New Specification

Rewarding Learning

ADVANCED
General Certificate of Education
2018

Centre Number

Candidate Number

Chemistry

Assessment Unit A2 2

assessing

Analytical, Transition Metals, Electrochemistry and Further Organic Chemistry

[ACH22]

ACH22

TUESDAY 12 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 eighteen** 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 eight** 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 **12(b)** and **13(a)(vi)**.
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.

11589

24ACH2201

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 When hydrogen peroxide is added to acidified potassium dichromate(VI) the following reaction occurs:

$$Cr_2O_7^{2-} + 3H_2O_2 + 8H^+ \rightarrow 2Cr^{3+} + 3O_2 + 7H_2O$$

Which statement is **not** correct?

A Hydrogen peroxide is acting as an oxidising agent

B The solution changes colour from orange to green

C The oxidation state of oxygen changes in the reaction

D The oxidation state of chromium changes in the reaction

2 Which compound has only singlet peaks in its proton nmr spectrum?

A Ethyl ethanoate

B Methyl propanoate

C Methyl ethanoate

D Propyl ethanoate

3 A painkiller, ibuprofen, produced effervescence when added to a solution of sodium carbonate. Which functional group is present in ibuprofen?

A -CHO

B -COOH

C -COOR

D $-CONH_2$

4 Which compound is the weakest base?

A Ammonia

B Methanamide

C Methylamine

D Phenylamine

5 What is the oxidation number of cobalt in $[Co(H_2O)_4en]Cl_2$?

A –2

B 0

C +2

D +3

[Turn over

6 Which atom has an unpaired electron in an s-orbital in the ground state?

A Chromium

B Cobalt

C Iron

D Manganese

7 Which compound will react most rapidly with 1,6-diaminohexane to form nylon?

A Hexane-1,6-diol

B Hexanedioic acid

C Hexanedioyl dichloride

D Sodium hexanedioate

8 A sample of chlorine gas was placed in a mass spectrometer. How many molecular ion peaks would be observed?

A 2

B 3

C 4

D 5

9 What mass of butanamide is required to synthesise 6.90 g of butanenitrile if the yield is 80%?

A 6.97 g

B 8.70 g

C 10.9 g

D 12.2 g

10 Some glycine is dissolved in a buffer solution of pH 11. What is the structure formed at this pH?

A $HOOCCH_2NH_3^+$

B NH_2CH_2COOH

C $NH_2CH_2COO^-$

D $NH^-CH_2COO^-$

Section B

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

11 Transition metal complexes are often coloured.

(a) State the colour of the following aqueous complexes:

aqueous complex	colour
$[Mn(H_2O)_6]^{2+}$	
$[Ni(H_2O)_6]^{2+}$	
$[Co(H_2O)_6]^{2+}$	
$[V(H_2O)_6]^{3+}$	
$[Ni(NH_3)_6]^{2+}$	

[5]

(b) Aqueous hexaaquacopper(II) ions can undergo ligand replacement with concentrated hydrochloric acid to form tetrachlorocuprate(II) ions.

(i) Write the electronic configuration of the copper ion in hexaaquacopper(II) ions and use this to explain why copper can be described as a transition metal.

_____

_____

_____ [2]

(ii) Define the term **ligand**.

_____

_____

_____ [1]

(iii) Suggest why the co-ordination number changes when hexaaquacopper(II) ions react with concentrated hydrochloric acid.

_____

_____

_____ [1]

(iv) Write the equation for the ligand substitution reaction which occurs when hexaaquacopper(II) ions form tetrachlorocuprate(II) ions.

_____

_____ [2]

(v) Write the colour change observed when this reaction occurs.

_____ [1]

(vi) Explain why this ligand replacement is thermodynamically feasible.

_____

_____ [2]

(c) Copper can form complexes with ammonia or ethylamine. State and explain which of these would be the stronger ligand.

_____

_____

_____ [2]

12 Two standard electrode potentials are given below:

(a)

half-cell	**$E^{\ominus}$/V**
$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn$	–0.76
$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu$	+0.34

(i) Define **standard electrode potential**.

_____

_____ [2]

(ii) When the two half-cells are connected zinc will reduce Cu^{2+} ions to Cu atoms. Write the equation for the reaction.

_____ [2]

(iii) Calculate the emf for this cell.

_____ [1]

(b) Describe how you would set up a standard hydrogen electrode and use it to measure the electrode potential for a half-cell.

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

_____

_____

_____

_____

_____

_____

_____

_____ [6]

[Turn over

13 A method of synthesising aspirin is given below using the following steps:

1. Add 7.5 cm^3 (an excess) of ethanoic anhydride to 3.0 g of salicylic acid in a conical flask
2. Add eight drops of concentrated phosphoric acid
3. Heat, with stirring, for 20 minutes in a water bath
4. Add 3 cm^3 of deionised water to the flask
5. Add 30 cm^3 of deionised water and cool to room temperature, allowing the aspirin to crystallise
6. Filter the crystals by Buchner filtration; continue to suck air through the Buchner funnel for five minutes after completion of the filtration

(a) **(i)** Suggest **two** reasons why ethanoic anhydride is used in this reaction in preference to ethanoic acid.

_____

_____

_____

_____ [2]

(ii) Write the equation for the reaction in step 1.

[2]

(iii) Why is concentrated phosphoric acid added?

_____ [1]

(iv) Suggest why water is added in step 4.

_____

_____ [1]

(v) Explain why air is sucked through the apparatus for five minutes.

_____

_____ [1]

(vi) Describe, giving full experimental detail, the TLC method which can be used to determine whether the reaction is complete after step 3. The solvent is ethyl ethanoate.

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

[6]

(b) Calculate the percentage yield if 2.3 g of aspirin is obtained (answer to one decimal place).

[3]

(c) Salicylic acid is a bifunctional molecule with a carboxylic acid group and a hydroxyl group attached to the benzene ring. The hydroxyl group displays acidic behaviour.

(i) Suggest why the hydroxyl group attached to a benzene ring is more acidic than the hydroxyl group in aliphatic alcohols.

_____

_____ [2]

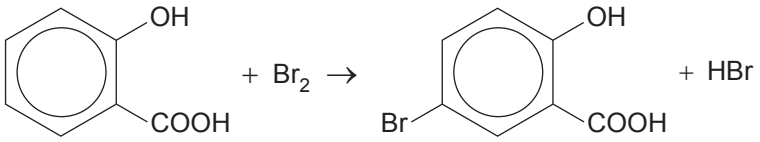
(ii) Write an equation for the reaction of salicylic acid with excess aqueous sodium hydroxide.

_____ [2]

(iii) State why it is preferable to use the sodium salt of aspirin.

_____ [1]

(d) Bromine will give an electrophilic substitution reaction with salicylic acid as shown below:



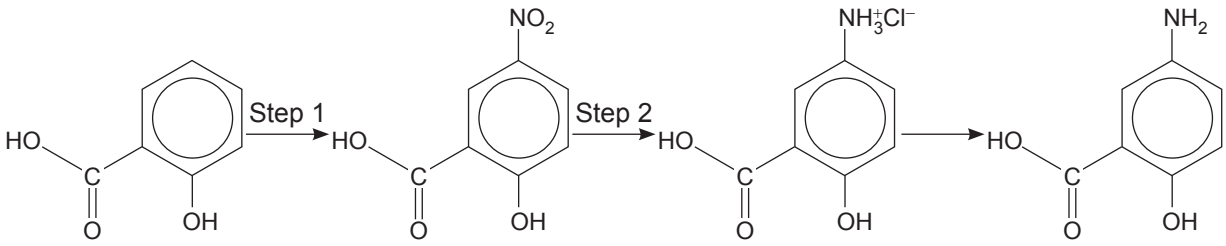
Salicylic acid will react with bromine without a catalyst being present. This differs from benzene, which requires a metal halide catalyst.

Name a catalyst which is used in the bromination of benzene.

_____ [1]

[Turn over

14 Mesalazine, an anti-inflammatory drug which is used to treat bowel disease, can be synthesised from 2-hydroxybenzoic acid using the flow scheme below.



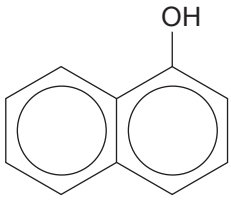
2-hydroxybenzoic acid mesalazine

(a) **(i)** State the reagents that could be used for Step 1 and Step 2.

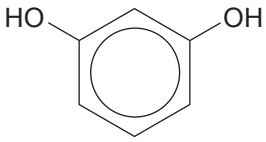
Step 1: _____

Step 2: _____ [2]

(ii) Mesalazine can be converted into azo dyes through reaction with naphth-1-ol or resorcinol:



naphth-1-ol



resorcinol

Draw the structure of the ion mesalazine must be converted into before the azo dye can be formed.

[2]

(iii) Draw the structure of the azo dye produced by the reaction with resorcinol.

[2]

(iv) Explain why azo dyes are coloured and suggest why the azo dyes produced by resorcinol and naphth-1-ol have slightly different colours.

_____

_____

_____

_____ [4]

(b) 2-hydroxybenzoic acid can be converted into an ester by reacting with an equimolar amount of ethane-1,2-diol. Write an equation for this reaction.

[2]

(c) Polyethylene terephthalate can be produced from ethane-1,2-diol.

(i) State a use for polyethylene terephthalate.

_____ [1]

(ii) Explain why polyethylene terephthalate is biodegradable.

_____ [1]

[Turn over

15 An ester, with the molecular formula $C_7H_{14}O_2$, produced three signals when analysed by proton nmr. The data is provided in the table below:

signal	**a**	**b**	**c**
chemical shift	4.1	1.2	1.1
integration ratio	2	3	9
splitting pattern	quartet	triplet	singlet

(a) **(i)** Explain why solvents which contain hydrogen atoms should not be used in nmr spectroscopy. Suggest a suitable solvent which could be used.

_____

_____ [2]

(ii) Give the name and formula of the molecule used in nmr spectroscopy as a standard.

_____ [2]

(iii) State **two** reasons why the molecule identified in part **(ii)** is used.

_____

_____ [2]

(b) **(i)** Explain which alkyl group in the ester produces signals **a** and **b** making reference to the spin-spin splitting pattern and the integration ratios.

_____

_____

_____

_____

_____ [3]

(ii) Draw the alkyl group that would give rise to signal **c**.

_____ [1]

(c) Draw the possible structure of the ester based upon the nmr data given.

[2]

[Turn over

16 The bromate(V) ion, BrO_3^-, is an oxidising agent produced by the reaction of bromine with a hot concentrated solution of sodium hydroxide.

(a) **(i)** Write the ionic equation for the reaction of bromine with sodium hydroxide.

_____ [2]

(ii) State the colour change observed for the above reaction.

_____ [1]

(b) Acidified bromate(V) ions will oxidise iodide ions to iodine.

(i) Write a half-equation for the reduction of bromate(V) ions to bromide.

_____ [1]

(ii) Write a half-equation for the oxidation of iodide ions to iodine.

_____ [1]

(iii) Write the overall equation for this reaction.

_____ [1]

(c) The iodine produced can then be reduced by thiosulfate ions. Titrations of the liberated iodine with sodium thiosulfate solution can be used to determine the concentration of bromate(V) ions. A 20.0 cm^3 solution containing acidified bromate(V) ions was added to a solution containing excess iodide ions and the resulting mixture made up to 1.0 dm^3. A 25.0 cm^3 aliquot was titrated against 0.10 M sodium thiosulfate, adding starch indicator just before the end point. The titre was found to be 23.8 cm^3.

(i) Explain why it is necessary to add the starch indicator just before the end point.

_____

_____ [1]

(ii) Calculate, to two significant figures, the concentration of the original bromate(V) solution.

_____

_____

_____

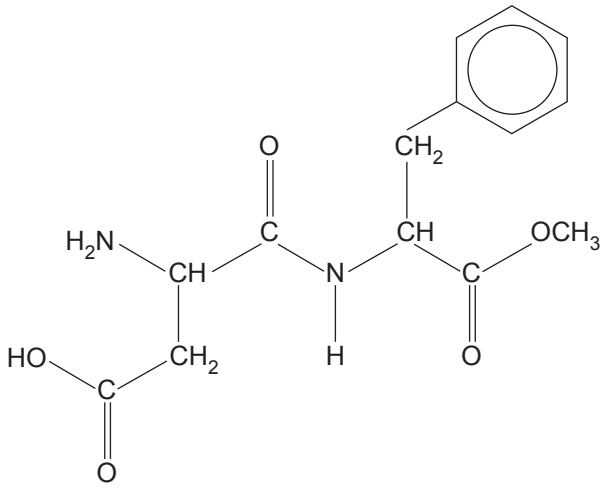
_____

_____

_____ [4]

[Turn over

17 Aspartame is used as a sweetener in many food products. It is a methyl ester of the dipeptide produced in the condensation reaction between aspartic acid and phenylalanine.



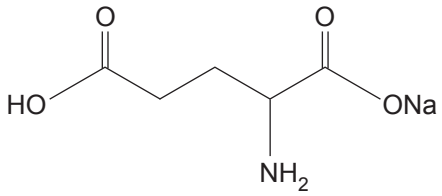
Aspartame

(a) Use the structure of aspartame to suggest structures for aspartic acid and phenylalanine.

aspartic acid phenylalanine

[2]

(b) Another amino acid derivative that is used as a food additive is monosodium glutamate which can be synthesised from glutamic acid.



monosodium glutamate

(i) Circle on the structure above any chiral centre present in monosodium glutamate. [1]

(ii) Draw the structure of the zwitterion formed by glutamic acid.

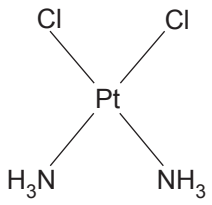
[1]

(iii) Write an equation for the reaction of glutamic acid with sodium carbonate to form monosodium glutamate.

_____ [2]

[Turn over

18 Cisplatin was first described by Peyrone in 1845 and was approved for use in the treatment of testicular and ovarian cancers in the USA in 1978.



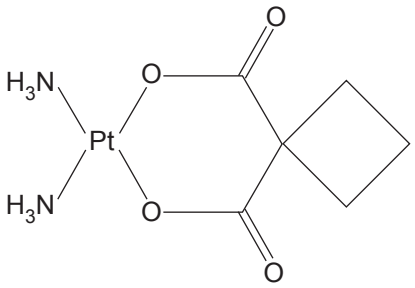
cisplatin

(a) Explain why cisplatin is effective in acting as an anticancer drug.

_____

_____ [1]

(b) Cisplatin has a number of undesired side-effects which are believed to be caused by the drug activating before it reaches the targeted tumour. Attempts to reduce these side-effects have included modifying the structure to give derivatives such as carboplatin.



carboplatin

Give the molecular formula of carboplatin.

_____ [1]

(c) Another method of developing more targetable platinum-based anticancer drugs has been through the development of photoactivable drugs which are activated through photoreduction by light. Early examples of these were diiodo complexes.

A **B**

(i) Explain, using oxidation states, why converting **A** into **B** is regarded as a reduction.

_____

_____ [2]

(ii) Describe the change in both shape and co-ordination number in converting **A** into **B**.

_____

_____

_____

_____ [4]

THIS IS THE END OF THE QUESTION PAPER

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237486

Rewarding Learning

Periodic Table of the Elements

For the use of candidates taking
Advanced Subsidiary and Advanced Level
Chemistry Examinations

Copies must be free from notes or additions of any kind. No other type of data booklet or information sheet is authorised for use in the examinations.

gce A/AS examinations

chemistry (advanced)

THE PERIODIC TABLE OF ELEMENTS
Group

One mole of any gas at 20 °C and a pressure of 1 atmosphere (10^5 Pa) occupies a volume of 24 dm^3.
Planck Constant = 6.63×10^{-34} J s
Gas Constant = 8.31 J mol^{-1} K^{-1}
Avogadro Constant = 6.02×10^{23} mol^{-1}

I	II											III	IV	V	VI	VII	0
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	99 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															

140 Ce Cerium 58	141 Pr Praseodymium 59	144 Nd Neodymium 60	147 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