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 20 January 2015 – Afternoon
Time: 1 hour 40 minutes

Paper Reference
WCH05/01

You must have: Data Booklet

Candidates may use a calculator.

Total Marks

Instructions

- Use **black** ink or 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.
- Keep an eye on the time.
- Try to answer every question.
- Check your answers if you have time at the end.

Turn over ▶

P45045A

5/5/5/5/2/1/

P 4 5 0 4 5 A 0 1 2 8

PEARSON

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 Manganese forms a complex with carbon monoxide, with the formula $Mn_2(CO)_{10}$. The oxidation number of manganese in $Mn_2(CO)_{10}$ is

☒ **A** 0

☒ **B** +2

☒ **C** +5

☒ **D** +10

(Total for Question 1 = 1 mark)

---

2 The reduction of nitrate(V) ions by aluminium in alkaline conditions may be represented by the equation below.

$$x\ NO_3^- + y\ Al + a\ OH^- + b\ H_2O \rightarrow x\ NH_3 + y\ Al(OH)_4^-$$

From the change in the oxidation numbers of nitrogen and aluminium, it can be deduced that the values of x and y are

☒ **A** x = 3 and y = 2

☒ **B** x = 2 and y = 3

☒ **C** x = 8 and y = 3

☒ **D** x = 3 and y = 8

(Total for Question 2 = 1 mark)

---

3 Which of the following is correct for the standard hydrogen electrode?

☒ **A** The temperature is kept at 273 K.

☒ **B** Sulfuric acid with a concentration of 0.5 mol dm^{-3} is used.

☒ **C** The metal electrode is copper foil.

☒ **D** The hydrogen pressure is 1 atmosphere.

(Total for Question 3 = 1 mark)

---

4 The standard electrode potentials of two electrode systems are given below.

$$Cr^{3+}(aq) + 3e^- \rightleftharpoons Cr(s) \qquad E^{\ominus} = -0.74\ V$$

$$Cd^{2+}(aq) + 2e^- \rightleftharpoons Cd(s) \qquad E^{\ominus} = -0.40\ V$$

Calculate the $E^{\ominus}_{cell}$ for the reaction

$$2Cr(s) + 3Cd^{2+}(aq) \rightarrow 3Cd(s) + 2Cr^{3+}(aq)$$

☒ **A** −0.34 V

☒ **B** +0.34 V

☒ **C** −0.28 V

☒ **D** +0.28 V

(Total for Question 4 = 1 mark)

5 The calculated $E^{\ominus}$ for a reaction is positive but no reaction occurs when the reagents are mixed under standard conditions. It can be deduced that

☒ **A** the reaction is thermodynamically feasible and the reaction mixture is kinetically stable.

☒ **B** the reaction is thermodynamically feasible and the reaction mixture is kinetically unstable.

☒ **C** the reaction mixture is thermodynamically and kinetically stable.

☒ **D** the reaction mixture is thermodynamically stable and kinetically unstable.

(Total for Question 5 = 1 mark)

6 The electronic configuration of the iron(II) ion, Fe^{2+}, is

		3d					4s
☒ **A**	[Ar]	↑↓	↑	↑			↑↓
☒ **B**	[Ar]	↑	↑	↑	↑		↑↓
☒ **C**	[Ar]	↑	↑	↑	↑	↑	↑
☒ **D**	[Ar]	↑↓	↑	↑	↑	↑	

(Total for Question 6 = 1 mark)

7 Transition metal compounds often have catalytic properties. The **best** explanation for this is that

☒ **A** transition metal compounds usually have a much larger surface area than other metal compounds.

☒ **B** transition metal ions readily promote electrons to higher energy levels by absorbing electromagnetic radiation in the visible region.

☒ **C** relatively small amounts of energy are required to change the oxidation state of a transition metal.

☒ **D** the ionization energies of transition metals are much lower than those of other metals.

(Total for Question 7 = 1 mark)

8 What are the shapes of the dichlorocuprate(I) ion, $CuCl_2^-$, and the tetrachlorochromate(III) ion, $CrCl_4^-$?

	$CuCl_2^-$	$CrCl_4^-$
☒ **A**	V shaped	tetrahedral
☒ **B**	linear	tetrahedral
☒ **C**	V shaped	square planar
☒ **D**	linear	square planar

(Total for Question 8 = 1 mark)

9 When dilute aqueous ammonia is added to an aqueous solution of a metal ion, a green precipitate is formed which dissolves slowly in excess ammonia to form a green solution. What is the metal ion present in the original solution?

☒ **A** Ni^{2+}

☒ **B** Fe^{2+}

☒ **C** Cu^{2+}

☒ **D** Cr^{3+}

(Total for Question 9 = 1 mark)

10 The iron(II) ion forms complexes with monodentate ethanoate ions and bidentate ethanedioate ions. The complexes with ethanedioate ions are more stable. What is the best explanation for this?

☒ **A** Ethanedioate ions form stronger bonds than ethanoate ions with iron(II) ions.

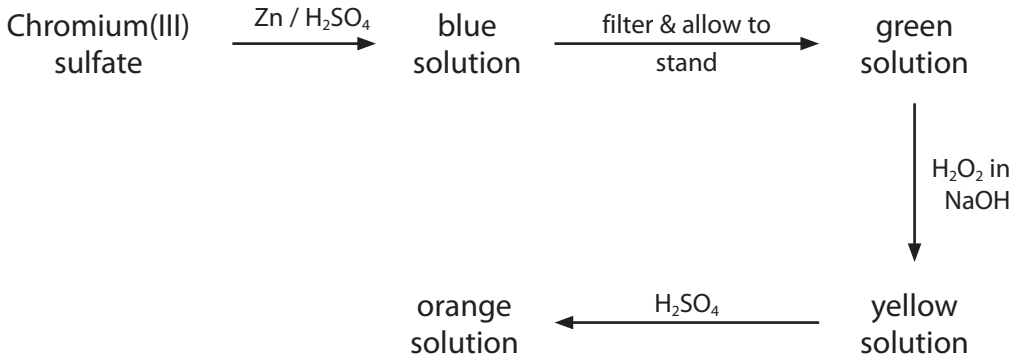
☒ **B** Ethanedioic acid is a stronger acid than ethanoic acid.

☒ **C** The formation of the ethanedioate complex produces more particles in solution.

☒ **D** Ethanedioic acid forms stronger hydrogen bonds than ethanoic acid.

(Total for Question 10 = 1 mark)

11 The diagram below summarises a sequence of reactions involving chromium compounds.



How many different oxidation states of chromium are involved in this sequence?

☒ **A** 2

☒ **B** 3

☒ **C** 4

☒ **D** 5

(Total for Question 11 = 1 mark)

12 All the bond angles in the benzene molecule are 120°. Which of the following provides the best evidence for this?

- ☒ **A** Valence shell electron pair repulsion theory
- ☒ **B** X-ray diffraction
- ☒ **C** High resolution nuclear magnetic resonance
- ☒ **D** Infrared spectroscopy

(Total for Question 12 = 1 mark)

13 Benzene burns with a very smoky flame. This is evidence for the extent to which the benzene molecule is

- ☒ **A** delocalised.
- ☒ **B** stabilised.
- ☒ **C** unsaturated.
- ☒ **D** activated.

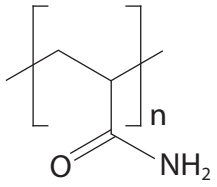
(Total for Question 13 = 1 mark)

14 When bromine water is added to benzene, no reaction occurs. However, when bromine water is added to an aqueous solution of phenol, a white precipitate with an antiseptic smell is formed. What is the explanation for this difference?

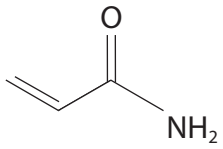
- ☒ **A** Bromine is a powerful electrophile.
- ☒ **B** The benzene ring in phenol is activated.
- ☒ **C** The reaction of phenol with bromine is similar to the iodoform reaction.
- ☒ **D** The OH group in phenol is much more acidic than that in ethanol.

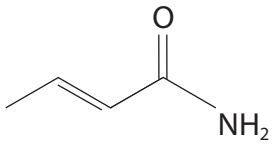
(Total for Question 14 = 1 mark)

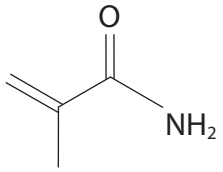
15 The repeat unit of a polymer is shown below.

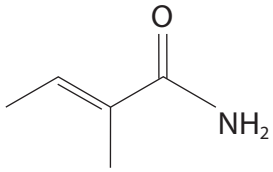


What is the structure of the monomer?

☒ **A** 

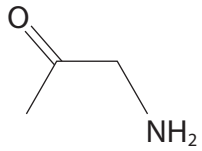
☒ **B** 

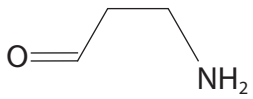
☒ **C** 

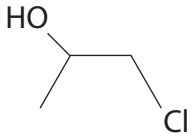
☒ **D** 

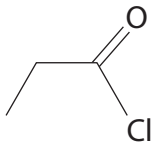
(Total for Question 15 = 1 mark)

16 An organic compound reacts with dilute sulfuric acid to form a colourless solution which produces a white solid on evaporation. It also gives a pale yellow solid on reaction with iodine in sodium hydroxide. The compound is

☒ **A** 

☒ **B** 

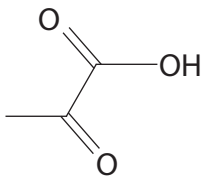
☒ **C** 

☒ **D** 

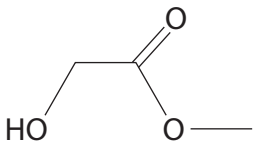
(Total for Question 16 = 1 mark)

17 An organic compound produces steamy fumes with phosphorus(V) chloride but does **not** react with 2,4-dinitrophenylhydrazine. The compound is

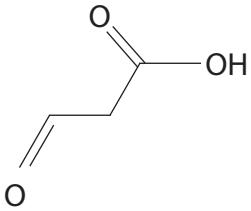
☒ **A**



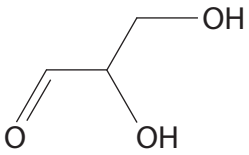
☒ **B**



☒ **C**



☒ **D**



(Total for Question 17 = 1 mark)

18 In the mass spectrum of an organic compound, the molecular ion occurs at *m/e* = 86.

Which of the following could be the **empirical formula** of the compound?

- ☒ **A** C_6H_{14}
- ☒ **B** $C_5H_{10}N$
- ☒ **C** $C_5H_{12}O$
- ☒ **D** C_5H_7F

(Total for Question 18 = 1 mark)

19 The high resolution proton nmr spectrum of propan-1-ol, $CH_3CH_2CH_2OH$, contains four peaks. What is the splitting pattern of the four peaks?

[Where 1 represents a singlet, 2 represents a doublet, etc.]

- ☒ **A** 3 2 2 1
- ☒ **B** 3 4 3 1
- ☒ **C** 3 6 3 1
- ☒ **D** 3 6 4 2

(Total for Question 19 = 1 mark)

20 Which of the following techniques would be the **least** effective as a control measure to reduce risk when heating a flammable liquid?

The use of

- ☒ **A** an electrical heater.
- ☒ **B** a fume cupboard.
- ☒ **C** a small quantity of the liquid.
- ☒ **D** a reflux condenser.

(Total for Question 20 = 1 mark)

TOTAL FOR SECTION A = 20 MARKS

SECTION B

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

21 Brass is an alloy of copper and zinc, often with traces of other metals. The copper content of brass can be determined by dissolving the metal in concentrated nitric acid and measuring, by titration, the concentration of the copper(II) ions formed.

(a) When concentrated nitric acid reacts with copper, the copper dissolves and one of the products is dinitrogen tetroxide, N_2O_4.

(i) Use the data on page 15 of the Data Booklet to write the ionic half-equations for this reaction of copper with concentrated nitric acid. State symbols are not required.

(2)

(ii) Write the overall equation for the reaction of copper with concentrated nitric acid and calculate $E^{\ominus}_{cell}$ for the reaction. State symbols are not required.

(2)

(iii) State **one** observation that you would expect to make when copper dissolves in concentrated nitric acid.

(1)

.....

.....

(b) 1.35 g of a sample of rivet brass was dissolved in concentrated nitric acid. The resulting mixture was boiled and then allowed to cool before being transferred to a volumetric flask. The solution was made up to 250 cm^3 with distilled water and mixed thoroughly.

Excess potassium iodide solution was added to 25.0 cm^3 samples of this solution, and the liberated iodine determined by titration with a solution of sodium thiosulfate of concentration 0.0505 mol dm^{-3}. The mean titre was 26.35 cm^3.

(i) Write the **ionic** equation for the reaction of the copper(II) ions with iodide ions to form copper(I) iodide and iodine. State symbols are not required.

(1)

(ii) Write the **ionic** equation for the reaction of iodine with thiosulfate ions. State symbols are not required.

(1)

(iii) Use the equations in (b)(i) and (b)(ii) to show that the amount of copper(II) ions is equal to the amount of thiosulfate ions.

(1)

.....

.....

.....

(iv) Calculate the percentage by mass of copper in the sample of rivet brass.

(4)

(c) (i) The reaction mixture in (b) was boiled before being transferred to a volumetric flask. This removed dissolved nitrogen oxides which would otherwise oxidize the iodide ions.

Explain the effect that omitting this step would have on the value obtained for the percentage of copper.

(2)

(ii) Any nitrogen oxides that remain after boiling can be removed by the addition of urea. When this was done, the mean titre changed by 0.25 cm^3.
By considering the uncertainties in the various measurements, explain whether the addition of urea is worthwhile.

(2)

(d) Both copper and zinc are d-block elements, but only copper is a transition metal.

(i) Explain the term **d-block element**.

(1)

(ii) Explain why copper is classed as a transition metal but zinc is not.

(1)

*(iii) Explain why the complexes of copper(II) ions are coloured.

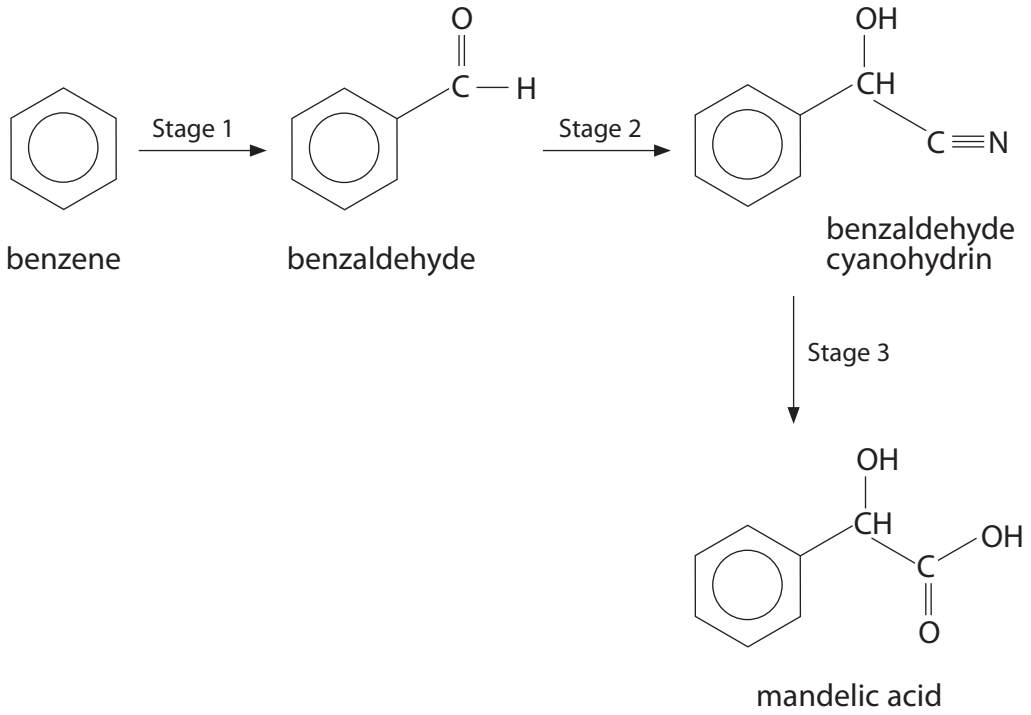
(4)

(iv) Although zinc is not a transition metal, zinc(II) ions form complexes. Explain why these complexes are colourless.

(1)

(Total for Question 21 = 23 marks)

22 Mandelic acid, 2-hydroxy-2-phenylethanoic acid, has a long history of medical use as an antibiotic and as a component of some cosmetic face creams. It was first obtained from an extract of bitter almonds and 'Mandel' is the German word for almond. Mandelic acid can be synthesized from benzene in the sequence shown below.



(a) (i) Use your knowledge of electrophilic substitution to suggest the identity of the electrophile in Stage 1 of the synthesis.

(1)

.....

(ii) Write the mechanism for the electrophilic substitution in Stage 1, using the electrophile that you have given in (a)(i).

(3)

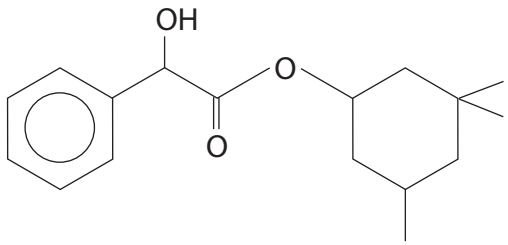
(iii) State the reagents and conditions required for Stage 2. You may assume that the reaction is carried out at a suitable temperature.

(2)

(iv) State the reagent (or reagents) required for Stage 3.

(1)

(b) Cyclandelate is a vasodilator (causes blood vessels to dilate) used in the treatment of arteriosclerosis (hardening of artery walls). The structure of cyclandelate is shown below.



(i) Suggest a single stage synthesis of cyclandelate from mandelic acid. Draw the skeletal formula of the organic compound that would be required and state any essential reagents and conditions.

(3)

(ii) Suggest a disadvantage of using the synthesis that you have suggested in (b)(i) for the large scale manufacture of cyclandelate.

(1)

(iii) An alternative **two** stage synthesis of cyclandelate was proposed. This involved reacting mandelic acid with phosphorus(V) chloride. Explain why this suggestion is unsatisfactory.

(1)

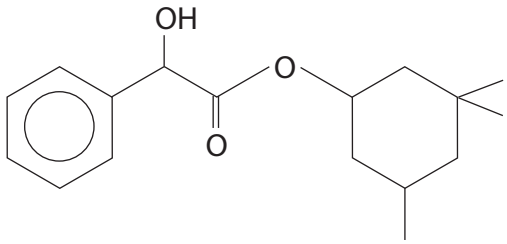
.....

.....

(c) Cyclandelate has **three** asymmetric carbon atoms.

(i) Circle these three asymmetric carbon atoms on the structure below.

(2)



(ii) Explain the possible problem that the presence of asymmetric carbon atoms might cause with the medical applications of cyclandelate.

(2)

.....

.....

.....

.....

.....

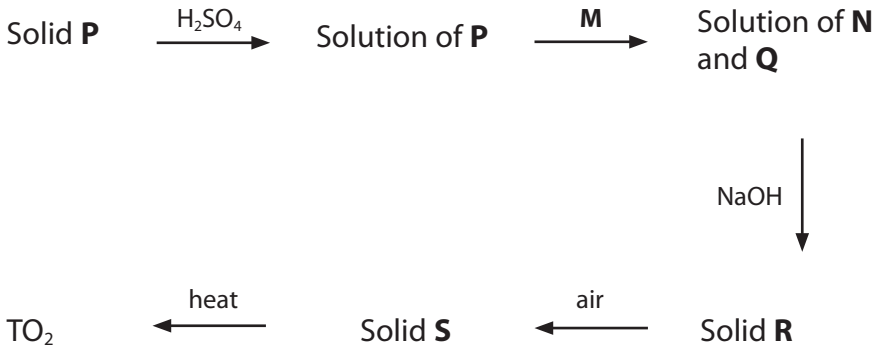
(Total for Question 22 = 16 marks)

23 Compound **P** is a very dark purple solid which gives a lilac flame in a flame test.

A sample of **P** was dissolved in dilute sulfuric acid to form a purple solution. A gaseous hydrocarbon, **M**, was bubbled into this solution which rapidly formed a colourless solution, containing an organic compound, **N**, and an inorganic compound, **Q**.

When aqueous sodium hydroxide was added to **Q**, a very pale brown precipitate, **R**, formed. **R** darkened on standing in air to form a dark brown solid, **S**, which was filtered off and heated to form a dark brown metal oxide, TO_2.

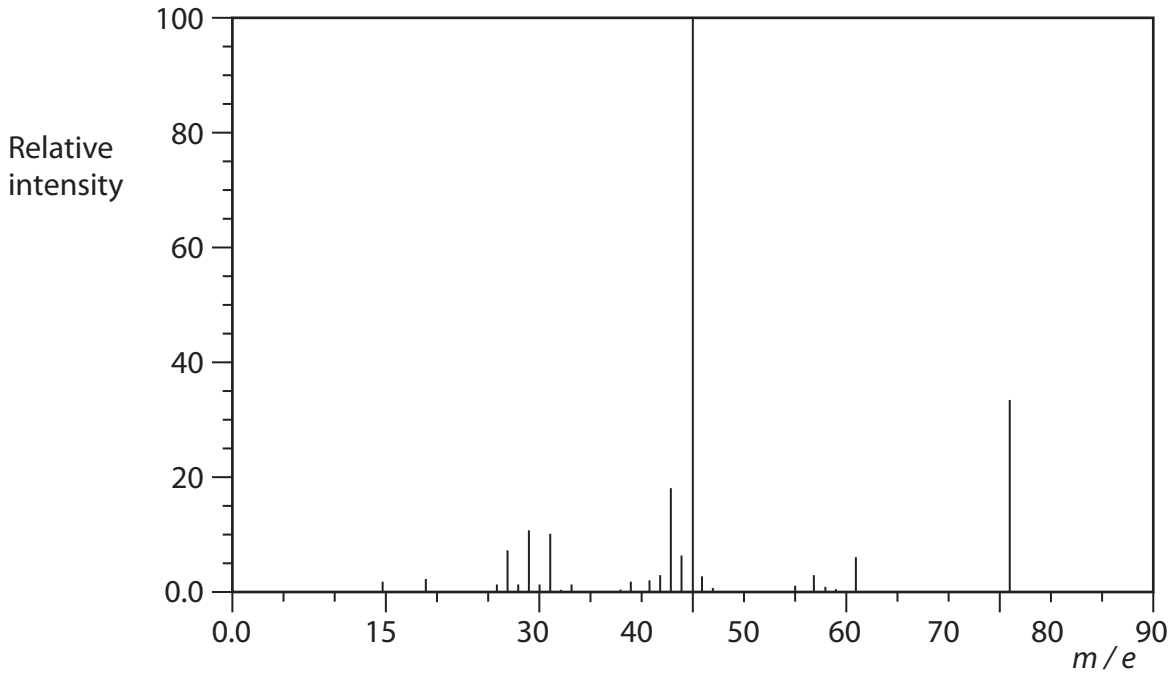
The reaction sequence is summarised below.



(a) Analysis of TO_2 showed that it contained 36.82% by mass of oxygen. Calculate the molar mass of the metal, T, and hence identify T. You **must** show your working.

(3)

(b) The mass spectrum of the organic product **N**, formed when **M** is reacted with the solution of **P**, is shown below.



(i) Label the molecular ion on the mass spectrum and deduce the molar mass of **N**.

(1)

.....

(ii) Identify, by name or formula, **M** and **N**.

(2)

M	
N	

(c) (i) Write an **ionic** equation for the formation of the very pale brown precipitate, **R**.
Include state symbols in your answer.

(2)

(ii) Suggest an equation for the conversion of the dark brown solid, **S**, to TO_2.
State symbols are not required.

(2)

(d) Write the formula of the cation in **P** and hence give the formula of compound **P**.

(2)

.....

.....

.....

(Total for Question 23 = 12 marks)

TOTAL FOR SECTION B = 51 MARKS

SECTION C

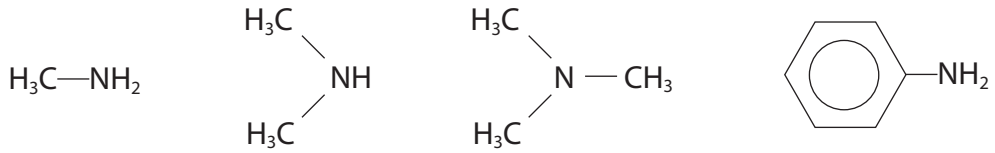
Answer ALL the questions. Write your answers in the spaces provided.

24

Organic Nitrogen Chemistry

Organic compounds that contain nitrogen are vital to life, but are also important in everyday applications of chemistry.

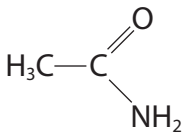
The simplest organic nitrogen compounds are amines, which may be regarded as derivatives of ammonia in which one or more of the hydrogen atoms of ammonia have been replaced by an alkyl group or an aryl group. Some simple amines are shown below.



methylamine dimethylamine trimethylamine phenylamine (aniline)

Amines with one alkyl group are called primary, with two alkyl groups secondary and with three alkyl groups tertiary. Because of the presence of nitrogen, the physical and chemical properties of alkyl amines are similar to those of ammonia but the similarities are less marked with phenylamine.

Amides are carboxylic acid derivatives which have a carbonyl group adjacent to an amine group. The simplest amide is ethanamide:



ethanamide

Because the two groups are adjacent, the chemical properties of amides are different from those of amines.

Amino acids are compounds with an amine group and a carboxylic acid group. The presence of these two functional groups gives amino acids properties that are also different from those of amines. The great significance of the amino acids is their ability to form polymers called polypeptides, leading to the formation of proteins, the building blocks of life. To form polypeptides, amino acids are joined by the amide group, sometimes called the peptide link.

(a) Methylamine boils at 267 K and dissolves in water to form an alkaline solution.

(i) Explain why methylamine has a higher boiling temperature than ammonia. A detailed description of the forces involved is **not** required.

(2)

*(ii) Explain why primary amines are soluble in water but their solubility decreases as molar mass increases.

(3)

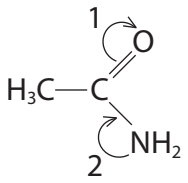
(iii) Write an equation for the reaction of methylamine with water to produce an alkaline solution. State symbols are not required.

(1)

(iv) Suggest why dimethylamine is more basic than methylamine and why both are **much** more basic than phenylamine.

(3)

(b) The interaction of the carbonyl group and the amine group in ethanamide may be shown by the following diagram.



(i) Explain what each of the two arrows represents.

(2)

Arrow 1 .....

.....

Arrow 2 .....

.....

(ii) Draw a diagram showing the ethanamide molecule if the changes indicated by the arrows go to completion.

(1)

(iii) Suggest why the carbonyl group in an amide does not react with 2,4-dinitrophenylhydrazine.

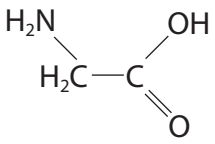
(1)

.....

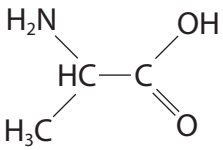
.....

.....

(c) The structures of the two simplest amino acids are shown below.



glycine



alanine

(i) Draw the structures of the **two** compounds, called dipeptides, that can be formed when glycine and alanine combine. Any double bonds **must** be displayed.

(2)

(ii) In practice, glycine and alanine do not combine readily. Suggest a reason for this.

(1)

*(iii) Describe in outline how a mixture of amino acids can be separated **and** identified using thin layer chromatography. You may assume that a suitable solvent is available.

(3)

(Total for Question 24 = 19 marks)

TOTAL FOR SECTION C = 19 MARKS
TOTAL FOR PAPER = 90 MARKS

The Periodic Table of Elements

1	2											3	4	5	6	7	0 (8) (18)
							1.0 H hydrogen 1										4.0 He helium 2
(1)	(2)		Key: relative atomic mass / atomic symbol / name / atomic (proton) number									(13)	(14)	(15)	(16)	(17)	
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	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(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