Write your name here

Surname	Other names

Pearson Edexcel GCE

Centre Number | Candidate Number

Chemistry

Advanced

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

Tuesday 17 June 2014 – Afternoon
Time: 1 hour 40 minutes

Paper Reference **6CH05/01R**

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

P 4 2 9 8 9 R 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 In which of the following ions does the metal have an oxidation number of +2?

☒ **A** MnO_4^{2-}

☒ **B** VO^{2+}

☒ **C** $[Fe(CN)_6]^{4-}$

☒ **D** $[CrCl_2(H_2O)_4]^+$

(Total for Question 1 = 1 mark)

2 Sulfur dioxide reacts with hydrogen sulfide to form water and sulfur. By considering the changes in the oxidation numbers of sulfur, it can be deduced that, in this reaction

☒ **A** 1 mol of sulfur dioxide oxidizes 2 mol of hydrogen sulfide.

☒ **B** 1 mol of sulfur dioxide reduces 2 mol of hydrogen sulfide.

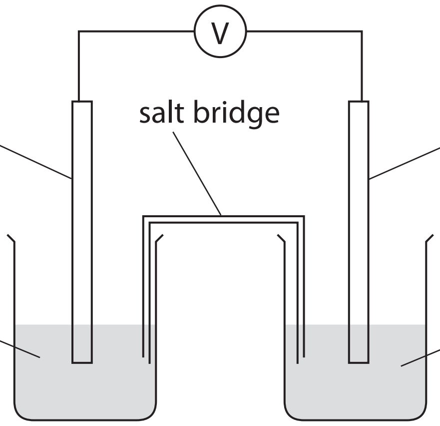
☒ **C** 2 mol of sulfur dioxide oxidizes 1 mol of hydrogen sulfide.

☒ **D** 2 mol of sulfur dioxide reduces 1 mol of hydrogen sulfide.

(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 diagram below shows a cell set up between a standard copper metal / copper(II) ion electrode and a silver metal / silver(I) ion electrode in which the silver ion concentration is 0.1 mol dm^{-3}.



At 298 K, the emf of this cell was +0.40 V. The electrode potential of the copper metal / copper(II) ion electrode is +0.34 V. What is the electrode potential of this silver metal / silver(I) ion electrode?

☒ **A** –0.74 V

☒ **B** –0.06 V

☒ **C** +0.06 V

☒ **D** +0.74 V

(Total for Question 3 = 1 mark)

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4 For the reaction

$$Zn(s) + Cu^{2+}(aq) \rightarrow Cu(s) + Zn^{2+}(aq)$$

$E^{\ominus}_{cell}$ is positive. From this it can be deduced that, for this reaction,

☒ **A** ΔS_{total} and $\ln K$ are positive.

☒ **B** ΔS_{total} and $\ln K$ are negative.

☒ **C** ΔS_{total} is positive and $\ln K$ is negative.

☒ **D** ΔS_{total} is negative and $\ln K$ is positive.

(Total for Question 4 = 1 mark)

5 Sodium thiosulfate was used to determine the concentration of iodine by titration.

(a) The sodium thiosulfate solution was prepared by dissolving 4.5 g of sodium thiosulfate in water and making the solution up to 250 cm^3 in a volumetric flask. The volumetric flask is accurate to ± 0.3 cm^3 so, to match this accuracy, the mass of the sodium thiosulfate should be accurate to at least

(1)

☒ **A** ± 0.5 g

☒ **B** ± 0.05 g

☒ **C** ± 0.005 g

☒ **D** ± 0.0005 g

(b) With the sodium thiosulfate in the burette, what is the colour of the solution in the conical flask at the end-point of the reaction?

(1)

☒ **A** Blue-black

☒ **B** Colourless

☒ **C** Red-brown

☒ **D** Yellow

(Total for Question 5 = 2 marks)

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6 In a hydrogen-oxygen fuel cell, hydrogen is

☒ **A** oxidized at the anode.

☒ **B** oxidized at the cathode.

☒ **C** reduced at the anode.

☒ **D** reduced at the cathode.

(Total for Question 6 = 1 mark)

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

7 The electronic configuration of iron is $[Ar]3d^6 4s^2$. What is the electronic configuration of the iron(II) ion, Fe^{2+}?

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

(Total for Question 7 = 1 mark)

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8 Chromium has the electronic configuration $[Ar]3d^5 4s^1$. Which of the following compounds is **unlikely** to exist?

☒ **A** K_3CrO_4

☒ **B** CrO_2Cl_2

☒ **C** $KCrO_2Cl$

☒ **D** $KCrO_4$

(Total for Question 8 = 1 mark)

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9 The shapes of the complexes $[CrCl_4]^-$ and $[CuCl_2]^-$ are

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

(Total for Question 9 = 1 mark)

10 When EDTA is added to $[Cu(NH_3)_4]^{2+}$ in aqueous solution, the copper(II)-EDTA complex, $[Cu(EDTA)]^{2-}$, predominates in the resulting solution.

This is **best** explained by the fact that when $[Cu(EDTA)]^{2-}$ is formed from $[Cu(NH_3)_4]^{2+}$

☒ **A** there are much stronger bonds between the ligands and the copper(II) ion.

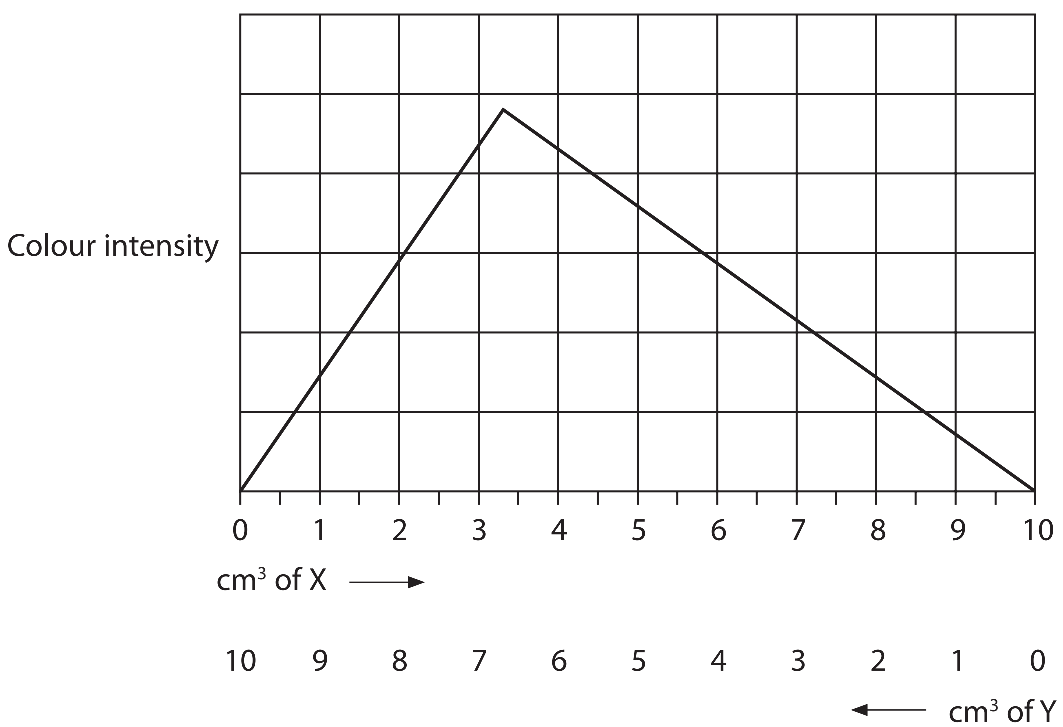
☒ **B** the reaction has a low activation energy.

☒ **C** the reaction is exothermic.

☒ **D** the total number of particles on the right-hand side of the equation is greater than on the left.

(Total for Question 10 = 1 mark)

11 The graph below shows the variation in the colour intensity of different solutions formed by mixing a 0.05 mol dm^{-3} solution of a metal ion **X** and a 0.05 mol dm^{-3} solution of a complexing agent **Y**, in the proportions shown on the graph.



The most likely formula of the complex formed is

☒ **A** X_2Y

☒ **B** XY_2

☒ **C** XY_3

☒ **D** X_3Y

(Total for Question 11 = 1 mark)

12 When benzene reacts with fuming sulfuric acid, which species is most likely to be the electrophile?

☒ **A** H_3O^+

☒ **B** SO_3

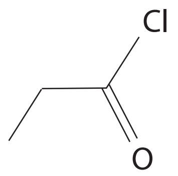
☒ **C** HSO_4^-

☒ **D** SO_4^{2-}

(Total for Question 12 = 1 mark)

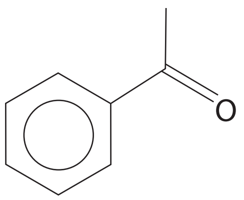
13 Benzene reacts with propanoyl chloride in the presence of a suitable catalyst.

The skeletal formula of propanoyl chloride is

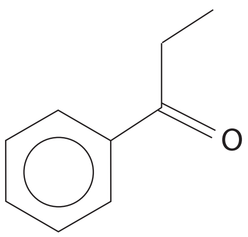


What is the organic product of this reaction?

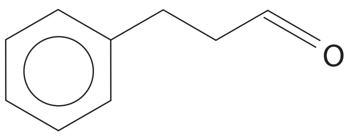
☒ **A**



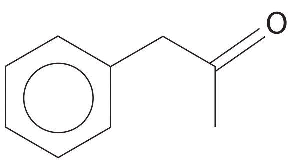
☒ **B**



☒ **C**



☒ **D**



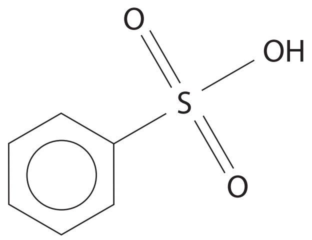
(Total for Question 13 = 1 mark)

P 4 2 9 8 9 R A 0 7 2 8

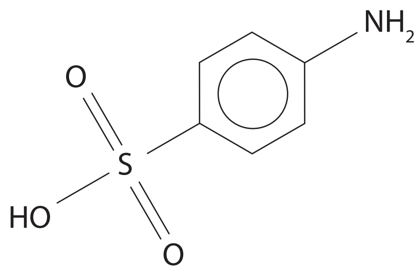
Turn over ▶

14 Excess dilute sulfuric acid is added to phenylamine. What is the product of the reaction?

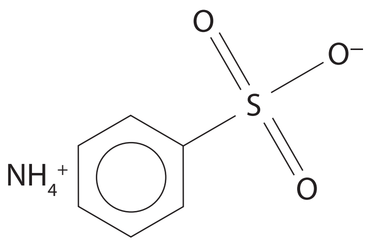
☒ **A**



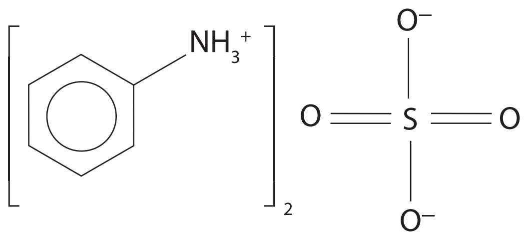
☒ **B**



☒ **C**



☒ **D**



(Total for Question 14 = 1 mark)

15 Butylamine (T_b = 77.8 °C) has a higher boiling temperature than propylamine (T_b = 47.7 °C). This is because the

☒ **A** hydrogen bonds of butylamine are stronger than the hydrogen bonds of propylamine.

☒ **B** London forces of butylamine are stronger than the hydrogen bonds of propylamine.

☒ **C** London forces of butylamine are stronger than the London forces of propylamine.

☒ **D** C—H bonds of butylamine are stronger than the C—H bonds of propylamine.

(Total for Question 15 = 1 mark)

16 Ninhydrin is used in thin-layer chromatography to help with the identification of amino acids. This is because the ninhydrin

☒ **A** reacts with amino acids to form a compound which has an intense colour.

☒ **B** reacts with amino acids to form compounds each of which has a characteristic colour.

☒ **C** increases the separation of the amino acids on the chromatogram.

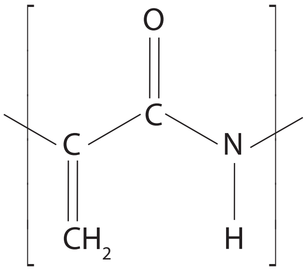
☒ **D** ensures that the mobile phase maintains a nearly constant pH for all the amino acids.

(Total for Question 16 = 1 mark)

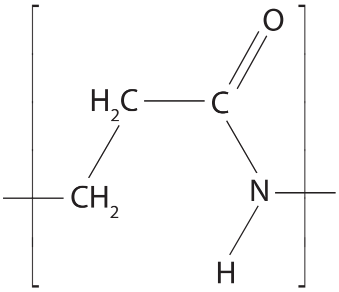
Use this space for any rough working. Anything you write in this space will gain no credit.

17 The monomer of the addition polymer poly(propenamide) is $CH_2{=}CHCONH_2$. The repeat unit of the polymer is

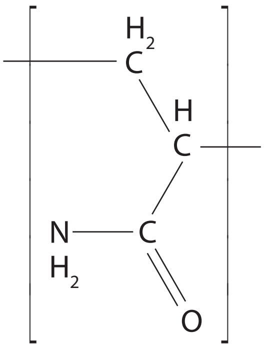
☒ **A**



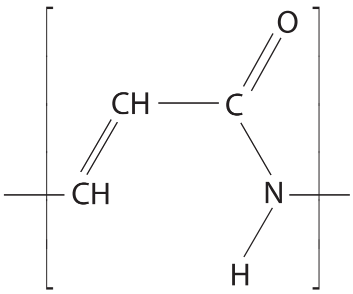
☒ **B**



☒ **C**



☒ **D**



(Total for Question 17 = 1 mark)

18 15 cm^3 of a gaseous hydrocarbon requires 90 cm^3 of oxygen for complete combustion, both volumes being measured at 15 °C and 1 atm. The formula of the hydrocarbon is

☒ **A** C_4H_6

☒ **B** C_4H_8

☒ **C** C_4H_{10}

☒ **D** impossible to calculate without knowing the molar volume of gases under these conditions.

(Total for Question 18 = 1 mark)

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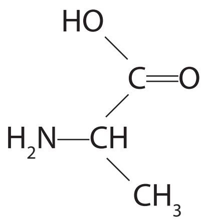
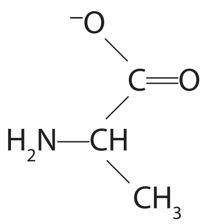
19 In an aqueous solution with a pH of 12, the amino acid alanine exists mainly as

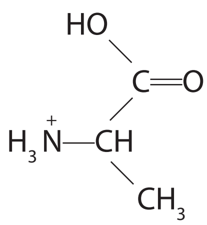
☒ **A**



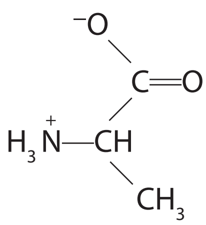
☒ **B**



☒ **C**



☒ **D**



(Total for Question 19 = 1 mark)

TOTAL FOR SECTION A = 20 MARKS

SECTION B

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

20 (a) When iron(II) sulfate is dissolved in water, the iron(II) ions are slowly oxidized to iron(III) ions by oxygen dissolved in the water.

(i) Write the two ionic half-equations for this redox reaction in **acid** conditions. State symbols are not required.

(1)

(ii) Hence write the overall ionic equation for the reaction. State symbols are not required.

(1)

(b) 6.90 g of iron(II) sulfate crystals ($FeSO_4.7H_2O$) was dissolved in distilled water and the solution made up to 250 cm^3 in a volumetric flask. After 24 hours, 25.0 cm^3 portions of this solution were pipetted into a conical flask and titrated against acidified potassium manganate(VII) solution with a concentration of 0.0195 mol dm^{-3}. The mean titre was 24.90 cm^3.

(i) Write the ionic equation showing that 1 mol of manganate(VII) ions oxidizes 5 mol of iron(II) ions in acid conditions. State symbols are not required.

(1)

(ii) What is the colour of the solution in the conical flask at the end-point of the titration?

(1)

....

*(iii) Calculate the amount of Fe^{2+} ions in 250 cm^3 of the solution after it had been left to stand for 24 hours. Hence calculate the percentage of the iron(II) ions that had been oxidized between the preparation of the solution and the titration. The molar mass of $FeSO_4 \cdot 7H_2O$ is 277.9 g mol^{-1}.

(5)

(iv) Suggest, with an explanation, the appropriate number of significant figures to give for the answer to (b)(iii).

(1)

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(c) The most stable oxidation states in iron compounds are +2 and +3, but others do exist, for example in the ferrate(VI) ion, FeO_4^{2-}. The ionic half-equation for the conversion of ferrate(VI) to iron(III) is

$$FeO_4^{2-}(aq) + 8H^+(aq) + 3e^- \rightleftharpoons Fe^{3+}(aq) + 4H_2O(l) \qquad E^\ominus = +2.20\ V$$

(i) Ferrate(VI) decomposes in neutral or acid solution, but is stable in alkali. Suggest why this is so.

(1)

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(ii) Write the equation for the disproportionation of iron(III) into iron(II) and ferrate(VI) in aqueous solution. State symbols are not required.

(2)

(iii) Use standard electrode potential values to determine the thermodynamic feasibility of this disproportionation.

(2)

(Total for Question 20 = 15 marks)

21 Chromium is a typical transition metal: it forms complexes, coloured compounds and exists in a range of stable oxidation states. Chromium and some of its compounds also show catalytic properties.

(a) Define the term **transition metal**.

(1)

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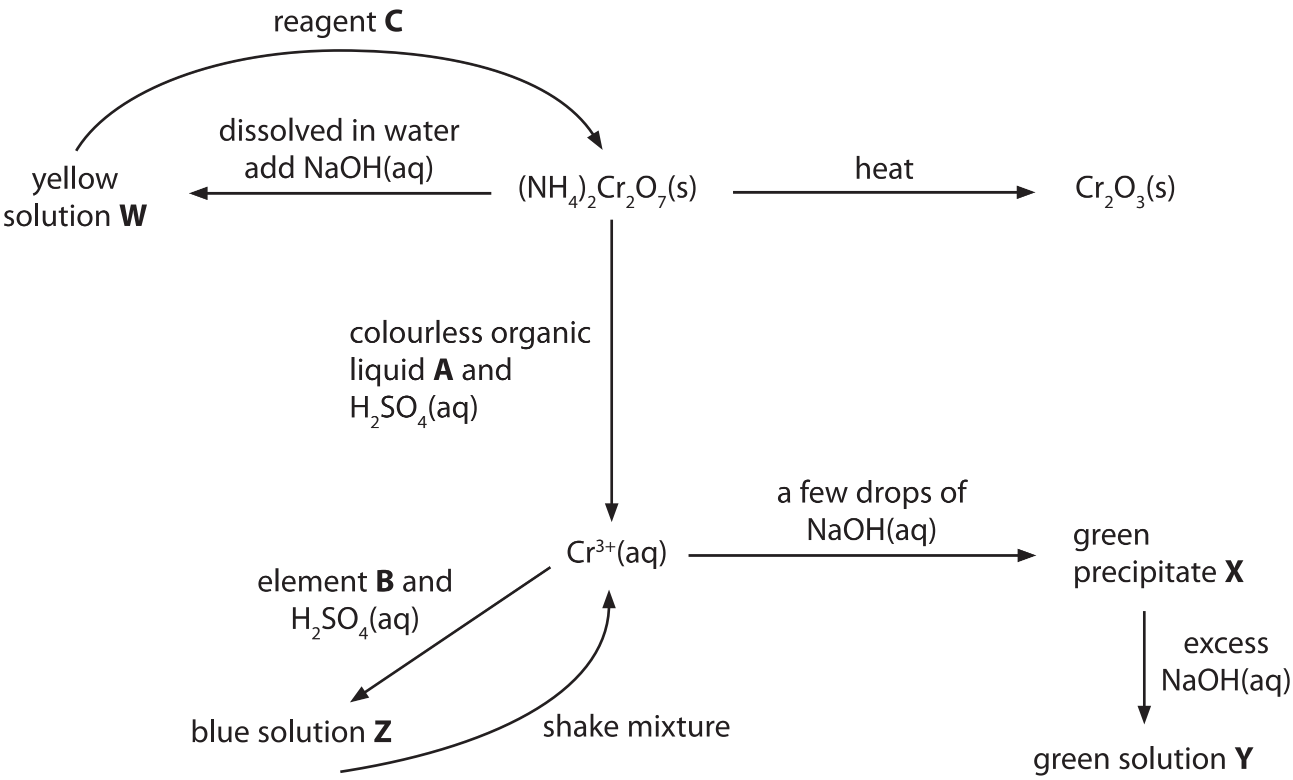
(b) The diagram below summarises some reactions of chromium compounds.



(i) Identify, by name (including the oxidation state where appropriate) or formula, the species containing **chromium** in the sequence.

(4)

W ....

X ....

Y ....

Z ....

(ii) Identify, by name or formula, suitable reagents for the sequence.

(3)

A ....

B ....

C ....

(iii) Write the ionic equation for the reaction between $(NH_4)_2Cr_2O_7$ and NaOH to form the yellow solution. State symbols are not required.

(1)

(iv) When $(NH_4)_2Cr_2O_7$ is heated, steam and nitrogen are formed as well as Cr_2O_3. Write the equation for this reaction. State symbols are not required.

Explain why this is a redox reaction, stating any changes in oxidation numbers that occur.

(3)

Equation

Explanation ....

....

....

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....

(v) Explain how shaking solution **Z** re-forms $Cr^{3+}(aq)$.

(1)

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(c) If excess aqueous ammonia is added to Cr^{3+}(aq), the ammonia acts as a ligand and the resulting green solution contains a chromium species which is different from the one found in **Y**.

(i) Explain the term 'ligand'.

(2)

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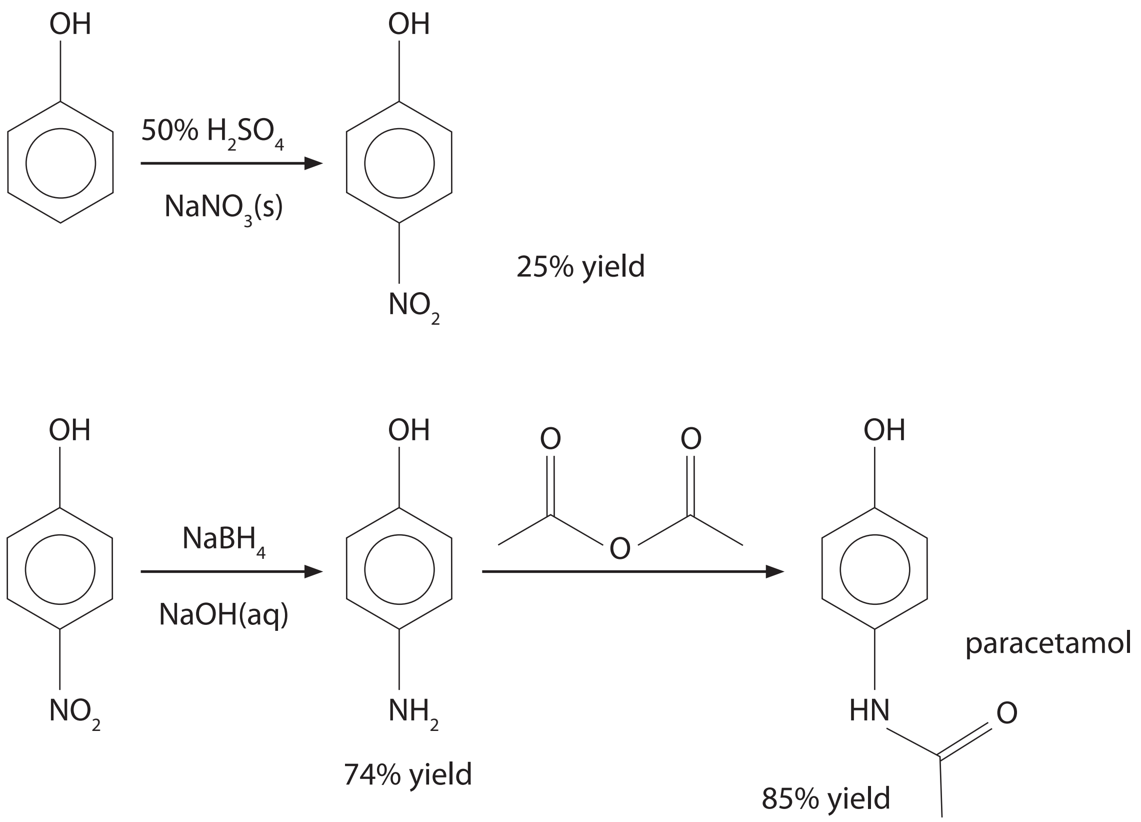
(ii) Write an equation for the reaction that occurs, showing **all** the ligands involved for both the chromium species in the reaction. State symbols are not required.

(2)

(Total for Question 21 = 17 marks)

22 Paracetamol is a mild painkiller which also reduces the temperature of patients with fever, actions known as analgesic and antipyretic respectively. The reaction scheme below summarises a laboratory synthesis of paracetamol starting from phenol. The yields shown are for the particular product of each step in the synthesis.



(a) The nitration of benzene is an electrophilic substitution reaction that requires concentrated nitric and sulfuric acids.

(i) Write an equation for the formation of the electrophile by the reaction between concentrated nitric and concentrated sulfuric acids.

(2)

(ii) Give the mechanism for the formation of nitrobenzene from benzene.

(3)

(iii) Explain why phenol is nitrated in much milder conditions than benzene.

(2)

(iv) Suggest why the yield for the nitration of phenol is so low.

(1)

(v) Suggest an alternative to $NaBH_4$ that could be used in aqueous solution.

(1)

(vi) Calculate the overall yield of the synthesis.

(1)

(b) The paracetamol, prepared by the synthesis shown at the start of the question, may be purified by recrystallization. In this process, the paracetamol is dissolved in a minimum volume of hot water, the hot mixture filtered, the filtrate cooled and the resulting crystals filtered and dried. The table below summarises the solubility of paracetamol in water at various temperatures.

Temperature / °C	5	10	20	95
Solubility / g / 100 g	0.82	0.94	1.3	5.2

(i) Explain the purpose of each of the filtrations in the recrystallization of paracetamol.

(2)

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(ii) From the temperatures given in the table, choose the pair of temperatures that will give the highest yield of paracetamol from the recrystallization. Explain your choice.

(2)

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(iii) Name the technique that could be used in a **school** laboratory to check the purity of the recrystallized paracetamol.

(1)

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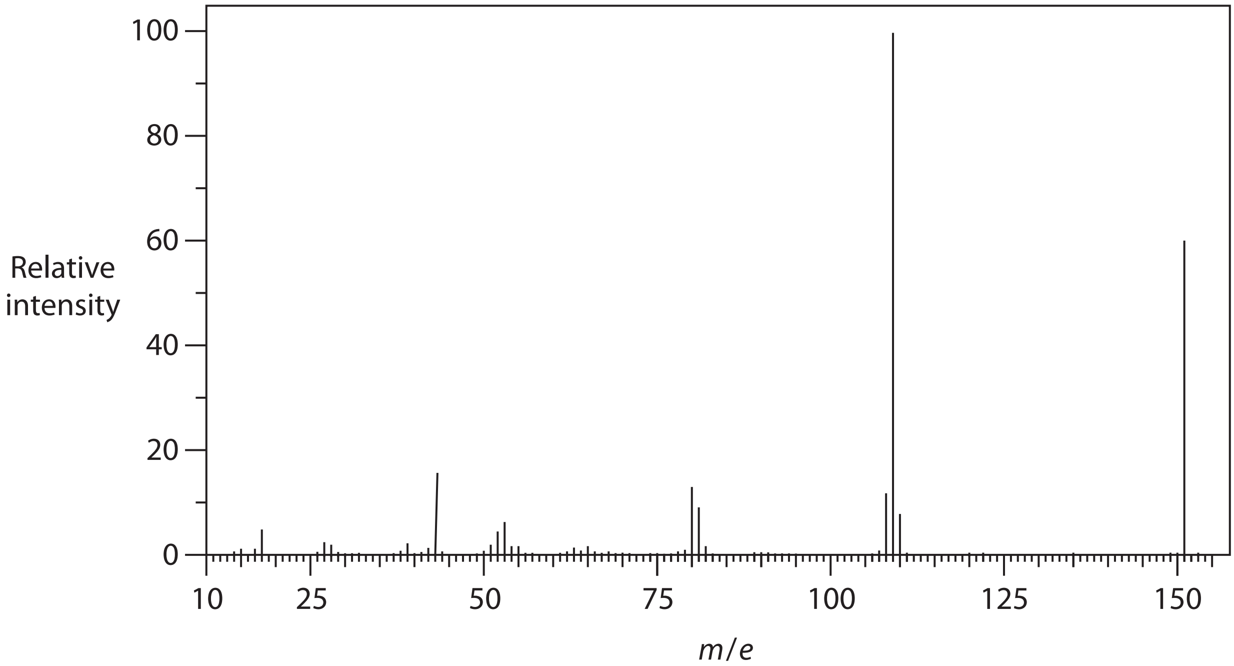
(c) The mass spectrum of paracetamol is shown below.



(i) Label the molecular ion peak, with an **M**, on the mass spectrum.

(1)

(ii) Suggest the formula of an ion that could cause the peak at m/e = 43.

(1)

(d) Paracetamol is highly toxic: overdosing causes irreversible liver damage. Despite this, paracetamol is readily available from pharmacies and even supermarkets. Suggest **one** control measure that sellers might employ to reduce the risk to paracetamol users.

(1)

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(Total for Question 22 = 18 marks)

TOTAL FOR SECTION B = 50 MARKS

SECTION C

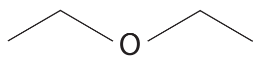
Answer ALL the questions. Write your answers in the spaces provided.

23

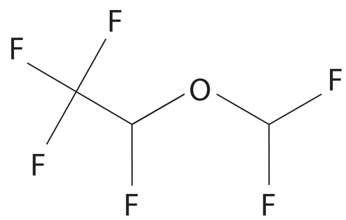
Anaesthetics

Substances have been used to relieve or eliminate pain during medical procedures for well over two thousand years. However, uncertainty about the nature and purity of the plant extracts being used and in standardising their application prompted Fallopius, a leading sixteenth century physician, to complain 'When soporifics are weak, they are useless, and when strong, they kill'. Modern analytical techniques have all but eliminated these problems.

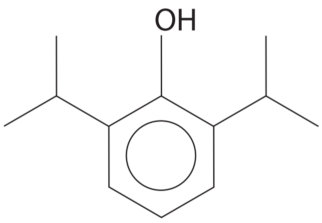
Anaesthetics are divided into two broad categories: general anaesthetics, which cause a reversible loss of consciousness, and local anaesthetics, which result in the absence of pain sensation in the area where they are applied. General anaesthetics may be delivered by inhalation or injection, while local anaesthetics may be injected or applied directly to the surface. The structures of some anaesthetics are shown below.



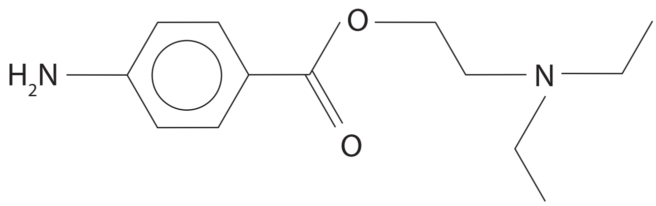
Ethoxyethane (T_b = 34.5 °C)



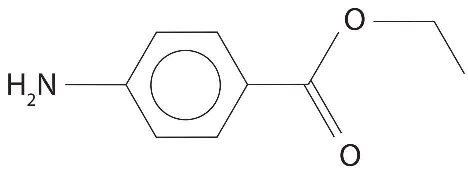
Desflurane (T_b = 23.5 °C)



Propofol



Procaine



Benzocaine

Ethoxyethane was first synthesized in 1540 by distilling a mixture of ethanol and concentrated sulfuric acid. Although its anaesthetic properties were established at this time, it was not until the nineteenth century that it was used as an inhalational general anaesthetic in medical procedures. However, ethoxyethane is highly flammable and has unpleasant side effects, so it has been entirely replaced by compounds like desflurane in modern medical practice. Propofol is a general anaesthetic which is administered by injection.

Procaine and benzocaine are local anaesthetics and are examples of aminoester anaesthetics.

(a) (i) Explain why ethoxyethane has a lower boiling temperature than ethanol (T_b = 78.5 °C) even though an ethanol molecule has fewer electrons. A detailed explanation of the forces involved is **not** required.

(3)

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*(ii) Desflurane is approximately 3700 times more potent as a greenhouse gas than carbon dioxide and it has been estimated that the worldwide use of inhalational anaesthetics contributes the equivalent of 1 million cars to global warming.

Suggest **three** factors that might be considered before deciding whether this type of general anaesthetic should be banned.

(3)

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(iii) Suggest why desflurane is much more stable than ethoxyethane and why the chemical stability of desflurane **increases** its potential to cause damage to the environment.

(2)

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....

*(b) Procaine is often used by dentists and administered by injection. Due to the presence of the amine groups, procaine is a basic compound.

Explain why the presence of an amine group makes a compound basic and hence compare the effect of each amine group on the basicity of procaine.

(3)

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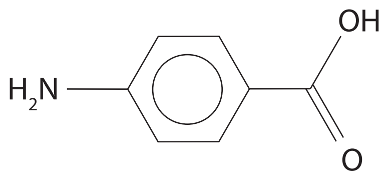
(c) The aminoester, benzocaine, is a local anaesthetic used in creams and cough drops. It can be made from 4-aminobenzoic acid, the structure of which is shown below.



4-aminobenzoic acid

(i) One possible preparation of benzocaine would be from 4-aminobenzoic acid using ethanol and a sulfuric acid catalyst. Suggest a **disadvantage** of this method.

(1)

....

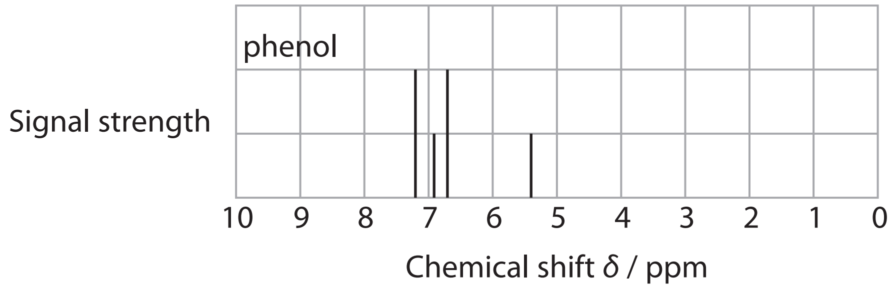
....

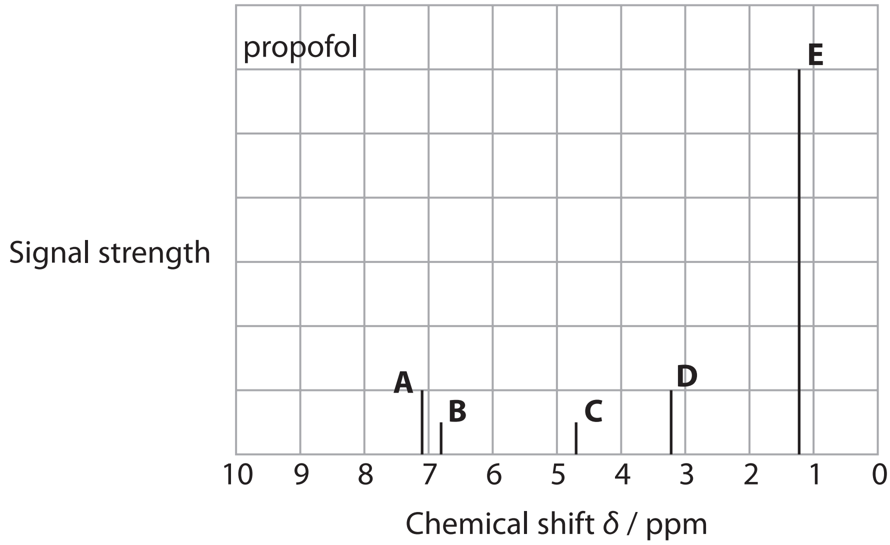
(ii) Suggest an alternative two-stage synthesis of benzocaine from 4-aminobenzoic acid. The reagents used must be identified and the structure of the intermediate compound given.

(3)

(d) The structure of an anaesthetic may be determined by proton nmr spectroscopy, while its purity may be established by high performance liquid chromatography.

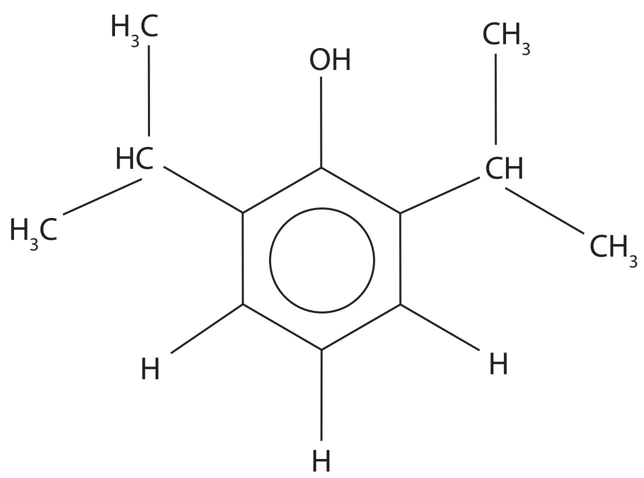
(i) Low resolution nmr spectra for phenol and for propofol are shown below. In these simplified spectra, the signal strength is proportional to the number of protons of each type, but only within each spectrum.





Use the phenol spectrum and your Data Booklet to identify the protons of propofol responsible for each of the peaks (**A** to **E**) in its nmr spectrum. Label **all** of the protons in the diagram below.

(3)



P 4 2 9 8 9 R A 0 2 6 2 8

(ii) Explain why high performance liquid chromatography, rather than nmr, is used to show that an anaesthetic contains no trace impurities.

(2)

(Total for Question 23 = 20 marks)

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

The Periodic Table of Elements

Key

relative atomic mass
atomic symbol
name
atomic (proton) number

1.0
H
hydrogen
1

1 (1)	2 (2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	3 (13)	4 (14)	5 (15)	6 (16)	7 (17)	0 (8) (18)
																	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