Rewarding Learning

ADVANCED
General Certificate of Education
2019

Centre Number

Candidate Number

Chemistry

StemUp Model Solution

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.

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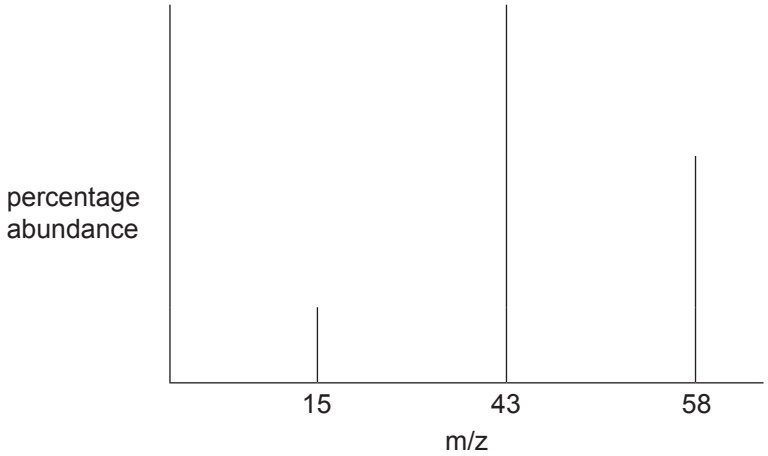
Section A

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.

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

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.

9 The systematic name for $LiAlH_4$ is

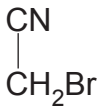
A lithal.

B lithium tetrahydridaluminate(III).

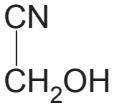
C lithium tetrahydridealuminate(III).

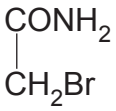
D lithium tetrahydridoaluminate(III).

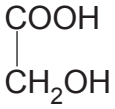
10 When the following compound is completely hydrolysed

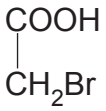


which product is formed?

A 

B 

C 

D 

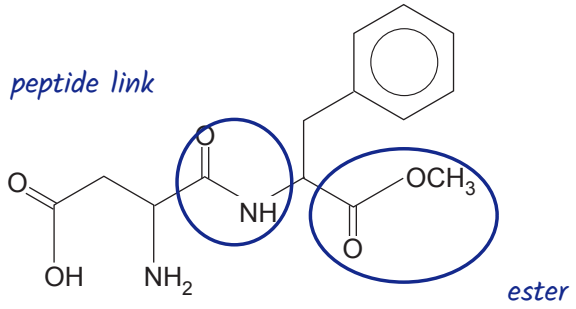
Section B

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**.

The amine ($-NH_2$) group and the carboxylic acid ($-COOH$) group are both attached to the same (first) carbon atom. [2]

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

Each contains a chiral centre: a carbon atom attached to four different groups. [1]

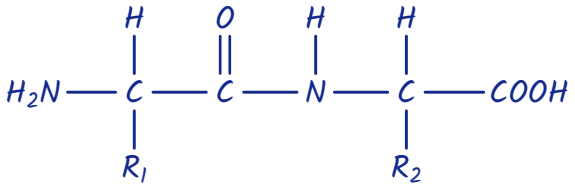
(d) Suggest why aspartic acid is classified as an acidic amino acid and phenylalanine is classified as a neutral amino acid.

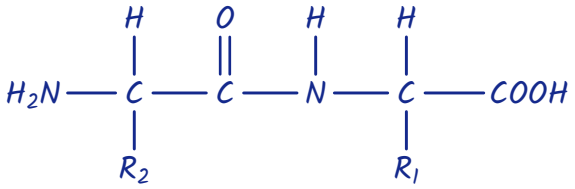
Aspartic acid has two acidic –COOH groups but only one basic $-NH_2$ group.

Phenylalanine has one basic $-NH_2$ group and one acidic –COOH group. [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.

(dilute) hydrochloric acid [1]

[Turn over

(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.

Spot the hydrolysis mixture onto a pencil base line on a TLC sheet, beside spots of pure phenylalanine and pure aspartic acid. Place the sheet in a beaker of a suitable solvent, e.g. ethanol, below the base line, and seal the beaker.

Run until the solvent nears the end of the sheet, mark the solvent front, dry and locate the spots under UV light, in iodine or by spraying with ninhydrin.

Compare the spots (R_f values) of the mixture with the pure samples: matching spots prove both amino acids are produced.

Methanol evaporates and is miscible with ethanol, so is not seen. [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.

Baking occurs at a high temperature, at which aspartame breaks down. Soft drinks are at room temperature and are acidic (pH 2.5 to 4.0), so aspartame is stable. [2]

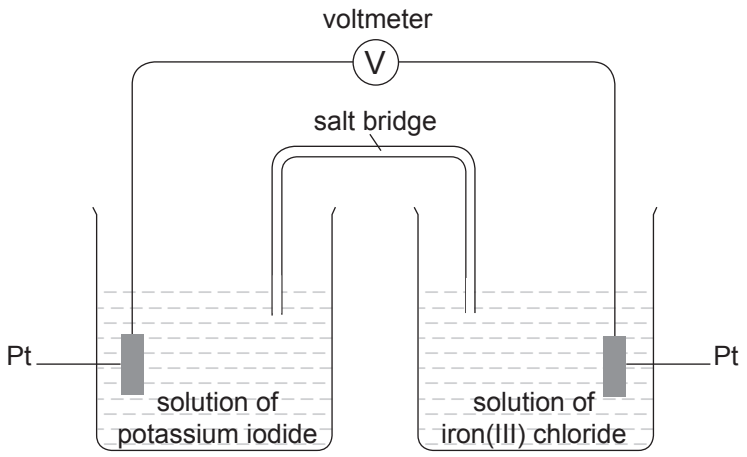
(i) When aspartame is made, it is important to use the correct chiral isomers of phenylalanine and aspartic acid. The binding sites for the taste receptors on the tongue act in a similar way to the mechanism of the action of enzymes. Explain the action of aspartame on taste receptors.

Only the correct chiral isomer of aspartame has the right shape to fit specifically into the binding site of the taste receptor, like a substrate fitting the active site of an enzyme (lock and key).

Binding to the receptor triggers the sweet taste.

[2]

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.

potassium chloride [1]

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

Soak a strip of filter paper in a saturated solution of potassium chloride. [1]

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

It completes the circuit (conducts) without introducing a metal.

It maintains the balance of anions and cations.

[2]

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

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

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

(i) Calculate the emf of the cell.

emf = +0.77 − (+0.54)

= +0.23 V [2]

(ii) Write a conventional representation for the cell.

$Pt \mid 2I^-(aq), I_2(aq) \parallel Fe^{3+}(aq), Fe^{2+}(aq) \mid Pt$ [2]

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

$2Fe^{3+}(aq) + 2I^-(aq) \rightarrow 2Fe^{2+}(aq) + I_2(aq)$ [1]

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

Electrons are produced in the iodine (I^-) half-cell and flow through the wire from left to right, to the iron(III) half-cell. [2]

[Turn over

(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+}

Add aqueous sodium hydroxide (or ammonia):

a brown precipitate forms. [2]

(ii) Fe^{2+}

Add aqueous sodium hydroxide (or ammonia):

a green precipitate forms. [2]

(iii) I^-

Add aqueous silver nitrate (with dilute nitric acid):

a yellow precipitate forms. [2]

(iv) I_2

Add starch solution:

it turns blue-black. [2]

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(Questions continue overleaf)

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**.

Isomers with the same molecular formula, but with the functional group (the C=C double bond) in a different position. [2]

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

$CH_3(CH_2)_7COOH$

$HOOC(CH_2)_7COOH$

[2]

(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.

The acid has hydrogen bonds between molecules (via –COOH), which are stronger than other intermolecular forces,but the ester has no O–H, so only weaker van der Waals forces. [2]

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

The methyl ester is more volatile, so it vaporises easily and passes through the GLC column faster.

[1]

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

Add together the areas under all the peaks on the trace.

% = area under the petroselinic (ester) peak ÷ total area × 100

[2]

(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.

$$\left[-OC(CH_2)_4CONH(CH_2)_6NH- \right]$$

[2]

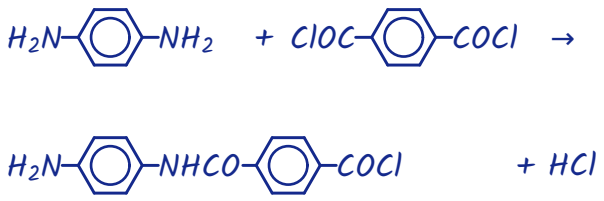
(ii) Explain what is meant by the term **condensation** polymer.

A polymer formed when monomers join with the elimination of a small molecule, e.g. water or HCl. [1]

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

Peptide links are only formed from amino acids; nylon is not made from amino acids. [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]

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

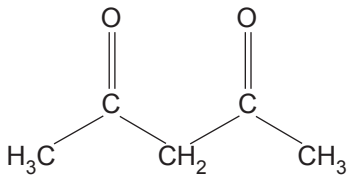
Both contain amide groups (–CONH–), which can be hydrolysed by microorganisms, breaking down the polymer chains. [2]

(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.

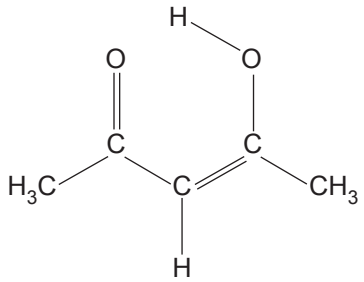
In this question you will be assessed on using your written communication skills including the use of specialist scientific terms.

The primary structure is the sequence of amino acids in the chain, joined by peptide links.
The secondary structure is the twisting or coiling of the chain into an α-helix, or β-pleated sheets, held by hydrogen bonds between C=O and N–H groups.
The tertiary structure is the further bending and folding of the secondary structure into a specific 3D shape, held by disulfide bridges, ionic bonds and hydrogen bonds.
At high temperature, or at low or high pH, these interactions are disrupted, the active site changes shape and the enzyme is denatured, losing its activity. At low temperature activity is low. [6]

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



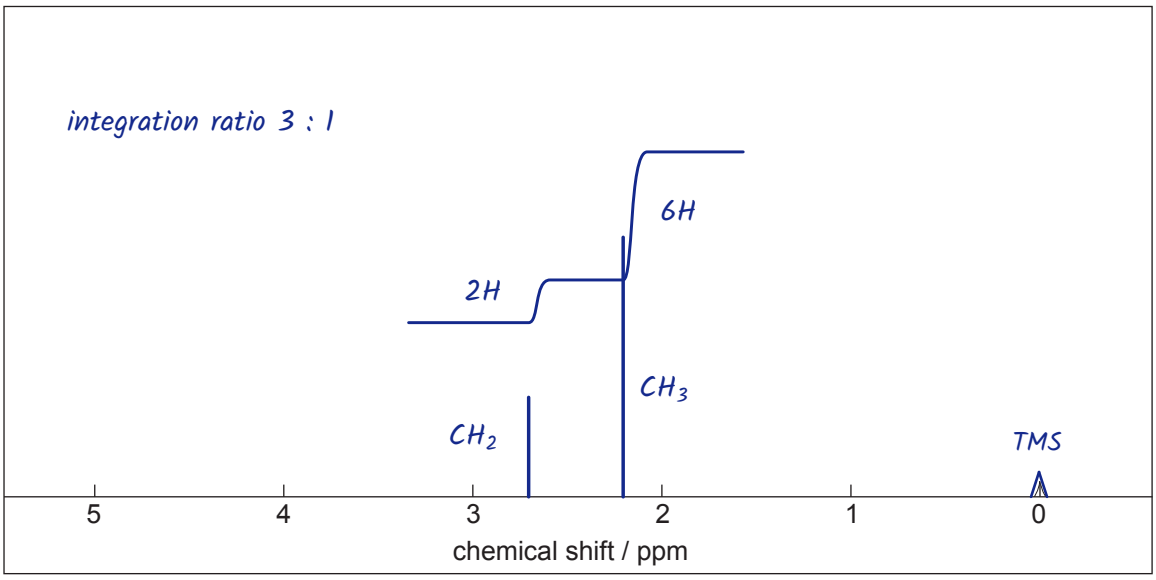
keto form



enol form

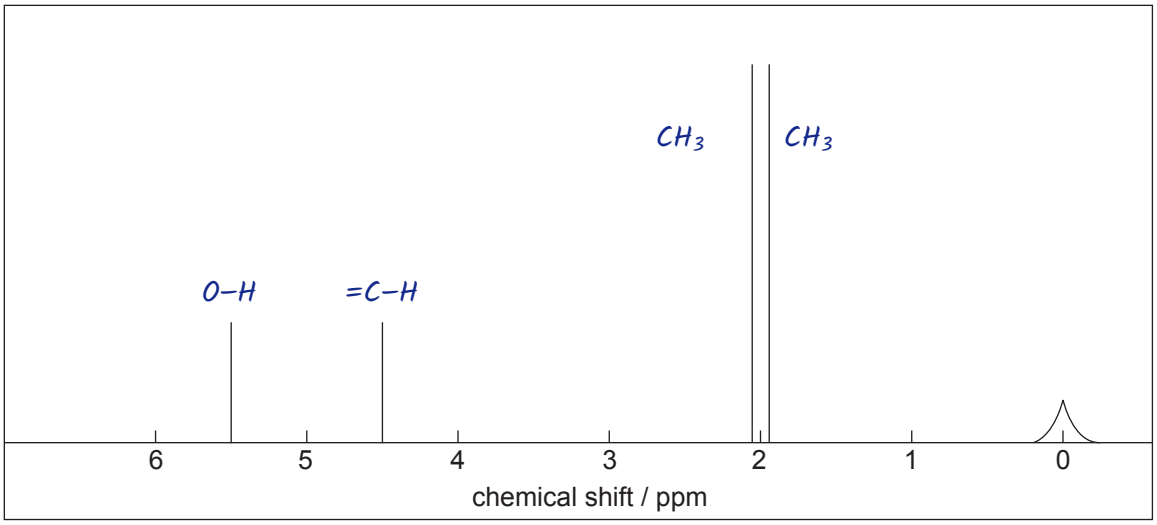
(a) The nmr spectrum of pentane-2,4-dione at room temperature shows that it is a mixture of isomers.

(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.



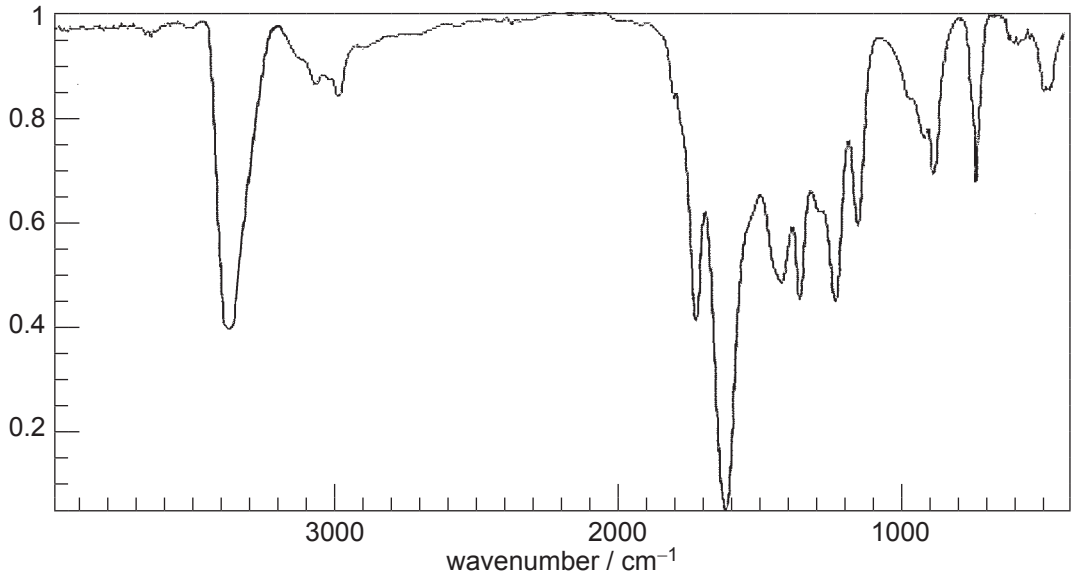
[2]

(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.



Peak at 3400 cm^{-1}: O–H in alcohols (3200 to 3600), enol;

peak at 1610: C=C in alkenes (1600 to 1700), enol;

peak at 1750: C=O in ketones (1650 to 1800), keto form. [2]

[Turn over

(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?

Wrap the flask in paper (keep it in the dark). [1]

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

The orange-brown colour of bromine remains. [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.

mol dione = $25.0 \times 10^{-3} \times 0.008 = 2.0 \times 10^{-4}$ mol

mol Br_2 = $4.6 \times 10^{-3} \times 0.002 = 9.2 \times 10^{-6}$ mol = mol enol

% enol = $9.2 \times 10^{-6} \div 2.0 \times 10^{-4} \times 100$

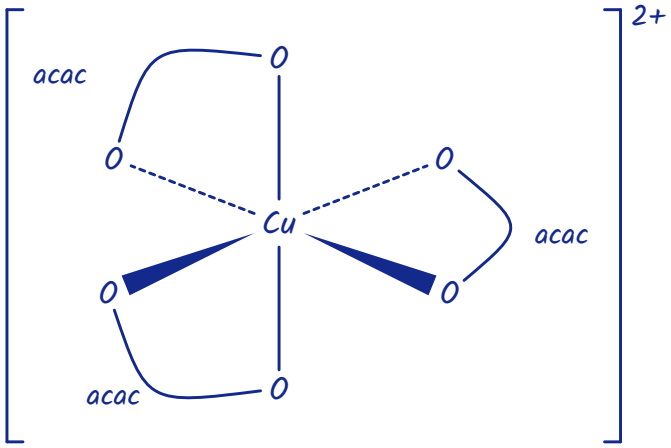
= 4.6% = 5% [4]

(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?

two [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.

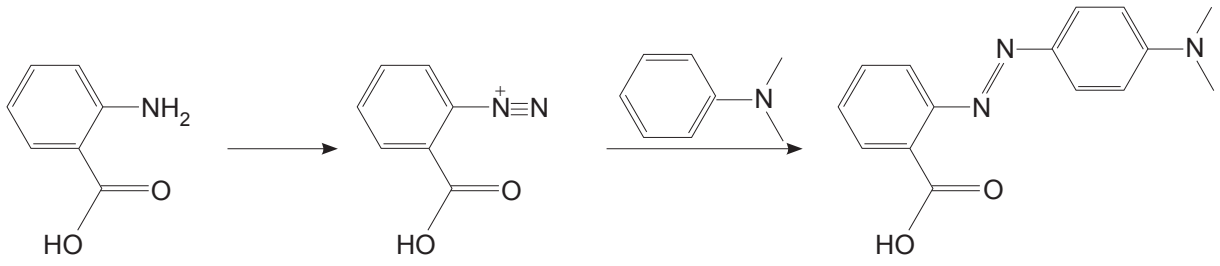
One edta replaces the three acac ligands, producing three molecules of acac (2 particles become 4), so there is an increase in entropy. [2]

(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.

React it with phenylhydrazine and measure the melting point of the product: if it is 107 to 108 °C, it must be pentane-2,4-dione. [1]

[Turn over

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.

sodium nitrite and dilute hydrochloric acid

at 0 to 10 °C (in ice) [2]

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

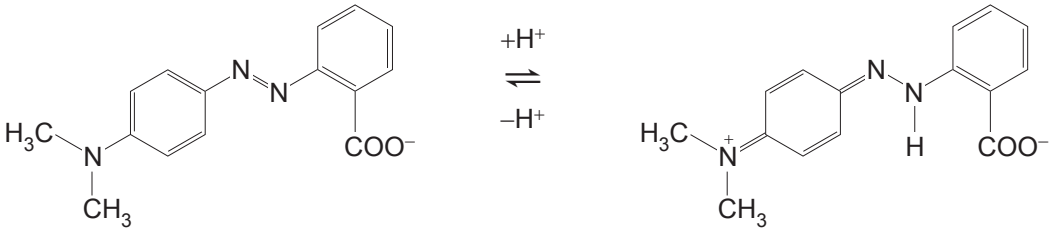
It has highly delocalised electrons across the molecule,

which gives closer proximity of the electronic energy levels,

so electrons are more easily promoted to higher levels.

A colour is removed from the (white) light. [4]

(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.

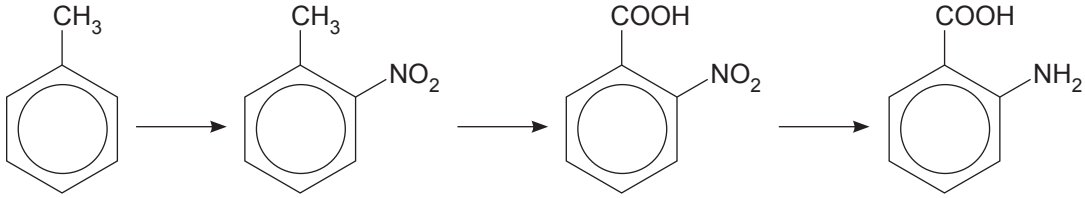
The delocalisation (double bond structure) differs in the two forms, so energy levels have a different proximity. [2]

(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.

The sodium salt is ionic, so it can bond with water; methyl red has no group to aid solubility except –COOH. [2]

[Turn over

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



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

concentrated nitric acid

concentrated sulfuric acid

[2]

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

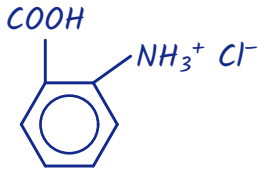
purple to colourless [2]

(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.

$Sn + 2HCl \rightarrow SnCl_2 + H_2$ [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.



NaOH reacts with $-NH_3^+Cl^-$ to give $-NH_2$ + NaCl,

and NaOH also reacts with $-COOH$ to give $-CO_2Na$. [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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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

Group

I	II											III	IV	V	VI	VII	0
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

$^{a}_{b}X$

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