate of Education
2019

Chemistry

Assessment Unit A2 2

assessing

Analytical, Transition Metals, Electrochemistry and Further Organic Chemistry

[ACH22]

ACH22

TUESDAY 11 JUNE, AFTERNOON

TIME

2 hours.

INSTRUCTIONS TO CANDIDATES

Write your Centre Number and Candidate Number in the spaces provided at the top of this page.
Answer **all fifteen** questions.
Answer **all ten** questions in **Section A**. Record your answers by marking the appropriate letter on the answer sheet provided. Use only the spaces numbered 1 to 10. Keep in sequence when answering.
Answer **all five** questions in **Section B**.
You must answer the questions in the spaces provided.
Do not write outside the boxed area on each page or on blank pages.
Complete in black ink only. **Do not write with a gel pen.**

INFORMATION FOR CANDIDATES

The total mark for this paper is 110.
Quality of written communication will be assessed in Questions **11(g)** and **13(d)**.
In Section A all questions carry equal marks, i.e. **one** mark for each question.
In Section B the figures in brackets printed down the right-hand side of pages indicate the marks awarded to each question or part question.
A Periodic Table of Elements, containing some data, is included with this question paper.

12188

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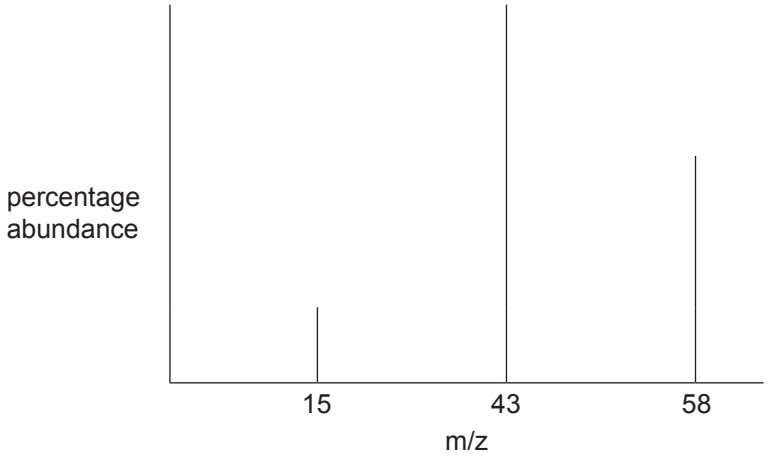
Section A

For each of the following questions only **one** of the lettered responses (A–D) is correct.

Select the correct response in each case and mark its code letter by connecting the dots as illustrated on the answer sheet.

1 Part of a mass spectrum is shown below.



The compound producing the mass spectrum is

A propane.

B propan-1-ol.

C propan-2-ol.

D propanone.

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2 Three acetylating agents, arranged in order of the vigour of their reaction with phenylamine, starting with the most reactive, are

A ethanoyl chloride, ethanoic acid, ethanoic anhydride.

B ethanoyl chloride, ethanoic anhydride, ethanoic acid.

C ethanoic anhydride, ethanoic acid, ethanoyl chloride.

D ethanoic anhydride, ethanoyl chloride, ethanoic acid.

3 Hydrogen sulfide is oxidised by acidified potassium manganate(VII) as shown by the following half-equation:

$$H_2S \longrightarrow S + 2H^+ + 2e^-$$

The volume, in cm^3, of 0.02 M $KMnO_4$ required to oxidise 0.001 mol of H_2S is

A 10.

B 20.

C 40.

D 50.

4 How many aromatic isomers of dichlorobenzene exist?

A 1

B 2

C 3

D 4

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5 On complete combustion, 6.0 g of an organic compound gave 8.8 g of carbon dioxide and 3.6 g of water as the only products. The empirical formula of the compound is

A CH_2.

B CHO.

C CH_2O.

D C_2H_4O.

6 Excess ethanoyl chloride reacts with $CH_2OHCH_2NH_2$ to produce

A $CH_2OHCH_2NHCOCH_3$.

B $CH_2OHCH_2N(COCH_3)_2$.

C $CH_3COOCH_2CH_2NH_2$.

D $CH_3COOCH_2CH_2NHCOCH_3$.

7 Which substance can exhibit geometrical isomerism?

A $[Co(NH_3)_5Cl]^{2+}$ octahedral structure

B $Cu(CN)_2$ linear structure

C $[Pt(NH_3)_2Cl_2]$ square planar structure

D $[Zn(NH_3)_2Cl_2]$ tetrahedral structure

8 Salicylic acid is used in the removal of warts because it

A alters the pH that warts grow in.

B attacks the warts and removes them.

C destroys the alkaline environment that warts flourish in.

D destroys the bacteria producing warts.

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9 The systematic name for $LiAlH_4$ is

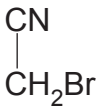
A lithal.

B lithium tetrahydridaluminate(III).

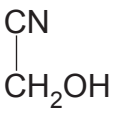
C lithium tetrahydridealuminate(III).

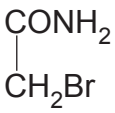
D lithium tetrahydridoaluminate(III).

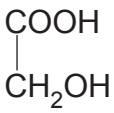
10 When the following compound is completely hydrolysed

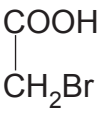


which product is formed?

A 

B 

C 

D 

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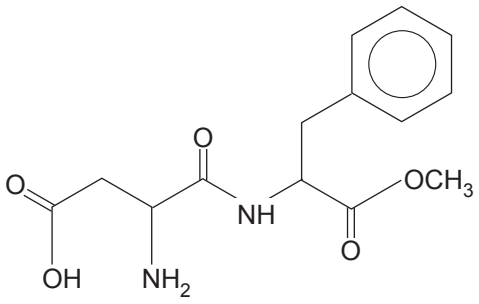
Section B

Answer **all five** questions in the spaces provided

11 Aspartame is an artificial sweetener which is about 200 times sweeter than sugar. It is a methyl ester of a dipeptide formed from the two α-amino acids, aspartic acid and phenylalanine.

Aspartic acid $HOOCCH_2CH(NH_2)COOH$

Phenylalanine $C_6H_5CH_2CH(NH_2)COOH$



aspartame

(a) On the structure of aspartame, shown above, circle and label:

(i) the ester group [1]

(ii) the peptide link [1]

(b) Both aspartic acid and phenylalanine are found in nature and are known as α-amino acids. Suggest the meaning of the term **α-amino acid**.

_____

_____ [2]

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(c) Explain why both aspartic acid and phenylalanine are optically active.

_____

_____ [1]

(d) Suggest why aspartic acid is classified as an acidic amino acid and phenylalanine is classified as a neutral amino acid.

_____

_____

_____ [2]

(e) Draw the structures of the **two** peptides which are produced when the following amino acids are reacted with each other.

$R_1CH(NH_2)COOH$ and $R_2CH(NH_2)COOH$

[2]

(f) Name **one** reagent that can be used to hydrolyse peptides.

_____ [1]

[Turn over

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(g) When aspartame is hydrolysed a mixture of aspartic acid, phenylalanine and methanol is produced. The mixture of products can be analysed using TLC. Explain, giving full experimental detail, how you would use TLC to prove that phenylalanine and aspartic acid are produced and why methanol cannot be detected.

In this question you will be assessed on using your written communication skills including the use of specialist scientific terms.

[6]

(h) Aspartame is stable at pH 4.3 but breaks down at elevated temperatures or at high pH. Suggest why it is not suitable to use as a sweetener in baking but is ideal for soft drinks.

[2]

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(i) When aspartame is made, it is important to use the correct chiral isomers of phenylalanine and aspartic acid. The binding sites for the taste receptors on the tongue act in a similar way to the mechanism of the action of enzymes. Explain the action of aspartame on taste receptors.

[2]

[Turn over

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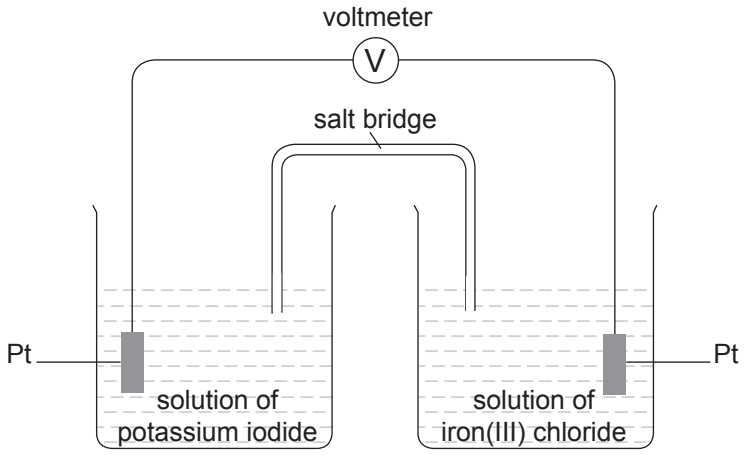
12 The reaction between iron(III) and iodide ions may be studied in a cell as shown below.



A solution of iron(III) chloride is placed in one beaker and a solution of potassium iodide in the other beaker. A salt bridge connects the beakers.

(a) The salt bridge can be made using a glass tube or paper.

(i) Name a chemical which is usually used to make a salt bridge.

_____ [1]

(ii) Describe how you would make a salt bridge from paper in the laboratory.

_____

_____ [1]

(iii) State **two** reasons for using a salt bridge in an electrochemical cell.

_____

_____

_____ [2]

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(b) The electrode potentials for the two half-cells taking place in the reaction are:

$Fe^{3+}(aq) + e \rightleftharpoons Fe^{2+}(aq)$ $+0.77$ V

$I_2(aq) + 2e \rightleftharpoons 2I^-(aq)$ $+0.54$ V

(i) Calculate the emf of the cell.

_____

_____ [2]

(ii) Write a conventional representation for the cell.

_____ [2]

(iii) Write the equation for the reaction taking place.

_____ [1]

(iv) Explain which way electrons will flow in the cell.

_____

_____ [2]

[Turn over

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(c) Before the cell operates Fe^{3+} ions and I^- ions are present. After the cell operates Fe^{2+} ions are present together with I_2 molecules. State how you would test for each of these species and the results expected for positive tests.

(i) Fe^{3+}

_____

_____ [2]

(ii) Fe^{2+}

_____

_____ [2]

(iii) I^-

_____

_____ [2]

(iv) I_2

_____

_____ [2]

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(Questions continue overleaf)

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13 Petroselinic acid is a long chain fatty acid which is found in coriander seeds.

$$CH_3(CH_2)_{10}CH{=}CH(CH_2)_4COOH$$

petroselinic acid

It is of interest because ozonolysis gives auric acid and adipic acid, used in the manufacture of nylon.

$$CH_3(CH_2)_{10}CH{=}CH(CH_2)_4COOH \xrightarrow{O_3} CH_3(CH_2)_{10}COOH + HOOC(CH_2)_4COOH$$

petroselinic acid — auric acid — adipic acid

(a) Petroselinic acid is a positional isomer of oleic acid. It has the double bond in position 6; in oleic acid it is in position 9.

(i) Suggest the meaning of the term **positional isomer**.

_____

_____ [2]

(ii) Draw the structures of the two fatty acids which are produced when oleic acid is ozonolysed.

[2]

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(b) The amount of petroselinic acid in coriander seeds can be determined by GLC. Petroselinic acid, which is a white solid, is first converted into its methyl ester which is a liquid.

(i) Suggest why petroselinic acid is a solid and methyl petroselinate is a liquid.

_____

_____

_____ [2]

(ii) Suggest why petroselinic acid is converted into the methyl ester for GLC analysis.

_____

_____

_____ [1]

(iii) Explain how the percentage of petroselinic acid in a sample can be determined from a GLC chromatography trace.

_____

_____

_____ [2]

[Turn over

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(c) Nylon is made from the reaction of adipic acid with 1,6-diaminohexane. It is a condensation polymer.

(i) Draw one repeating unit of the nylon polymer formed when adipic acid reacts with 1,6-diaminohexane.

[2]

(ii) Explain what is meant by the term **condensation** polymer.

_____

_____ [1]

(iii) Explain why nylon contains an amide bond and not a peptide link despite the fact that both bonds have the same structure.

_____

_____ [1]

(iv) Kevlar is a polymer formed by the reaction of 1,4-diaminobenzene with terephthaloyl dichloride. Write the equation for the reaction of one molecule of 1,4-diaminobenzene with one molecule of terephthaloyl dichloride.

[3]

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(v) Explain why both nylon and kevlar are biodegradable.

[2]

(d) Enzymes are also condensation polymers. Explain the primary, secondary and tertiary structures of enzymes. Include in your answer an explanation of the effect of pH and temperature on enzyme activity.

In this question you will be assessed on using your written communication skills including the use of specialist scientific terms.

[6]

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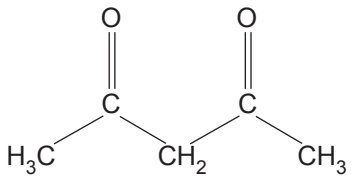
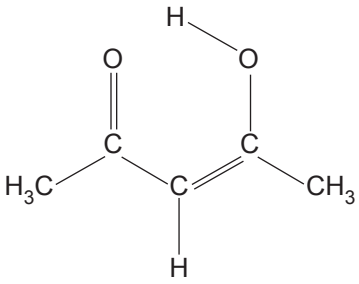
14 Pentane-2,4-dione (acetylacetone) is an unusual compound. It exists as a mixture of isomers.



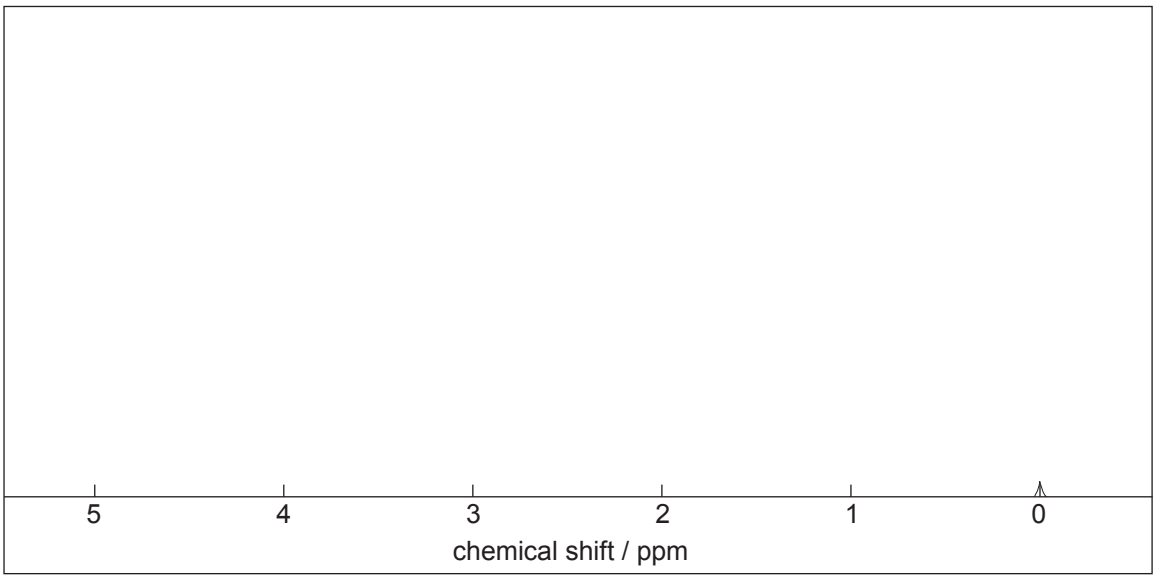
keto form



enol form

(a) The nmr spectrum of pentane-2,4-dione at room temperature shows that it is a mixture of isomers.

(i) On the following nmr axes draw the expected nmr spectrum, including an integration curve, of pentane-2,4-dione as the keto form. Use the data leaflet for your answer.



[2]

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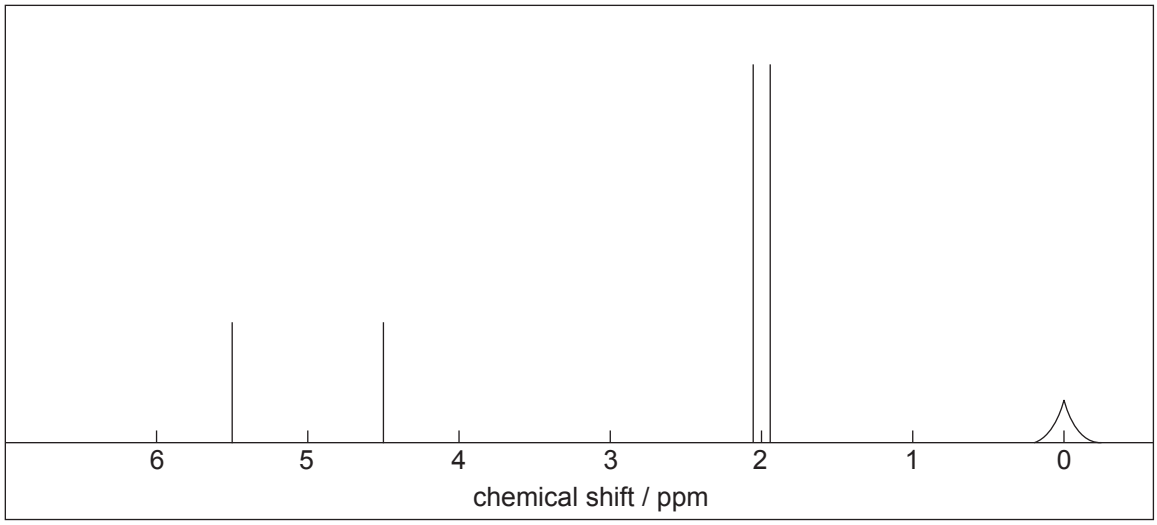
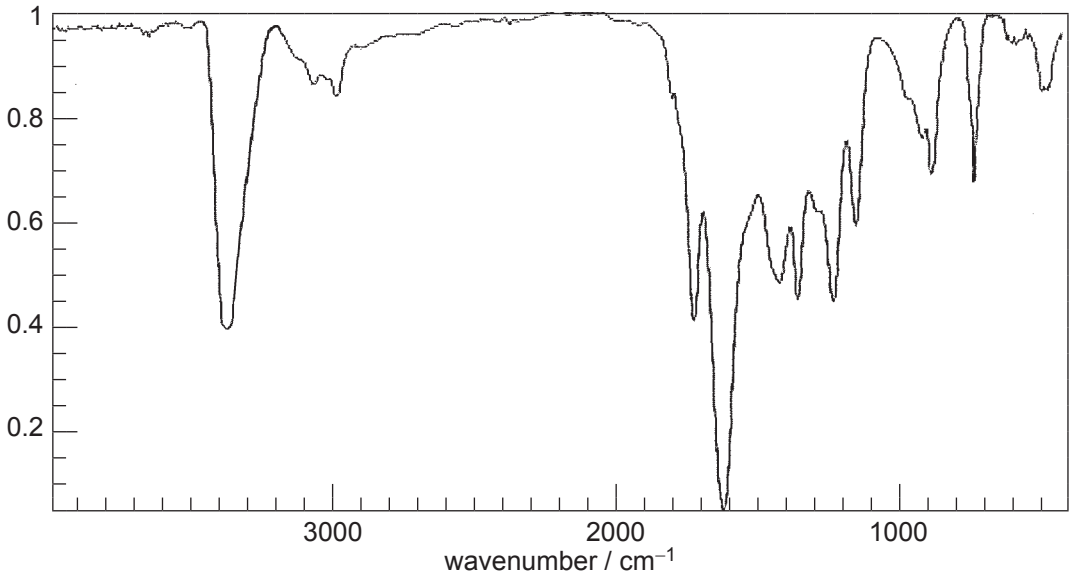
(ii) The following is the nmr spectrum of pentane-2,4-dione as an enol at room temperature. Using the data in the data leaflet, label the peaks in the spectrum with the appropriate hydrogen atoms from the enol form.



[2]

(b) The infrared spectrum of pentane-2,4-dione is shown below. Explain how it suggests that pentane-2,4-dione is a mixture of isomers.



[2]

[Turn over

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(c) It is possible to titrate the enol isomer of pentane-2,4-dione using bromine because the C═C bond reacts faster in an addition reaction than in any possible substitution reaction with bromine.

(i) How would you slow down the substitution reaction before the titration was carried out?

_____ [1]

(ii) How would you know that the end point had been reached?

_____ [1]

(iii) In a titration, 25.0 cm^3 of a 0.008 M solution of pentane-2,4-dione was reacted with a 0.002 M solution of bromine. The titration value was 4.6 cm^3 of bromine solution. Use these values to calculate the percentage of pentane-2,4-dione which exists in the enol form.

_____

_____

_____

_____ [4]

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(d) Pentane-2,4-dione is a ligand represented by the symbol acac. It combines with many transition metal ions to form complexes.

(i) How many coordinate bonds can pentane-2,4-dione form?

_____ [1]

(ii) It reacts with copper(II) ions to form $[Cu(acac)_3]^{2+}$ which has an octahedral structure. Draw a 3D structure of this octahedral complex using dotted lines and wedges.

[2]

(iii) Explain why $[Cu(acac)_3]^{2+}$ reacts with edta.

_____

_____ [2]

(e) Pentane-2,4-dione does not form a hydrazone with phenylhydrazine. Instead, it forms a substituted pyrazole which has a melting point of 107–108 °C. Explain how this reaction can be used to identify pentane-2,4-dione.

_____

_____ [1]

[Turn over

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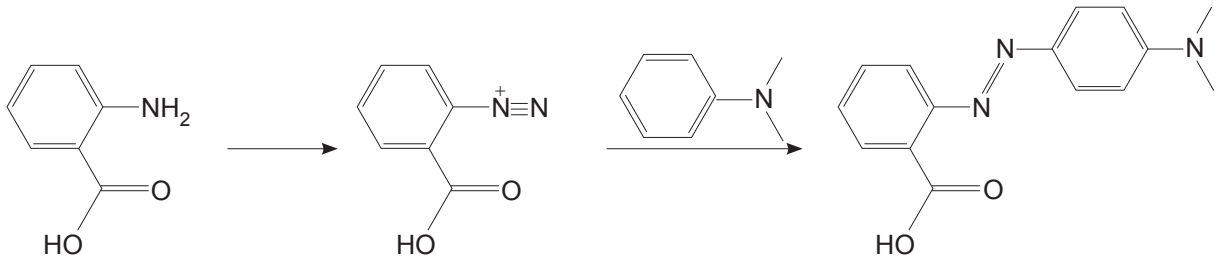
15 Methyl red is a dye and can be used as an indicator. It is synthesised by the reaction of dimethylaniline with the diazonium salt of anthranilic acid.



methyl red

(a) Name the reagents used to produce the diazonium ion and the condition under which they are used.

_____

_____ [2]

(b) **(i)** Explain why methyl red is a coloured compound.

_____

_____

_____

_____ [4]

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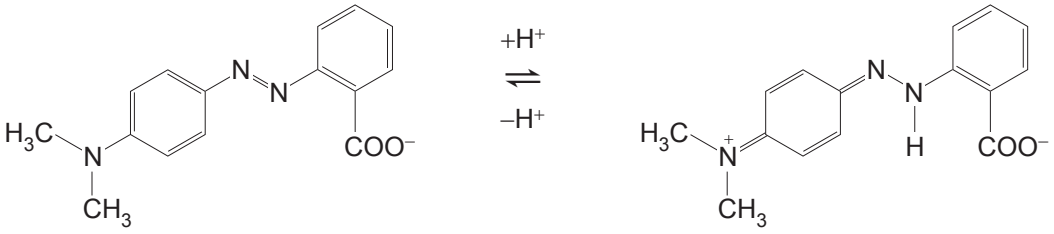
(ii) Methyl red is red in its acidic form and yellow in its basic form.



basic form

acidic form

Suggest why the two forms have different colours.

_____

_____ [2]

(c) Methyl red is insoluble in water. It forms a sodium salt which has a solubility of 800 mg in 1 cm^3 of water. Explain why methyl red is insoluble in water but the sodium salt is soluble in water.

_____

_____ [2]

[Turn over

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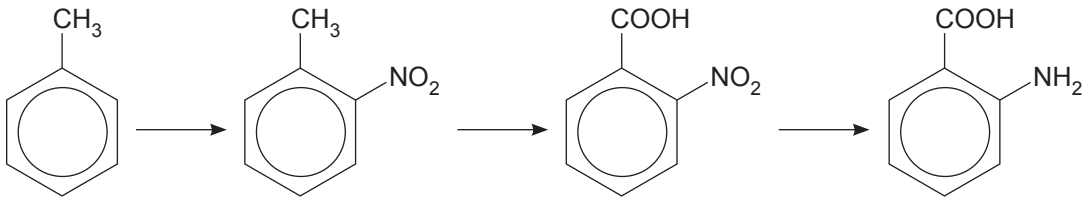
(d) The synthesis of anthranilic acid may be carried out as follows.



(i) Name the reagents used to carry out the nitration of methylbenzene.

_____

_____

_____ [2]

(ii) The reagent used to oxidise the 2-methylnitrobenzene is acidified potassium manganate(VII). State the colour change observed.

_____ [2]

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(e) The reduction of the nitrobenzoic acid is carried out using tin and concentrated hydrochloric acid.

(i) Write the equation for the reaction of tin with hydrochloric acid.

_____ [2]

(ii) The anthranilic acid is obtained as the phenylammonium salt. Draw the structure of the salt and explain why the addition of sodium hydroxide solution liberates the amino group but does not produce anthranilic acid.

_____

_____ [3]

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General Information

1 tonne = 10^6 g
1 metre = 10^9 nm
One mole of any gas at 293 K and a pressure of 1 atmosphere (10^5 Pa) occupies a volume of 24 dm^3
Avogadro Constant = 6.02×10^{23} mol^{-1}
Planck Constant = 6.63×10^{-34} J s
Specific Heat Capacity of water = 4.2 J g^{-1} K^{-1}
Speed of Light = 3×10^8 m s^{-1}

Characteristic absorptions in IR spectroscopy

Wavenumber/cm^{-1}	Bond	Compound
550–850	C–X (X = Cl, Br, I)	Haloalkanes
750–1100	C–C	Alkanes, alkyl groups
1000–1300	C–O	Alcohols, esters, carboxylic acids
1450–1650	C=C	Arenes
1600–1700	C=C	Alkenes
1650–1800	C=O	Carboxylic acids, esters, aldehydes, ketones, amides, acyl chlorides
2200–2300	C≡N	Nitriles
2500–3200	O–H	Carboxylic acids
2750–2850	C–H	Aldehydes
2850–3000	C–H	Alkanes, alkyl groups, alkenes, arenes
3200–3600	O–H	Alcohols
3300–3500	N–H	Amines, amides

Proton Chemical Shifts in Nuclear Magnetic Resonance Spectroscopy (relative to TMS)

Chemical Shift	Structure	
0.5–2.0	–C**H**	Saturated alkanes
0.5–5.5	–O**H**	Alcohols
1.0–3.0	–N**H**	Amines
2.0–3.0	–CO–C**H**	Ketones
	–N–C**H**	Amines
	C_6H_5–C**H**	Arene (aliphatic on ring)
2.0–4.0	X–C**H**	X = Cl or Br (3.0–4.0)
		X = I (2.0–3.0)
4.5–6.0	–C=C**H**	Alkenes
5.5–8.5	RCON**H**	Amides
6.0–8.0	–C_6**H**$_5$	Arenes (on ring)
9.0–10.0	–C**H**O	Aldehydes
10.0–12.0	–COO**H**	Carboxylic acids

These chemical shifts are concentration and temperature dependent and may be outside the ranges indicated above.

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Data Leaflet

Including the Periodic Table of the Elements

For the use of candidates taking
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gce a/as examinations

chemistry

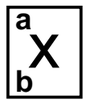
For first teaching from September 2016
For first award of AS Level in Summer 2017
For first award of A Level in Summer 2018
Subject Code: 1110

THE PERIODIC TABLE OF ELEMENTS

I	II											III	IV	V	VI	VII	0
Group																	
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H Hydrogen 1																	4 He Helium 2
7 Li Lithium 3	9 Be Beryllium 4											11 B Boron 5	12 C Carbon 6	14 N Nitrogen 7	16 O Oxygen 8	19 F Fluorine 9	20 Ne Neon 10
23 Na Sodium 11	24 Mg Magnesium 12											27 Al Aluminium 13	28 Si Silicon 14	31 P Phosphorus 15	32 S Sulfur 16	35.5 Cl Chlorine 17	40 Ar Argon 18
39 K Potassium 19	40 Ca Calcium 20	45 Sc Scandium 21	48 Ti Titanium 22	51 V Vanadium 23	52 Cr Chromium 24	55 Mn Manganese 25	56 Fe Iron 26	59 Co Cobalt 27	59 Ni Nickel 28	64 Cu Copper 29	65 Zn Zinc 30	70 Ga Gallium 31	73 Ge Germanium 32	75 As Arsenic 33	79 Se Selenium 34	80 Br Bromine 35	84 Kr Krypton 36
85 Rb Rubidium 37	88 Sr Strontium 38	89 Y Yttrium 39	91 Zr Zirconium 40	93 Nb Niobium 41	96 Mo Molybdenum 42	98 Tc Technetium 43	101 Ru Ruthenium 44	103 Rh Rhodium 45	106 Pd Palladium 46	108 Ag Silver 47	112 Cd Cadmium 48	115 In Indium 49	119 Sn Tin 50	122 Sb Antimony 51	128 Te Tellurium 52	127 I Iodine 53	131 Xe Xenon 54
133 Cs Caesium 55	137 Ba Barium 56	139 La* Lanthanum 57	178 Hf Hafnium 72	181 Ta Tantalum 73	184 W Tungsten 74	186 Re Rhenium 75	190 Os Osmium 76	192 Ir Iridium 77	195 Pt Platinum 78	197 Au Gold 79	201 Hg Mercury 80	204 Tl Thallium 81	207 Pb Lead 82	209 Bi Bismuth 83	210 Po Polonium 84	210 At Astatine 85	222 Rn Radon 86
223 Fr Francium 87	226 Ra Radium 88	227 Ac† Actinium 89	261 Rf Rutherfordium 104	262 Db Dubnium 105	266 Sg Seaborgium 106	264 Bh Bohrium 107	277 Hs Hassium 108	268 Mt Meitnerium 109	271 Ds Darmstadtium 110	272 Rg Roentgenium 111	285 Cn Copernicium 112						

140 Ce Cerium 58	141 Pr Praseodymium 59	144 Nd Neodymium 60	145 Pm Promethium 61	150 Sm Samarium 62	152 Eu Europium 63	157 Gd Gadolinium 64	159 Tb Terbium 65	162 Dy Dysprosium 66	165 Ho Holmium 67	167 Er Erbium 68	169 Tm Thulium 69	173 Yb Ytterbium 70	175 Lu Lutetium 71
232 Th Thorium 90	231 Pa Protactinium 91	238 U Uranium 92	237 Np Neptunium 93	242 Pu Plutonium 94	243 Am Americium 95	247 Cm Curium 96	245 Bk Berkelium 97	251 Cf Californium 98	254 Es Einsteinium 99	253 Fm Fermium 100	256 Md Mendelevium 101	254 No Nobelium 102	257 Lr Lawrencium 103

* 58 – 71 Lanthanum series
† 90 – 103 Actinium series



a = relative atomic mass (approx)
x = atomic symbol
b = atomic number