Write your name here

Surname	Other names

Pearson Edexcel
International
Advanced Level

Centre Number	Candidate Number

Chemistry

Advanced

Unit 5: General Principles of Chemistry II – Transition Metals and Organic Nitrogen Chemistry (including synoptic assessment)

Tuesday 12 June 2018 – Afternoon
Time: 1 hour 40 minutes

Paper Reference
WCH05/01

Candidates must have: Data Booklet
Scientific calculator

Total Marks

Instructions

- Use **black** ink or **black** ball-point pen.
- **Fill in the boxes** at the top of this page with your name, centre number and candidate number.
- Answer **all** questions.
- Answer the questions in the spaces provided – *there may be more space than you need.*

Information

- The total mark for this paper is 90.
- The marks for **each** question are shown in brackets – *use this as a guide as to how much time to spend on each question.*
- Questions labelled with an **asterisk** (*****) are ones where the quality of your written communication will be assessed – *you should take particular care with your spelling, punctuation and grammar, as well as the clarity of expression, on these questions.*
- A Periodic Table is printed on the back cover of this paper.

Advice

- Read each question carefully before you start to answer it.
- Check your answers if you have time at the end.
- Show all your working in calculations and give units where appropriate.

Turn over ▶

SECTION A

Answer ALL the questions in this section. You should aim to spend no more than 20 minutes on this section. For each question, select one answer from A to D and put a cross in the box ☒. If you change your mind, put a line through the box ☒ and then mark your new answer with a cross ☒.

1 In the complex ion $[Fe(CN)_6]^{4-}$, the oxidation number of the iron is

☒ **A** +2

☒ **B** +3

☒ **C** +4

☒ **D** +6

(Total for Question 1 = 1 mark)

2 Aluminium reacts with aqueous alkali to produce hydrogen gas.
By considering the changes in the oxidation numbers of aluminium and hydrogen, it can be deduced that, in this reaction, 1 mol of aluminium produces

☒ **A** 1 mol of hydrogen gas.

☒ **B** 1.5 mol of hydrogen gas.

☒ **C** 2 mol of hydrogen gas.

☒ **D** 3 mol of hydrogen gas.

(Total for Question 2 = 1 mark)

Use this space for any rough working. Anything you write in this space will gain no credit.

3 The standard reduction potentials of two systems are

$$Sn^{4+}(aq) + 2e^- \rightleftharpoons Sn^{2+}(aq) \qquad E^\ominus = +0.15\,V$$

$$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq) \qquad E^\ominus = +0.77\,V$$

(a) What are the components of the half-cell required to measure the standard reduction potential of the Fe^{3+}/ Fe^{2+} system?

(1)

	Ion(s) in the solution	Metal electrode
☒ **A**	Fe^{2+}	iron
☒ **B**	Fe^{3+}	iron
☒ **C**	Fe^{2+} and Fe^{3+}	iron
☒ **D**	Fe^{2+} and Fe^{3+}	platinum

(b) What is the value of $E^\ominus_{cell}$ for the system below?

$$Sn^{4+}(aq) + 2Fe^{2+}(aq) \rightarrow Sn^{2+}(aq) + 2Fe^{3+}(aq)$$

(1)

☒ **A** −1.39 V

☒ **B** −0.62 V

☒ **C** +0.62 V

☒ **D** +1.39 V

(Total for Question 3 = 2 marks)

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4 The value of $E^\ominus_{cell}$ for a reaction is positive. It can be deduced that the

☒ **A** entropy change for the system, $\Delta S^\ominus_{system}$, must be positive.

☒ **B** entropy change for the surroundings, $\Delta S^\ominus_{surroundings}$, must be positive.

☒ **C** total entropy change, $\Delta S^\ominus_{total}$, must be positive.

☒ **D** entropy change for the system, $\Delta S^\ominus_{system}$, and the entropy change for the surroundings, $\Delta S^\ominus_{surroundings}$, must **both** be positive.

(Total for Question 4 = 1 mark)

Use this space for any rough working. Anything you write in this space will gain no credit.

5 In a hydrogen-oxygen fuel cell, the oxygen is

☒ **A** oxidised at the negative electrode.

☒ **B** oxidised at the positive electrode.

☒ **C** reduced at the negative electrode.

☒ **D** reduced at the positive electrode.

(Total for Question 5 = 1 mark)

6 Iodide ions are oxidised by peroxodisulfate ions in aqueous solution:

$$2I^- + S_2O_8^{2-} \rightarrow I_2 + 2SO_4^{2-}$$

This reaction is catalysed by Fe^{3+} ions. This catalysis is effective because

☒ **A** Fe^{3+} is readily reduced to Fe^{2+} which is then oxidised to Fe^{3+}.

☒ **B** Fe^{3+} has many electrons in its outermost subshells.

☒ **C** Fe^{3+} has many active sites on which the reaction can occur.

☒ **D** Fe^{3+} will oxidise peroxodisulfate ions to sulfate ions.

(Total for Question 6 = 1 mark)

7 Which has the greatest number of unpaired electrons in each of its atoms?

☒ **A** Vanadium

☒ **B** Chromium

☒ **C** Manganese

☒ **D** Iron

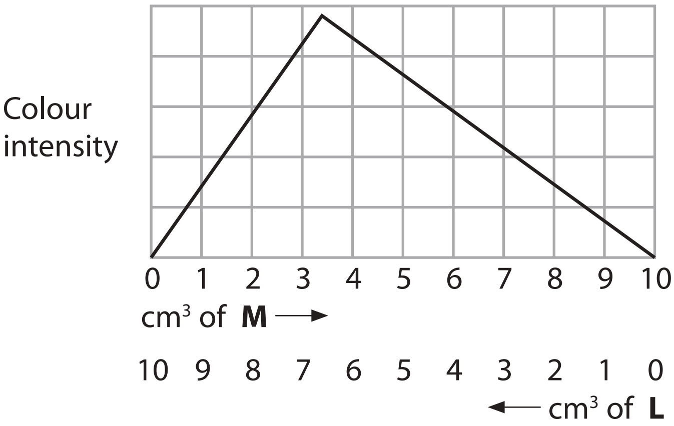
(Total for Question 7 = 1 mark)

Use this space for any rough working. Anything you write in this space will gain no credit.

8 A transition metal ion, **M**, forms a coloured complex with a monodentate ligand **L**.

Portions of a 0.05 mol dm^{-3} solution of **M** are mixed with portions of a solution containing 0.05 mol dm^{-3} of **L** so that the total volume of the resulting mixture is always 10 cm^3. The colour intensity of the complex in each mixture is measured using a colorimeter.

The graph of the results is



What is the formula of the complex?

☒ **A** **ML**

☒ **B** **ML_2**

☒ **C** **ML_3**

☒ **D** **ML_4**

(Total for Question 8 = 1 mark)

Use this space for any rough working. Anything you write in this space will gain no credit.

9 What is the total number of different oxidation numbers of vanadium that occurs in the white solid and the three solutions shown in the following sequence?

$$\underset{\text{white solid}}{NH_4VO_3(s)} \xrightarrow{\text{add water}} \text{pale yellow solution} \xrightarrow{\text{add } H_2SO_4} \text{dark yellow solution} \xrightarrow{\text{add zinc powder}} \text{pale purple solution}$$

☒ **A** 1

☒ **B** 2

☒ **C** 3

☒ **D** 4

(Total for Question 9 = 1 mark)

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10 The enthalpy change of hydrogenation of but-1-ene is $-126.9\,\text{kJ mol}^{-1}$ and the enthalpy change of hydrogenation of buta-1,3-diene is $-236.4\,\text{kJ mol}^{-1}$.

The delocalisation structure of buta-1,3-diene is more stable than the molecule with two isolated $C{=}C$ bonds by

☒ **A** $363.3\,\text{kJ mol}^{-1}$

☒ **B** $109.5\,\text{kJ mol}^{-1}$

☒ **C** $17.4\,\text{kJ mol}^{-1}$

☒ **D** $8.7\,\text{kJ mol}^{-1}$

(Total for Question 10 = 1 mark)

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11 Aluminium chloride catalyses the reaction of benzene and ethanoyl chloride. This is because aluminium chloride

☒ **A** has significant covalent character.

☒ **B** exists as a dimer in non-polar solvents.

☒ **C** is an electron pair acceptor.

☒ **D** is rapidly hydrolysed.

(Total for Question 11 = 1 mark)

Use this space for any rough working. Anything you write in this space will gain no credit.

12 Phenylamine reacts rapidly with dilute sulfuric acid. The reaction is

☒ **A** electrophilic addition.

☒ **B** electrophilic substitution.

☒ **C** hydrolysis.

☒ **D** neutralisation.

(Total for Question 12 = 1 mark)

13 Alanine is an amino acid. It is a crystalline solid at room temperature because the strongest forces between the molecules of alanine are

☒ **A** dipole-dipole forces.

☒ **B** London forces.

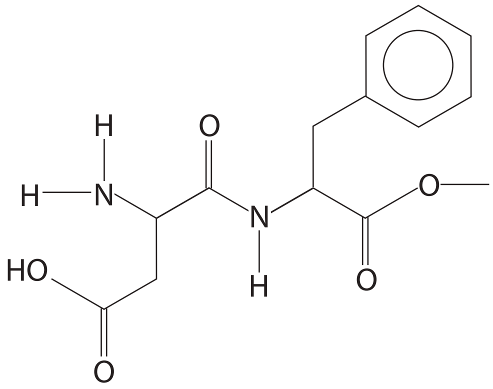
☒ **C** hydrogen bonds.

☒ **D** ionic bonds.

(Total for Question 13 = 1 mark)

Use this space for any rough working. Anything you write in this space will gain no credit.

14 Aspartame is an artificial sweetener. The structure of aspartame is



(a) Which functional group is **not** present in aspartame?

(1)

☒ **A** Amine

☒ **B** Ester

☒ **C** Ketone

☒ **D** Phenyl

(b) How many asymmetric carbon atoms are there in a molecule of aspartame?

(1)

☒ **A** Two

☒ **B** Three

☒ **C** Four

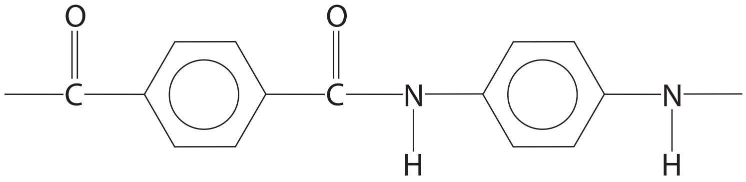
☒ **D** Six

(Total for Question 14 = 2 marks)

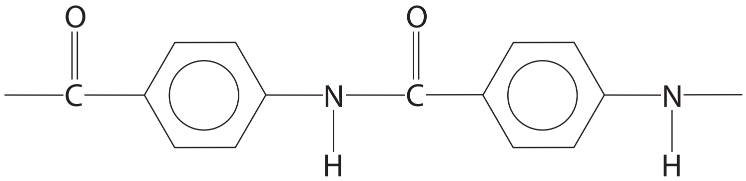
Use this space for any rough working. Anything you write in this space will gain no credit.

15 The repeat unit of the polymer Kevlar has the structure

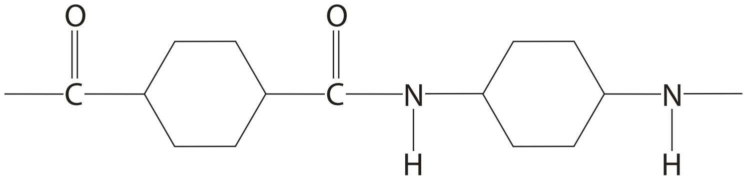
☒ **A**



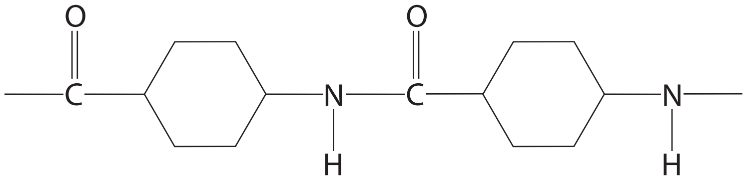
☒ **B**



☒ **C**



☒ **D**



(Total for Question 15 = 1 mark)

16 Which of these isomers would be expected to have mass spectrum peaks at $m/e = 30$ and $m/e = 73$?

☒ **A** $CH_3CH_2CH_2CH_2NH_2$

☒ **B** $CH_3CH(NH_2)CH_2CH_3$

☒ **C** $(CH_3)_3CNH_2$

☒ **D** $CH_3CH_2NHCH_2CH_3$

(Total for Question 16 = 1 mark)

Use this space for any rough working. Anything you write in this space will gain no credit.

17 An important advantage of the use of polymer supports in organic synthesis by the pharmaceutical industry is that

☒ **A** the equilibrium yield of the reaction is usually higher.

☒ **B** polymeric support materials are always inexpensive to prepare.

☒ **C** a range of side reactions occur on the polymer support.

☒ **D** the products are easily separated from the polymer support.

(Total for Question 17 = 1 mark)

18 Which piece of apparatus is normally used in solvent extraction?

☒ **A** Buchner funnel

☒ **B** Evaporating basin

☒ **C** Liebig condenser

☒ **D** Separating funnel

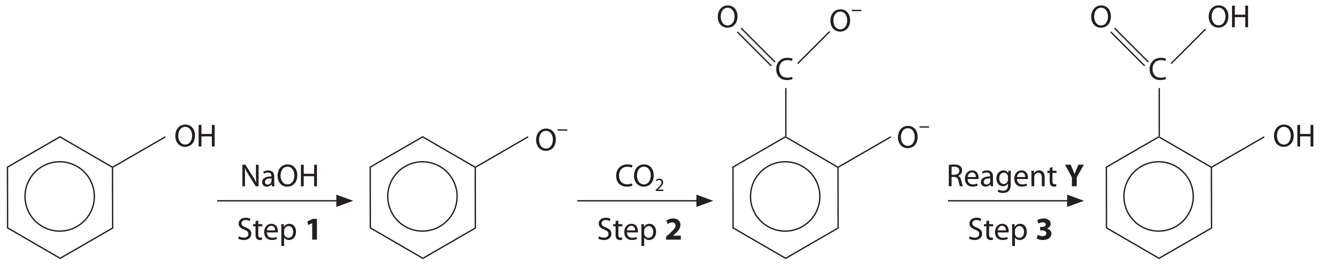
(Total for Question 18 = 1 mark)

TOTAL FOR SECTION A = 20 MARKS

SECTION B

Answer ALL the questions. Write your answers in the spaces provided.

19 Salicylic acid (2-hydroxybenzoic acid) is a starting material in the manufacture of aspirin; it is synthesised from phenol in the Kolbe-Schmitt process outlined.



(a) Step **2** of the Kolbe-Schmitt process involves an electrophilic substitution.

(i) Using your knowledge of electrophilic substitutions, draw the mechanism for the reaction in Step **2**.
Show the displayed formula of the electrophile CO_2, and all relevant curly arrows.
(4)

(ii) Identify Reagent **Y**.
(1)

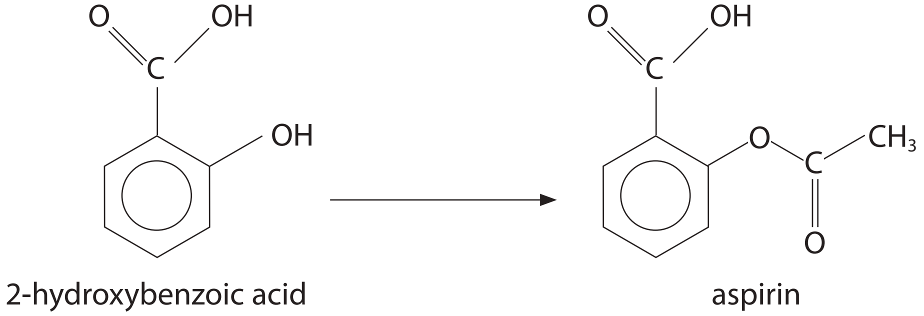
....

*(b) The Kolbe-Schmitt process is carried out at 125 °C and high pressure. State how, if at all, these conditions for electrophilic substitution would have to change if the Kolbe-Schmitt process was carried out with benzene in place of phenol.

Fully justify your answer in terms of the relative reactivity of benzene and phenol.

(4)

(c) In the final stage of the synthesis, 2-hydroxybenzoic acid is converted into aspirin in a single step:



(i) Name the type of reaction occurring.

(1)

*(ii) One student suggested that ethanoic acid would be a suitable reagent for this final reaction. A second student suggested using ethanoyl chloride. Compare the suitability of these two reagents, stating any advantages or disadvantages of each.

(3)

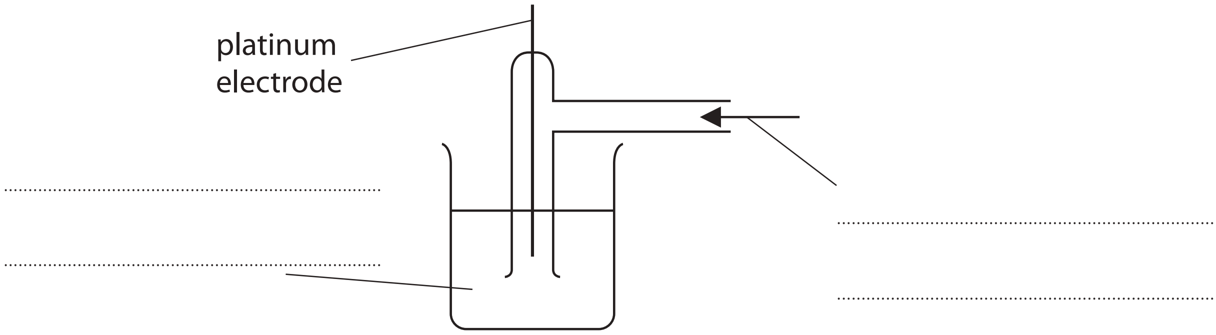
(Total for Question 19 = 13 marks)

20 Standard electrode potentials are used to predict the thermodynamic feasibility of chemical reactions.

(a) Standard electrode potentials can be determined by using the standard hydrogen electrode as a reference standard.

(i) Label the diagram of the standard hydrogen electrode, indicating the essential conditions associated with each substance used.

(2)



(ii) The platinum electrode of the standard hydrogen electrode is coated in finely divided platinum ('platinum black'). Suggest why platinum is used as the electrode and why it is coated in platinum black.

(2)

(iii) State the value assigned to the electrode potential of the standard hydrogen electrode.

(1)

(iv) Explain why a reference electrode is needed to measure the electrode potentials of chemical systems.

(1)

(v) Sometimes the calculated value of $E^{\ominus}_{cell}$ for a reaction shows it to be thermodynamically feasible but, in the laboratory, no reaction occurs. Give **two** possible explanations for this.

(2)

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....

(b) Potassium dichromate(VI) in acid conditions is a laboratory oxidising agent widely used in organic chemistry. Some electrode potentials relating to the use of this reagent are given in the table below.

Electrode reaction	*E* / V
$CH_3COOH(aq) + 2H^+(aq) + 2e^- \rightleftharpoons CH_3CHO(aq) + H_2O(l)$	–0.94
$CH_3CHO(aq) + 2H^+(aq) + 2e^- \rightleftharpoons C_2H_5OH(aq)$	–0.61
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightleftharpoons 2Cr^{3+}(aq) + 7H_2O(l)$	+1.33

(i) Deduce the ionic equation for the oxidation of ethanol to ethanal by potassium dichromate(VI) in acid conditions. State symbols are not required.

(2)

(ii) Calculate E_{cell} for the oxidation by acidified potassium dichromate(VI) of

- ethanol to ethanal
- ethanal to ethanoic acid.

(2)

(iii) Use your answer to (b)(ii) to suggest why it is necessary to distil ethanal directly out of the reaction mixture in the preparation of ethanal by the oxidation of ethanol.

(1)

(c) Potassium manganate(VII) is another laboratory oxidising agent used in organic chemistry. Use the data on page 17 of your Data Booklet to answer the questions about manganese compounds.

(i) Suggest why potassium manganate(VII) is **not** used to oxidise alcohols such as ethanol, whereas potassium dichromate(VI) is used. Give the relevant electrode reaction and its standard electrode potential. No calculation is required.

(2)

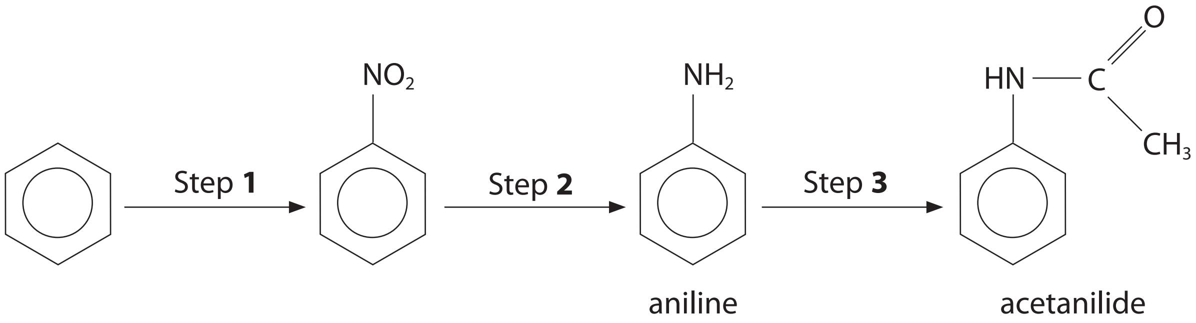
(ii) Write the equation for the disproportionation of manganate(VI) ions, MnO_4^{2-}, and calculate whether or not the reaction is thermodynamically feasible. State symbols are not required.

(3)

(Total for Question 20 = 18 marks)

21 Acetanilide (*N*-phenylethanamide) was the first aniline (phenylamine) derivative discovered to have analgesic properties. It was first used as a painkiller in 1886 but quickly discarded because of a range of toxic effects. Nowadays it is important in the manufacture of 'sulfa' antibacterial drugs.

(a) A laboratory synthesis of acetanilide from benzene is outlined below.



Give the reagents for each step and the conditions for Step **1** and Step **2**.

(5)

Step **1** ……………………………………………………………………………

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Step **2** ……………………………………………………………………………

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Step **3** ……………………………………………………………………………

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(b) The mass spectrum of acetanilide contains peaks at *m* / *e* = 43, *m* / *e* = 77 and *m* / *e* = 135.

(i) Give the **molecular formulae** of the species that produce the peaks at *m* / *e* = 135 and *m* / *e* = 77.

(2)

(ii) Give the **structure** of the species responsible for the peak at *m* / *e* = 43.

(1)

(c) Use your Data Booklet to suggest the wavenumber range of **two** peaks that would be present in the infrared spectrum of acetanilide but not in the infrared spectrum of aniline. Identify the bond stretches responsible for each of your chosen peaks.

(2)

(Total for Question 21 = 10 marks)

22 A volatile organic compound **X** has the percentage by mass composition:

C = 61.0%; H = 15.3%; N = 23.7%.

0.105 g of **X** was vaporised and the volume of dry air displaced measured. After adjustment to room temperature and pressure, the volume of air displaced was 42.7 cm^3.

(a) Calculate the empirical formula of **X**. You **must** show your working.

(3)

(b) Calculate the molar mass of **X** and hence deduce its molecular formula. You **must** show your working.

Molar volume of gas at room temperature and pressure = 24.0 $dm^3\ mol^{-1}$

(2)

(c) Draw two of the possible structures for **X**.

(2)

(d) The low resolution proton nmr spectrum of **X** has three peaks of relative area 6:2:1. Identify the structure of **X** and explain how your structure is consistent with the nmr spectrum.

(2)

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(Total for Question 22 = 9 marks)

TOTAL FOR SECTION B = 50 MARKS

SECTION C

Answer ALL the questions. Write your answers in the spaces provided.

23 The importance of the element copper ($Z = 29$) is due to its limited chemical reactivity and high thermal and electrical conductivity. Copper compounds have significant biological activity. Like silver and gold, copper can occur in nature as the pure element, although it is mostly obtained from one of the minerals that contain copper compounds.

The physical properties of copper have resulted in its widespread use in electrical wiring and in plumbing. Due to its cost and relative softness, the use of pure copper in coinage has largely been superseded by alloys, some of which contain no copper at all.

Copper is placed in the d-block of the Periodic Table and forms compounds with two stable oxidation states: copper(I), which resembles silver(I), and copper(II). The characteristics of copper(II) lead to the classification of copper as a transition element. Both copper(I) and copper(II) form a range of complex ions; copper(I) complexes are colourless but copper(II) complexes are coloured, often blue.

(a) (i) Complete the electronic structures of Cu, Cu^+ and Cu^{2+}, using the 'electrons-in-boxes' notation.

(2)

		3d					4s
Cu	(Ar)						
Cu^+	(Ar)						
Cu^{2+}	(Ar)						

(ii) Explain why copper is classified as a d-block element.

(1)

(iii) Explain why the electronic structure of Cu^{2+} leads to copper being classified as a transition element.

(1)

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(b) Anhydrous copper(II) sulfate is a white crystalline solid which dissolves in water to form a solution that has a pale blue colour.

(i) Explain fully why it becomes coloured when it is dissolved in water.

(5)

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(ii) Explain why anhydrous copper(II) sulfate has no colour.

(1)

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(c) The percentage of copper in a piece of copper tubing was determined by a titration method. The tubing was weighed, dissolved in concentrated nitric acid and the solution with all the washings transferred to a 250.0 cm^3 volumetric flask. The pH of the solution was adjusted before it was made up to the mark with deionised water and mixed thoroughly. 25.0 cm^3 portions of this solution were titrated with a solution of edta until concordant results were obtained. The equation for the reaction in the titration is

$$[Cu(H_2O)_6]^{2+} + edta^{4-} \rightarrow [Cu(edta)]^{2-} + 6H_2O$$

The results of the experiment are summarised in the table.

Measurement	Value
Mass of tubing / g	3.63
Concentration of edta solution / mol dm^{-3}	0.205
Mean titre / cm^3	27.50

(i) Suggest what might be added to the solution to adjust the pH.

(1)

....

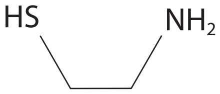
(ii) Calculate the percentage by mass of copper in the tubing.

(3)

(iii) Copper coins are often made using alloys of copper and nickel. Suggest why titration with edta is **not** a suitable method of measuring the amount of copper in such coins.

(1)

(d) Cysteamine is naturally present in human body cells and is the product of the metabolism of the amino acid L-cysteine.
The structure of cysteamine is



Cysteamine forms complexes with Cu^+, in which it is a monodentate ligand, and with Cu^{2+}, in which it is bidentate. It has been suggested that the copper(I) complexes of cysteamine might be used in the treatment of deep cancers.

(i) Explain, by reference to cysteamine, the meaning of 'bidentate'.

(2)

(ii) Draw a diagram showing how **one** molecule of cysteamine complexes with a Cu^{2+} ion.

(1)

*(iii) Use your knowledge of the shape of copper(I) complexes to suggest why cysteamine does **not** act as a bidentate ligand with Cu^+.

(2)

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(Total for Question 23 = 20 marks)

TOTAL FOR SECTION C = 20 MARKS
TOTAL FOR PAPER = 90 MARKS

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The Periodic Table of Elements

Key

relative atomic mass
atomic symbol
name
atomic (proton) number

1	2											3	4	5	6	7	0 (8)
(1)	*(2)*	*(3)*	*(4)*	*(5)*	*(6)*	*(7)*	*(8)*	*(9)*	*(10)*	*(11)*	*(12)*	*(13)*	*(14)*	*(15)*	*(16)*	*(17)*	*(18)*
							1.0 **H** hydrogen 1										4.0 **He** helium 2
6.9 **Li** lithium 3	9.0 **Be** beryllium 4											10.8 **B** boron 5	12.0 **C** carbon 6	14.0 **N** nitrogen 7	16.0 **O** oxygen 8	19.0 **F** fluorine 9	20.2 **Ne** neon 10
23.0 **Na** sodium 11	24.3 **Mg** magnesium 12											27.0 **Al** aluminium 13	28.1 **Si** silicon 14	31.0 **P** phosphorus 15	32.1 **S** sulfur 16	35.5 **Cl** chlorine 17	39.9 **Ar** argon 18
39.1 **K** potassium 19	40.1 **Ca** calcium 20	45.0 **Sc** scandium 21	47.9 **Ti** titanium 22	50.9 **V** vanadium 23	52.0 **Cr** chromium 24	54.9 **Mn** manganese 25	55.8 **Fe** iron 26	58.9 **Co** cobalt 27	58.7 **Ni** nickel 28	63.5 **Cu** copper 29	65.4 **Zn** zinc 30	69.7 **Ga** gallium 31	72.6 **Ge** germanium 32	74.9 **As** arsenic 33	79.0 **Se** selenium 34	79.9 **Br** bromine 35	83.8 **Kr** krypton 36
85.5 **Rb** rubidium 37	87.6 **Sr** strontium 38	88.9 **Y** yttrium 39	91.2 **Zr** zirconium 40	92.9 **Nb** niobium 41	95.9 **Mo** molybdenum 42	[98] **Tc** technetium 43	101.1 **Ru** ruthenium 44	102.9 **Rh** rhodium 45	106.4 **Pd** palladium 46	107.9 **Ag** silver 47	112.4 **Cd** cadmium 48	114.8 **In** indium 49	118.7 **Sn** tin 50	121.8 **Sb** antimony 51	127.6 **Te** tellurium 52	126.9 **I** iodine 53	131.3 **Xe** xenon 54
132.9 **Cs** caesium 55	137.3 **Ba** barium 56	138.9 **La*** lanthanum 57	178.5 **Hf** hafnium 72	180.9 **Ta** tantalum 73	183.8 **W** tungsten 74	186.2 **Re** rhenium 75	190.2 **Os** osmium 76	192.2 **Ir** iridium 77	195.1 **Pt** platinum 78	197.0 **Au** gold 79	200.6 **Hg** mercury 80	204.4 **Tl** thallium 81	207.2 **Pb** lead 82	209.0 **Bi** bismuth 83	[209] **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							

Elements with atomic numbers 112-116 have been reported but not fully authenticated

* Lanthanide series	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	163 **Dy** dysprosium 66	165 **Ho** holmium 67	167 **Er** erbium 68	169 **Tm** thulium 69	173 **Yb** ytterbium 70	175 **Lu** lutetium 71
* Actinide series	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