Write your name here

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Edexcel GCE

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Candidate Number ☐☐☐☐

Chemistry

Advanced

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

Monday 28 June 2010 – Morning
Time: 1 hour 40 minutes

Paper Reference
6CH05/01

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 ▶

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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 reaction of manganate(VII) ions with reducing agents in strongly acidic solution, the half-reaction for the reduction is

☒ **A** $MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$

☒ **B** $MnO_4^- + 4H^+ + 5e^- \rightarrow Mn^{2+} + 2H_2O$

☒ **C** $MnO_4^- + 8H^+ + 3e^- \rightarrow Mn^{2+} + 4H_2O$

☒ **D** $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$

(Total for Question 1 = 1 mark)

2 In the titration of iodine with standard sodium thiosulfate solution, starch is often used as an indicator. The starch should **not** be added until nearly all the iodine has reacted because

☒ **A** it is decomposed by high concentrations of iodine.

☒ **B** the blue complex formed is bleached by high concentrations of iodine.

☒ **C** the blue complex formed with high concentrations of iodine is insoluble and does not re-dissolve as more thiosulfate is added.

☒ **D** the starch reacts with the thiosulfate ions being added.

(Total for Question 2 = 1 mark)

3 The conditions needed for the $E^\ominus$ value of the standard hydrogen electrode to be exactly 0 V are

☒ **A** 1 mol dm^{-3} solution of hydrogen ions, 1 atm pressure of hydrogen, 25 °C.

☒ **B** 1 mol dm^{-3} solution of hydrogen ions, 1 atm pressure of hydrogen, room temperature.

☒ **C** 1 mol dm^{-3} solution of hydrogen ions, laboratory pressure of hydrogen, 25 °C.

☒ **D** 0.1 mol dm^{-3} solution of hydrogen ions, 1 atm pressure of hydrogen, 25 °C.

(Total for Question 3 = 1 mark)

4 The electrode potential for a cell can be used to calculate the equilibrium constant for the cell reaction. This is because

☒ **A** $E^{\ominus}_{\text{cell}}$ is proportional to $\ln K$.

☒ **B** $E^{\ominus}_{\text{cell}}$ is proportional to K.

☒ **C** $\ln E^{\ominus}_{\text{cell}}$ is proportional to $\ln K$.

☒ **D** $\ln E^{\ominus}_{\text{cell}}$ is proportional to K.

(Total for Question 4 = 1 mark)

5 Which of the following successive ionization energies (values in kJ mol^{-1}) could have come from a transition element?

☒	**A**	496	4563	6913	9544	13352	16611	20115	25941
☒	**B**	590	1145	4912	6474	8144	10496	12320	14207
☒	**C**	717	1509	3249	4940	6985	9200	11508	18956
☒	**D**	2081	3952	6122	9370	12177	15239	19999	23069

(Total for Question 5 = 1 mark)

6 Although platinum is very unreactive, it is used as a catalyst in catalytic converters in motor cars. Which of the following is true?

☒ **A** It converts nitrogen oxides and carbon monoxide to nitrogen and carbon dioxide by adsorbing the reactants on its surface so weakening their bonds.

☒ **B** It converts nitrogen oxides and carbon monoxide to nitrogen and carbon dioxide by being able to change its oxidation state.

☒ **C** It oxidizes unburnt fuel to carbon monoxide.

☒ **D** It oxidizes unburnt fuel to carbon dioxide.

(Total for Question 6 = 1 mark)

7 Which of the following gives the electronic configuration for chromium and for the Cr^{3+} ion?

		Cr	Cr^{3+}
☒	**A**	$[Ar]3d^4 4s^2$	$[Ar]3d^3 4s^0$
☒	**B**	$[Ar]3d^5 4s^1$	$[Ar]3d^2 4s^1$
☒	**C**	$[Ar]3d^5 4s^1$	$[Ar]3d^3 4s^0$
☒	**D**	$[Ar]3d^4 4s^2$	$[Ar]3d^1 4s^2$

(Total for Question 7 = 1 mark)

8 Which of the following gives the colours of solutions containing $Cr_2O_7^{2-}$, CrO_4^{2-}, hydrated Cr^{3+} and hydrated Cr^{2+}, in this order?

☒ **A** Yellow, orange, green, blue

☒ **B** Orange, yellow, green, blue

☒ **C** Orange, yellow, blue, green

☒ **D** Orange, green, yellow, blue

(Total for Question 8 = 1 mark)

9 When dichromate(VI) ions, $Cr_2O_7^{2-}$, react with iron(II) ions in acidic solution, the products are chromium(III) ions and iron(III) ions. In what ratio do the dichromate(VI) ions and the iron(II) ions react?

☒ **A** 1:6

☒ **B** 1:5

☒ **C** 2:5

☒ **D** 1:3

(Total for Question 9 = 1 mark)

10 The compound $[Pt(NH_3)_2Cl_2]$ is

☒ **A** tetrahedral with no isomers.

☒ **B** square planar with no isomers.

☒ **C** tetrahedral with two isomers.

☒ **D** square planar with two isomers.

(Total for Question 10 = 1 mark)

11 The hexaaquacopper(II) ion, $[Cu(H_2O)_6]^{2+}$, is blue because the water ligands

☒ **A** split the *p*-orbital energies and *p-p* electron transitions emit blue light.

☒ **B** split the *d*-orbital energies and *d-d* electron transitions absorb all but blue light.

☒ **C** split the *p*-orbital energies and *p-p* electron transitions absorb all but blue light.

☒ **D** split the *d*-orbital energies and *d-d* electron transitions emit blue light.

(Total for Question 11 = 1 mark)

12 If phenol and benzene are tested separately with bromine water, you would expect to see that

☒ **A** benzene and phenol would both decolorize bromine water.

☒ **B** benzene would decolorize bromine water, but phenol would not do so.

☒ **C** neither benzene nor phenol would decolorize bromine water.

☒ **D** benzene would not decolorize bromine water, but phenol would do so.

(Total for Question 12 = 1 mark)

13 An organic compound **X** is much more soluble in dilute hydrochloric acid than in water. Compound **X** forms a coloured complex with aqueous copper(II) ions.

Compound **X** could be

☒ **A** C_6H_5COOH

☒ **B** $C_6H_5NO_2$

☒ **C** $C_6H_5NH_2$

☒ **D** C_6H_5OH

(Total for Question 13 = 1 mark)

14 Which of the following shows the generation of the electrophile in the reaction of benzene with ethanoyl chloride in the presence of anhydrous aluminium chloride?

☒ **A** $CH_3COCl + AlCl_3 \rightarrow [CH_3CO]^+ + AlCl_4^-$

☒ **B** $CH_3COCl + AlCl_3 \rightarrow [CH_3CO]^- + AlCl_4^+$

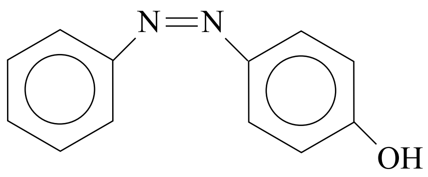
☒ **C** $CH_3CH_2Cl + AlCl_3 \rightarrow [CH_3CH_2]^+ + AlCl_4^-$

☒ **D** $CH_3COOCl + AlCl_3 \rightarrow [CH_3COO]^- + AlCl_4^+$

(Total for Question 14 = 1 mark)

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

15 Which of the following reagents and conditions would enable phenylamine to be converted to the yellow dye 4-hydroxyazobenzene in a good yield?



☒ **A** Sodium nitrite, $NaNO_2$, in concentrated HCl, between 0 °C and 10 °C; followed by an alkaline solution of phenol.

☒ **B** Sodium nitrite, $NaNO_2$, in concentrated HCl, between 0 °C and 10 °C; followed by an acidic solution of phenol.

☒ **C** Sodium nitrate, $NaNO_3$, in concentrated HCl, between 0 °C and 10 °C; followed by an alkaline solution of phenol.

☒ **D** Sodium nitrite, $NaNO_2$, in concentrated HCl, room temperature; followed by an alkaline solution of phenol.

(Total for Question 15 = 1 mark)

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16 1-butylamine, $CH_3CH_2CH_2CH_2NH_2$, reacts with ethanoyl chloride to form

☒ **A** $CH_3CH_2CH_2CH_2NH_3^+Cl^-$

☒ **B** $CH_3CH_2CH_2CH_2NHCOCH_3$

☒ **C** $CH_3CH_2CH_2CH_2NHCH_2CH_3$

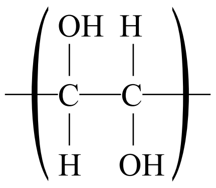
☒ **D** $CH_3CH_2CH_2CH(COCH_3)NH_2$

(Total for Question 16 = 1 mark)

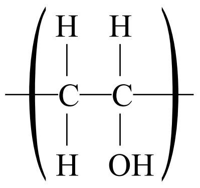
Use this space for any rough working. Anything you write in this space will gain no credit.

17 The addition polymer poly(ethenol) is water-soluble. The repeating unit of poly(ethenol) is

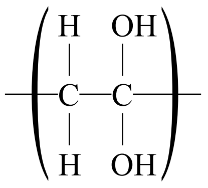
☒ **A**



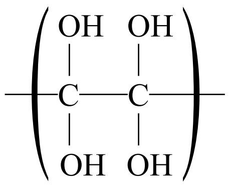
☒ **B**



☒ **C**



☒ **D**



(Total for Question 17 = 1 mark)

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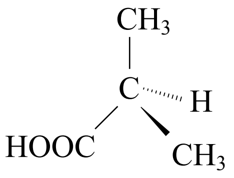
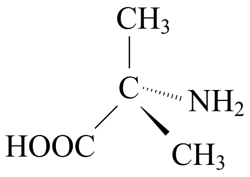
18 A white organic compound, **X**, is optically active and reacts with ninhydrin to give a coloured product. The structural formula of **X** could be

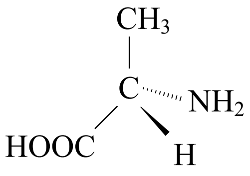
☒ **A**



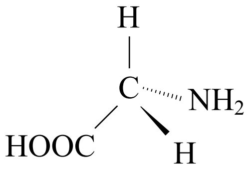
☒ **B**



☒ **C**



☒ **D**



(Total for Question 18 = 1 mark)

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

19 Glycine, H_2NCH_2COOH, is a solid that has a melting temperature of about 250 °C, and it is very soluble in water. This is because of the

☒ **A** formation of intermolecular hydrogen bonds in the solid and hydrogen bonds with water.

☒ **B** formation of $H_3N^+CH_2COO^-$ ions which interact strongly with each other in the solid and with water.

☒ **C** dissociation of the molecule to form $H_2NCH_2COO^-$ and H^+ ions in the solid and the solution.

☒ **D** protonation of the molecule to form $H_3N^+CH_2COOH$ ions in both the solid and the solution.

(Total for Question 19 = 1 mark)

20 Organic solids are often purified by recrystallization. This technique works on the basis that

☒ **A** the impurities must be insoluble in the solvent used.

☒ **B** the impurities must react with the solvent used.

☒ **C** the impurities crystallize first when the hot solution is cooled.

☒ **D** the cooled solution is saturated with the desired material but not with the impurities.

(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, zinc and, in some cases, other metals too. There are over 30 varieties of brass for different applications.

The amount of copper in a brass can be found as follows:

- A weighed sample of brass is reacted with the minimum amount of concentrated nitric acid.
- The solution is neutralized, a portion of it pipetted into a conical flask, and excess potassium iodide solution is added.
- The iodine produced is titrated with a solution of sodium thiosulfate of known concentration.

(a) The ionic equation for the reaction between copper metal and concentrated nitric acid is shown below.

$$Cu(s) + 2NO_3^-(aq) + 4H^+ (aq) \rightarrow Cu^{2+}(aq) + 2NO_2(g) + 2H_2O(l)$$

(i) Give the oxidation numbers of the copper and nitrogen in both the reactants and products.

(2)

Copper: from .... **to** ....

Nitrogen: from .... **to** ....

(ii) Write the two half-equations that can be combined to give the ionic equation shown above.

(2)

(iii) Explain why the standard electrode potentials for the two ionic half-equations that you have written give an incorrect value for E_{cell} for this reaction as described above.

(2)

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(b) The solution produced contains a mixture of zinc ions and copper ions.

(i) State TWO observations that you would **see** if concentrated ammonia solution were to be added, drop by drop, to the solution until in excess.

(2)

....

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....

(ii) Copper ions can be separated from the zinc ions in the solution by adding sodium hydroxide solution in excess, followed by filtration of the mixture.

Write equations, including state symbols, for the THREE reactions that occur.

(3)

Equation 1

Equation 2

Equation 3

*(iii) Give examples of amphoteric behaviour and ligand exchange, by reference to the reactions of zinc compounds.

(3)

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(c) A sample of Admiralty Brass of mass 3.00 g was treated with nitric acid and made up to a neutral solution of volume 250 cm^3. Excess potassium iodide was added to 25.0 cm^3 portions of this solution, and the liberated iodine was titrated with sodium thiosulfate solution, concentration 0.100 mol dm^{-3}. The mean titre was 33.10 cm^3.

(i) Write the ionic equation for the reaction between thiosulfate ions and iodine.

(1)

*(ii) The equation for the reaction between copper(II) ions and iodide ions is shown below.

$$2Cu^{2+} + 4I^{-} \rightarrow 2CuI + I_2$$

Hence calculate the percentage by mass of copper in Admiralty Brass. Give your answer to **three** significant figures.

(6)

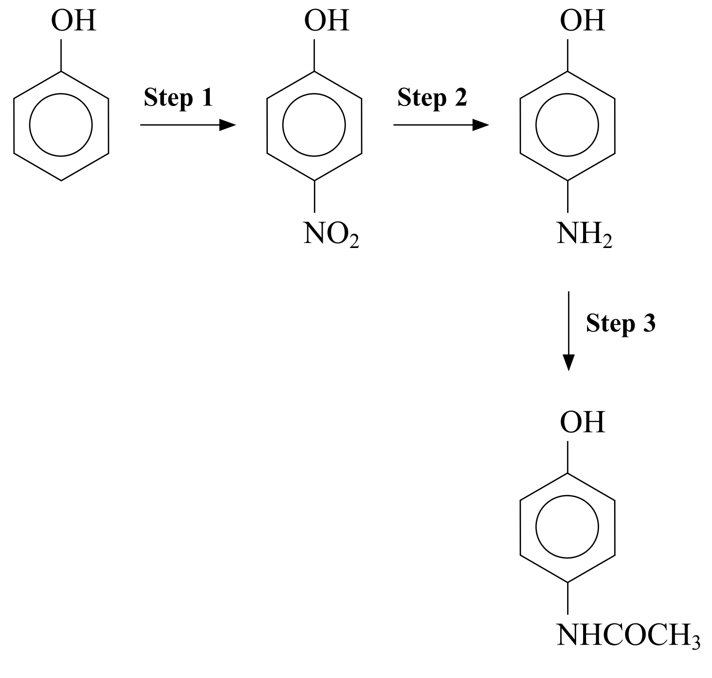
(iii) When setting up the burette, a student failed to fill the jet of the burette. Explain the effect that this would have on the value of the first titre.

If this first titre was included in the calculation of the mean titre, what effect would this have on the value for the percentage of copper in the brass?

(2)

(Total for Question 21 = 23 marks)

22 Paracetamol is possibly the most widely used analgesic (painkiller) in the world. It can be made from phenol as shown below.



Paracetamol

(a) The nitration of phenol in **step 1** uses dilute nitric acid at room temperature, whereas the nitration of benzene requires a mixture of concentrated nitric and sulfuric acids at about 55 °C.

(i) Give the mechanism for the nitration of **benzene**, including the equation for the reaction that produces the electrophile.

(4)

*(ii) Explain why phenol can be nitrated under much milder conditions than those required to nitrate benzene.

(2)

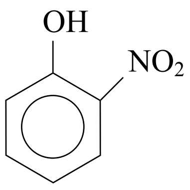
(iii) Suggest reagents that could be used for **step 2**.

(2)

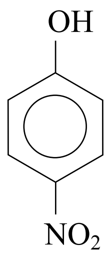
(iv) Suggest the name or formula of a reagent that could be used in **step 3**.

(1)

*(b) In the nitration of phenol, **step 1**, two compounds are produced.



2-nitrophenol



4-nitrophenol

These compounds can be separated by steam distillation, since 2-nitrophenol is volatile in steam but 4-nitrophenol is not.

Describe briefly the technique of steam distillation and give ONE advantage of steam distillation over normal distillation.

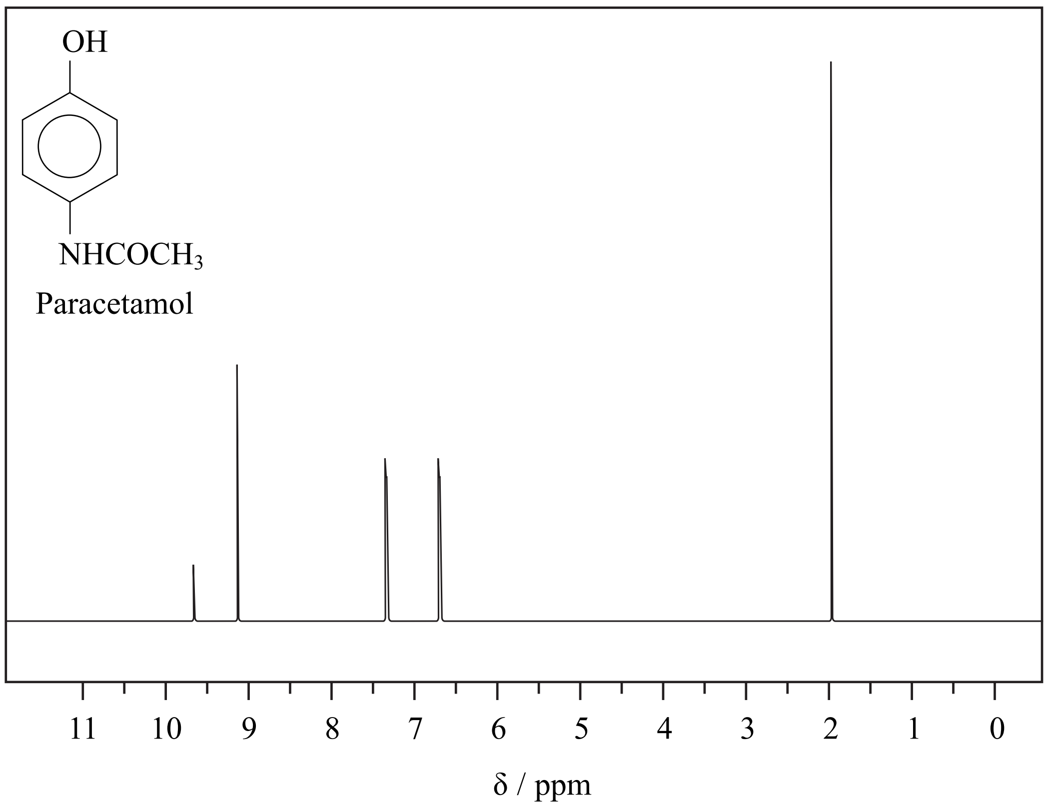
(3)

(c) The nmr spectrum of paracetamol is given below. The peaks at 6.7 and 7.4 ppm are due to the protons on the benzene ring and are both doublets.

Explain why these two peaks are doublets but all the other peaks are singlets.

[There is no need to refer to your data booklet]

(2)



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(Total for Question 22 = 14 marks)

23 More than half of the elements in the Periodic Table are transition elements. Vanadium, element 23, is a typical transition element.

(a) (i) Give TWO properties shown by vanadium **compounds** that are characteristic of transition metal chemistry, other than variable oxidation state.

(2)

(ii) Vanadium(III) ions in aqueous solution exist as $[V(H_2O)_6]^{3+}$.

Draw this ion so as to clearly show its shape. Name the type of bond between the ligand and the vanadium ion and state the feature of the ligand that enables this bond to be formed.

(3)

(b) Vanadium ions exist in oxidation states from (V) to (II).

(i) Use your data booklet (page 15) to find the standard electrode (reduction) potential for the reduction of vanadium(IV), VO^{2+}, to vanadium(III), V^{3+}.

(1)

*(ii) Explain the term **disproportionation.**

(2)

(iii) Use your answer to (b)(i), and the data below, to calculate $E^{\ominus}_{\text{cell}}$ for the formation of vanadium(V) and vanadium(III) from vanadium(IV) in acidic solution. State if the reaction is feasible under standard conditions and justify your answer.

$$VO_2^{+}(aq) + 2H^{+}(aq) + e^{-} \rightleftharpoons VO^{2+}(aq) + H_2O(l) \quad E^{\ominus} = +1.00\text{ V}$$

(2)

(Total for Question 23 = 10 marks)

TOTAL FOR SECTION B = 47 MARKS

SECTION C

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

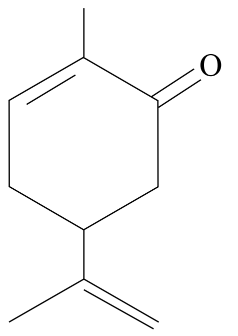
24

A major function of the chemical industry is the manufacture of perfumes and flavourings. Perfumes were originally made from natural products, such as spermaceti from whales or civetone from the civet cat. The use of synthetic equivalents is generally cheaper and the supply is more reliable, and does not require the animals to be killed which obtaining spermaceti did. Synthetic perfumes and flavourings are usually nature-identical, although naturally-occurring molecules that have stereoisomers are sometimes produced synthetically as mixtures since the stereospecific synthesis required might be difficult to achieve economically.

Some chiral molecules have a different taste depending on which enantiomer is present. The enantiomer (–)-carvone tastes and smells of spearmint, and its mirror-image, (+)-carvone, of caraway or dill. In some cases only one enantiomer has any taste; this is true for glucose. The mirror image molecule of naturally occurring glucose has no taste and cannot even be absorbed or metabolized. Many drug molecules are chiral, though paracetamol is not. The wrong isomer present in a drug may be positively damaging, which was the case with thalidomide. In order to synthesize optically-pure drug molecules, it is important to understand the mechanism of any reaction used. Using an S_N1 reaction which involves the chiral centre would result in the product mixture being racemic. It is advantageous to use stereospecific catalysts wherever possible, and industry on the whole prefers to use heterogeneous rather than homogeneous catalysts.

(a) The skeletal formula of carvone is shown below. Draw a circle around the chiral carbon atom.

(1)



(b) Explain why the synthesis of paracetamol is more efficient than the synthesis of a single enantiomer such as (–)-carvone.

(3)

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(c) Carvone contains two types of functional group. For each of these, give a suitable chemical test to show its presence, and state what you would see in each case.

(4)

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(d) Carvone can be reduced in a variety of ways.

(i) On reduction with hydrogen, in the presence of a platinum catalyst, 4.5 g of carvone reacted with 1.44 dm^3 of hydrogen. Use these data to deduce the skeletal formula of the reduction product.

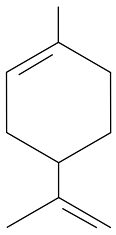
[Molar mass of carvone is 150 g mol^{-1}; molar volume of hydrogen at the temperature and pressure of the experiment is 24 dm^3 mol^{-1}.]

(3)

Working

Hence skeletal formula of reduction product.

(ii) Reduction of carvone, using hydrazine in potassium hydroxide solution, gives limonene.



How would you show from a comparison of the infra-red spectra of carvone and of limonene that this reduction had occurred? You should quote appropriate data, from the data booklet, to support your answer.

(2)

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(e) (i) Draw the skeletal formula of the molecule that would be obtained if carvone were to be reacted with an excess of hydrogen bromide in an inert solvent.

(2)

(ii) If the product from (e)(i) were to be heated with ethanolic potassium hydroxide solution, elimination would occur and HBr would be lost. Would the resulting molecule necessarily be carvone? Explain your answer.

(2)

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(f) *(i) Give the mechanism of one nucleophilic reaction of your choice, which **either** gives rise to a racemic mixture **or** results in the inversion of the chirality of the starting material. Explain what your mechanism predicts about the stereochemistry of the product.

(5)

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(ii) Suggest why industrial chemists prefer to use heterogeneous rather than homogeneous catalysts.

(1)

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(Total for Question 24 = 23 marks)

TOTAL FOR SECTION C = 23 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 *(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)*
							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