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<h1>Chemistry</h1> <h2>Advanced</h2> <h3>Unit 5: General Principles of Chemistry II – Transition Metals and Organic Nitrogen Chemistry (including synoptic assessment)</h3>									
Tuesday 17 June 2014 – Afternoon							Paper Reference		
Time: 1 hour 40 minutes							6CH05/01		
You must have: Data Booklet								Total Marks	
Candidates may use a calculator.									

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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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 +3?

- A MnO_4^{2-}
- B VO^{2+}
- C $[\text{Fe}(\text{CN})_6]^{4-}$
- D $[\text{CrCl}_2(\text{H}_2\text{O})_4]^+$

(Total for Question 1 = 1 mark)

2 Copper metal is oxidized to Cu^{2+} by nitrate(V) ions which are reduced to nitrogen monoxide, NO. By considering the changes to the oxidation numbers of copper and nitrogen, it can be deduced that in this reaction

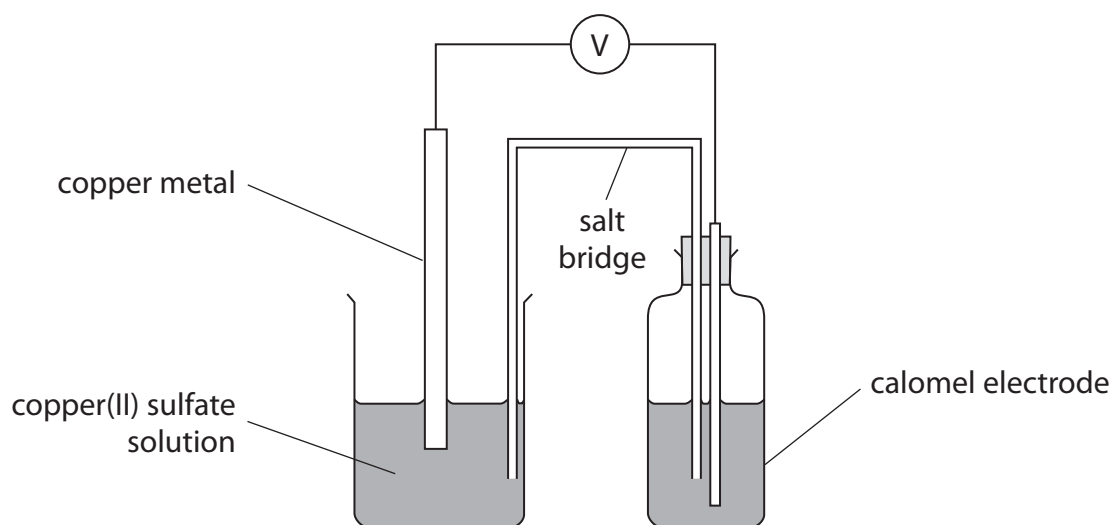
- A 2 mol of copper reacts with 3 mol of nitrate(V) ions.
- B 2 mol of copper reacts with 5 mol of nitrate(V) ions.
- C 3 mol of copper reacts with 2 mol of nitrate(V) ions.
- D 5 mol of copper reacts with 2 mol of nitrate(V) ions.

(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 copper metal / copper(II) ion electrode and a reference electrode, known as a calomel electrode.

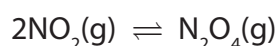


Under standard conditions, the emf of this cell was -0.07 V . The standard electrode potential of the copper metal / copper(II) ion electrode is $+0.34\text{ V}$. Hence the standard electrode potential of the calomel electrode is

- A -0.41 V
 B -0.27 V
 C $+0.27\text{ V}$
 D $+0.41\text{ V}$

(Total for Question 3 = 1 mark)

- 4 For the reaction



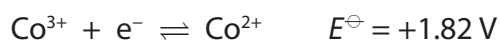
at 450 K the total entropy change, ΔS_{total} , is negative. Hence the equilibrium constant, K_p , for this reaction at 450 K is

- A zero.
 B positive and greater than 1.
 C positive and less than 1.
 D negative.

(Total for Question 4 = 1 mark)



5 The standard electrode potentials of two half reactions are shown below.



Which of the following processes is thermodynamically favourable? The reaction of

- A Co^{2+} with Cl_2 to form Cl^-
- B Co^{2+} with Cl^- to form Cl_2
- C Co^{3+} with Cl_2 to form Cl^-
- D Co^{3+} with Cl^- to form Cl_2

(Total for Question 5 = 1 mark)

6 A solution of potassium manganate(VII) was used to determine the concentration of iron(II) ions in solution by titration in the presence of excess dilute sulfuric acid.

(a) With the potassium manganate(VII) in the burette, the end-point of the reaction is when the solution in the conical flask turns

(1)

- A colourless.
- B pink.
- C green.
- D orange.

(b) If insufficient acid is added, the titre value is

(1)

- A low and a brown precipitate forms.
- B low and a green precipitate forms.
- C high and a brown precipitate forms.
- D high and a green precipitate forms.

(Total for Question 6 = 2 marks)

7 What is the electronic configuration of the stable scandium ion?

- A $[\text{Ar}] 3\text{d}^0 4\text{s}^2$
- B $[\text{Ar}] 3\text{d}^1 4\text{s}^1$
- C $[\text{Ar}] 3\text{d}^0 4\text{s}^1$
- D $[\text{Ar}] 3\text{d}^0 4\text{s}^0$

(Total for Question 7 = 1 mark)



8 The shapes of the complexes $[\text{CrCl}_4]^-$ and $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ are

	$[\text{CrCl}_4]^-$	$[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$
<input type="checkbox"/> A	square planar	square planar
<input type="checkbox"/> B	tetrahedral	tetrahedral
<input type="checkbox"/> C	square planar	tetrahedral
<input type="checkbox"/> D	tetrahedral	square planar

(Total for Question 8 = 1 mark)

9 The compound 1,2-diaminoethane, $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$, is a bidentate ligand; in formulae, it is usually abbreviated to 'en'.

When 1,2-diaminoethane is added to $[\text{Co}(\text{NH}_3)_6]^{2+}$ in aqueous solution, $[\text{Co}(\text{en})_3]^{2+}$ is formed. What is the **best** explanation for this?

- A There are much stronger bonds between the ligands and the cobalt(II) ion in $[\text{Co}(\text{en})_3]^{2+}$ than in $[\text{Co}(\text{NH}_3)_6]^{2+}$.
- B When $[\text{Co}(\text{en})_3]^{2+}$ is formed from $[\text{Co}(\text{NH}_3)_6]^{2+}$ the reaction is exothermic.
- C When $[\text{Co}(\text{en})_3]^{2+}$ is formed from $[\text{Co}(\text{NH}_3)_6]^{2+}$ the total entropy change is positive.
- D When $[\text{Co}(\text{en})_3]^{2+}$ is formed from $[\text{Co}(\text{NH}_3)_6]^{2+}$ the reaction has a low activation energy.

(Total for Question 9 = 1 mark)

10 When aqueous sodium hydroxide is added to an aqueous solution of a transition metal compound, a green precipitate is formed which dissolves in excess sodium hydroxide forming a green solution. The transition metal ion present in the original solution is

- A Cr^{3+}
- B Fe^{3+}
- C Fe^{2+}
- D Ni^{2+}

(Total for Question 10 = 1 mark)



11 Benzene reacts with a nitrating mixture of concentrated nitric and sulfuric acids. Which species is **least** likely to be present in the nitrating mixture?

- A NO_3^-
- B H_3O^+
- C HSO_4^-
- D NO_2^+

(Total for Question 11 = 1 mark)

12 Benzene ($T_b = 80.1^\circ\text{C}$) has a higher boiling temperature than ethanol ($T_b = 78.5^\circ\text{C}$). This is because the

- A benzene ring is stabilised.
- B London forces between benzene molecules are stronger than the hydrogen bonds between ethanol molecules.
- C hydrogen bonds between benzene molecules are stronger than the hydrogen bonds between ethanol molecules.
- D C–H bonds in benzene are stronger than the C–H bonds in ethanol.

(Total for Question 12 = 1 mark)

13 Separate 0.1 mol dm^{-3} aqueous solutions of ammonia, methylamine and phenylamine were prepared. Which of the following sequences shows the solutions in order of **increasing** pH?

- A phenylamine, methylamine, ammonia
- B phenylamine, ammonia, methylamine
- C methylamine, ammonia, phenylamine
- D methylamine, phenylamine, ammonia

(Total for Question 13 = 1 mark)

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



14 The benzenediazonium ion, $C_6H_5N_2^+$, is an intermediate in the preparation of azo dyes.

(a) In the formation of an azo dye, the benzenediazonium ion is

(1)

- A** an electrophile.
- B** a nucleophile.
- C** a carbocation.
- D** a substituent.

(b) The temperature of the aqueous reaction mixture must be kept below $10^\circ C$ to prevent the benzenediazonium ion being converted into

(1)

- A** benzene.
- B** nitrobenzene.
- C** phenylamine.
- D** phenol.

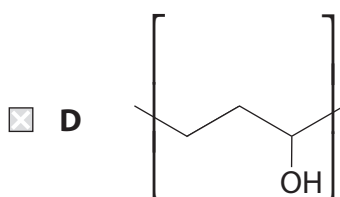
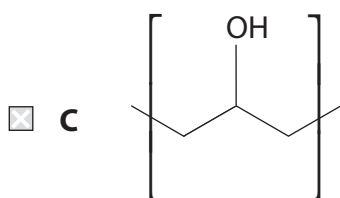
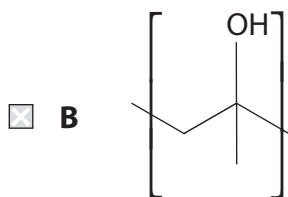
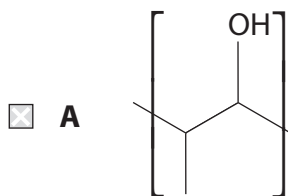
(Total for Question 14 = 2 marks)

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



15 The monomer of the addition polymer poly(propenol) may be represented as $\text{CH}_3\text{-CH=CHOH}$.

The repeat unit of the addition polymer is



(Total for Question 15 = 1 mark)

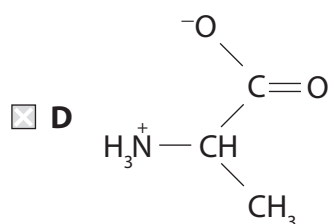
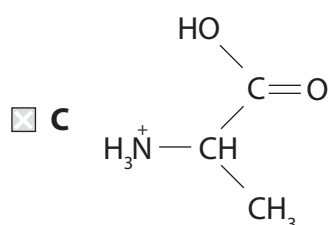
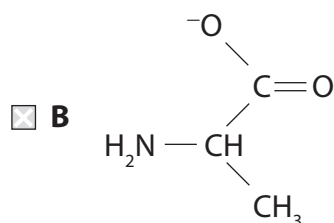
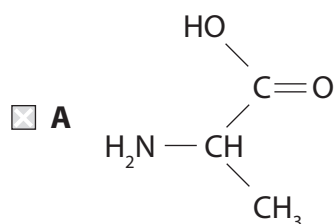
16 Chromatography may be used to separate mixtures of amino acids. This is best explained by the fact that different amino acids have different interactions with

- A the mobile phase only.
- B the stationary phase only.
- C the mobile phase **and** the stationary phase.
- D ninhydrin.

(Total for Question 16 = 1 mark)



17 In an aqueous solution with a pH of 7, the amino acid alanine exists mainly as



(Total for Question 17 = 1 mark)

18 When a solid is purified by recrystallization, the procedure involves the removal of impurities by filtration of the hot mixture followed by filtration of the cold mixture. Which impurities are removed by these two filtrations?

	Hot filtration	Cold filtration
<input type="checkbox"/> A	insoluble impurities	insoluble impurities
<input type="checkbox"/> B	insoluble impurities	soluble impurities
<input type="checkbox"/> C	soluble impurities	insoluble impurities
<input type="checkbox"/> D	soluble impurities	soluble impurities

(Total for Question 18 = 1 mark)

TOTAL FOR SECTION A = 20 MARKS

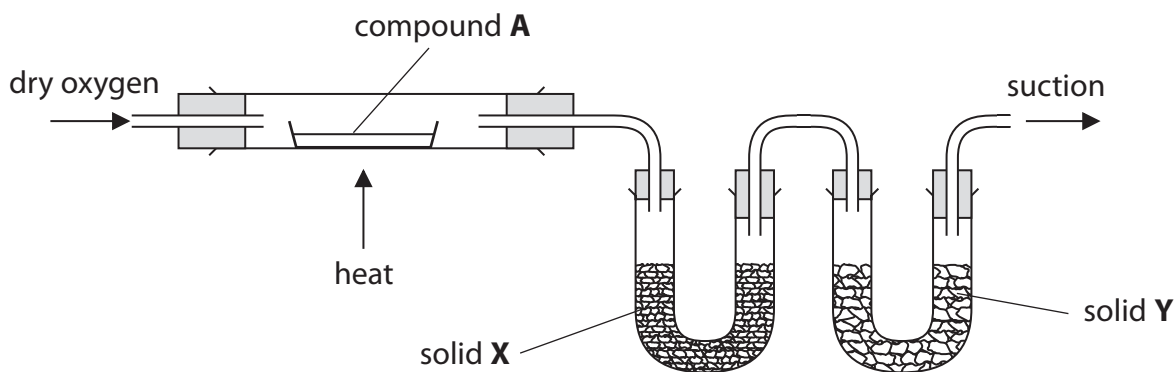


SECTION B

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

19 A compound **A**, known to contain only the elements carbon, hydrogen and oxygen, was subjected to detailed analysis.

(a) A sample of **A** was burned completely in the apparatus shown below. Solid **X** absorbed the water formed in the combustion and solid **Y** absorbed the carbon dioxide.



(i) Explain why the oxygen must be dry.

(1)

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(ii) Suggest a suitable substance to use as solid **X**.

(1)

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(iii) Suggest a suitable substance to use as solid **Y**.

(1)

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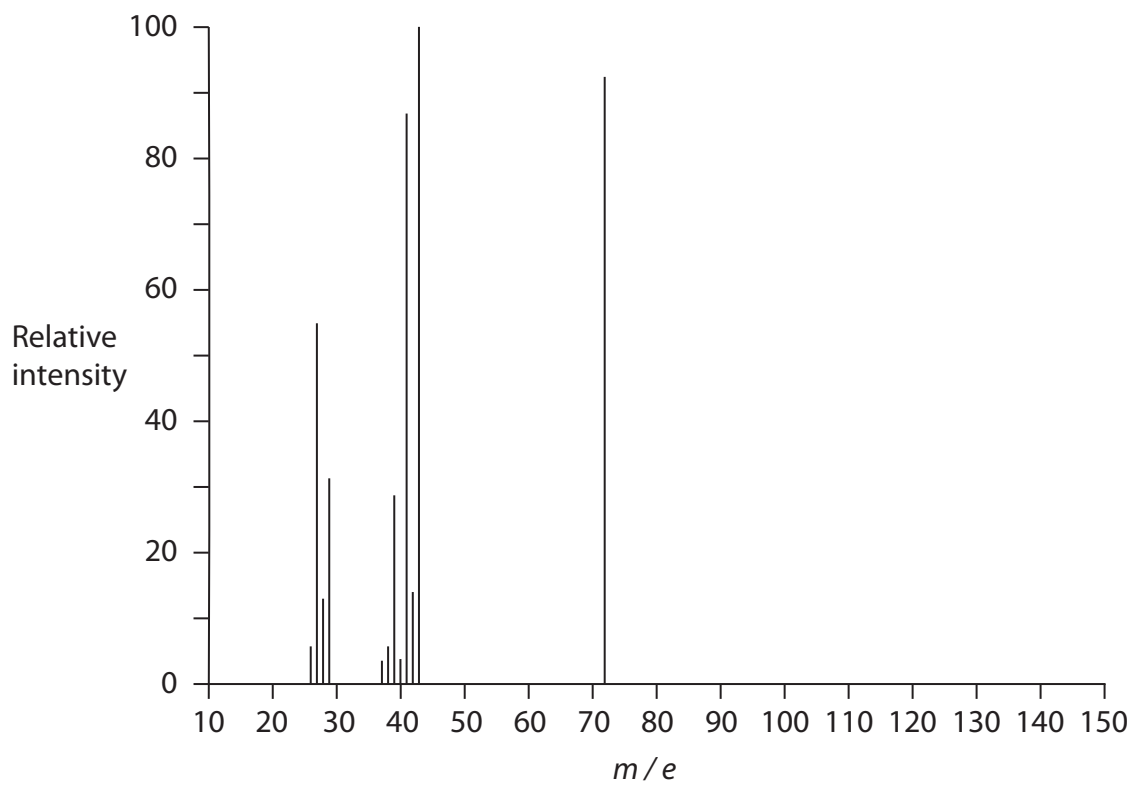
(iv) 3.60 g of compound **A** was burned completely. The mass of solid **X** increased by 3.60 g and the mass of solid **Y** increased by 8.80 g.

Use these data to calculate the empirical formula of compound **A**.
You **must** show your working.

(5)



(b) The mass spectrum of **A** is shown below.



(i) Identify the molecular ion peak and hence deduce the molecular formula of **A**.

(2)



(ii) Given that **A** does **not** have a ring structure, suggest the **structural** formulae of three of the species that might cause the peak at $m/e = 43$ in the mass spectrum of **A**.

(3)

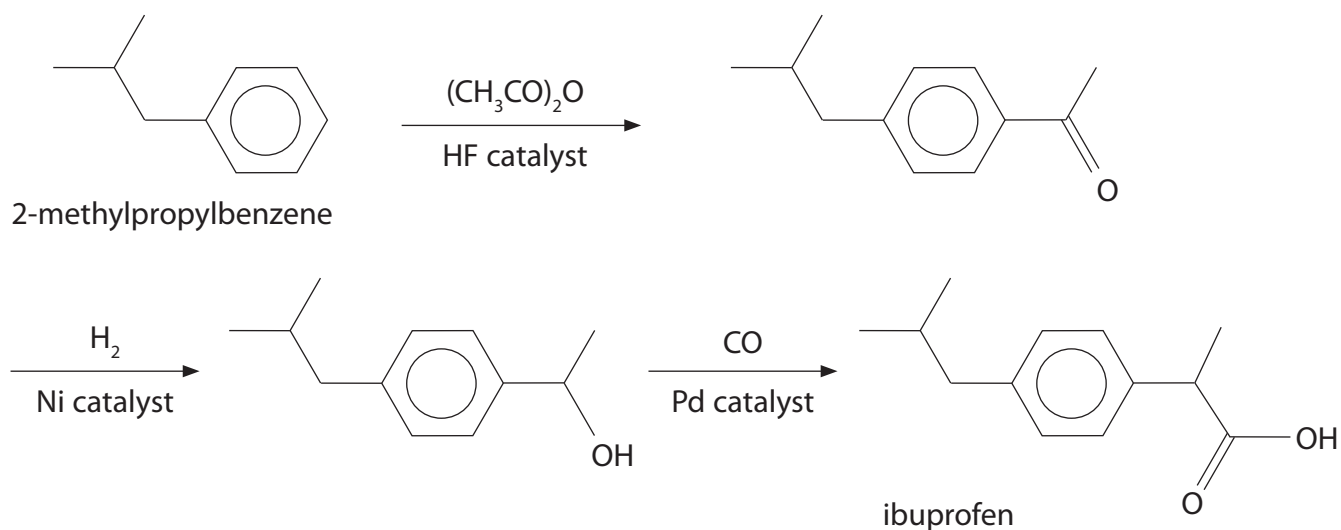
*(c) The low resolution nmr spectrum of **A** has three peaks in the ratio 6:1:1. Draw the structure of **A** and show how your structure is consistent with the nmr data.

(3)

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(Total for Question 19 = 16 marks)



20 Ibuprofen is a nonsteroidal anti-inflammatory drug (NSAID) widely used as an analgesic (pain reliever). It was discovered in the 1960s by the Boots Group which developed a six step synthesis from 2-methylpropylbenzene. The synthesis shown below was introduced in the 1990s by the BHC Company and received a Presidential Green Chemistry Challenge award in 1997. The citation noted that the synthesis has just three steps, all of which are catalytic, and an effective atom economy of 99%. Both syntheses are carried out in solution.



(a) (i) Suggest why a three step synthesis is likely to be 'greener' than a six step process.

(1)

(ii) Why does the use of catalysts make processes 'greener' (as well as faster)?

(1)



(b) The first step of the synthesis is an electrophilic substitution which is usually carried out in a school laboratory using ethanoyl chloride and an aluminium chloride catalyst.

(i) Write an equation showing the formation of the electrophile in the **school** experiment.

(1)

(ii) Give the mechanism for the electrophilic substitution of 2-methylpropylbenzene by ethanoyl chloride, using the electrophile you have given in (b)(i).

(3)

(iii) Suggest **one** environmental benefit of using $(\text{CH}_3\text{CO})_2\text{O}$, rather than ethanoyl chloride, in the manufacture of ibuprofen.

(1)

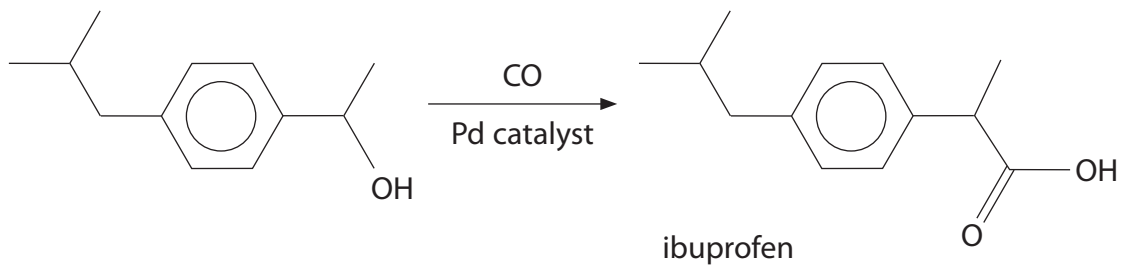
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(c) The final stage of the modern synthesis for ibuprofen is shown below.



(i) Suggest a benefit of using a **solid** catalyst in this reaction.

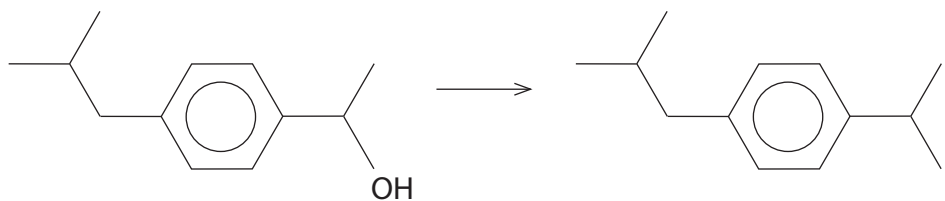
(1)



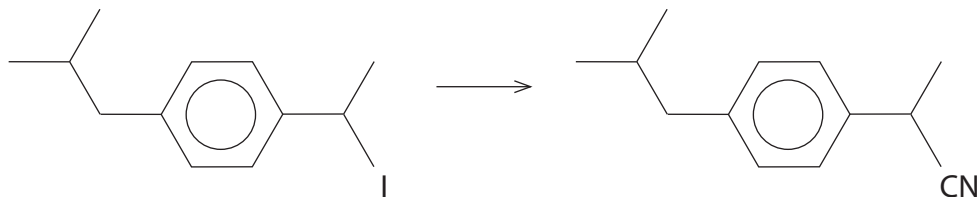
(ii) The preparation in part (c) can be carried out in a laboratory in three reactions.

(3)

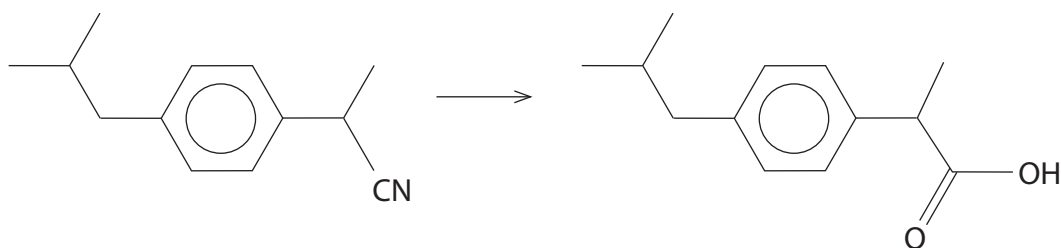
Reaction 1



Reaction 2



Reaction 3



Give:

The reagents for **Reaction 1**

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The reagents and conditions for **Reaction 3**

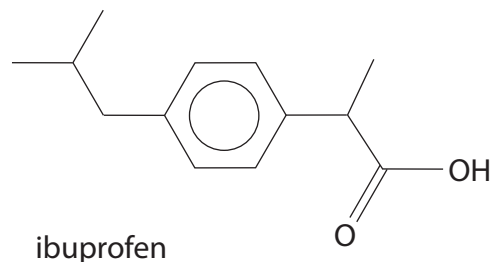
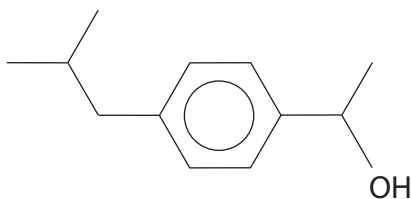
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(iii) Using your Data Booklet, explain how infrared spectroscopy can be used to distinguish between the two structures shown below.

(2)



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(d) Ibuprofen is a chiral molecule and only one of its enantiomers is biologically active. However, although the synthesis produces a racemic mixture, an isomerase enzyme in the body converts the inactive enantiomer into the active enantiomer.

(i) Explain the term 'chiral molecule'.

(1)

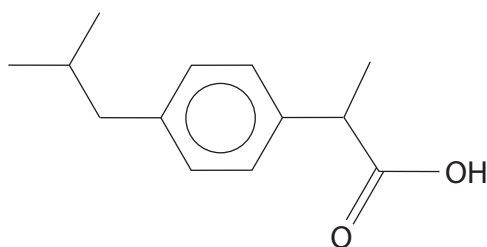
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(ii) Mark with an asterisk (*) the chiral centre on the structure of ibuprofen below.

(1)



(iii) Explain the term 'racemic mixture'.

(1)

(iv) Suggest **two** benefits that arise from the isomerization of the inactive enantiomer of ibuprofen.

(2)

(Total for Question 20 = 18 marks)



- 21 (a) The following method was used to estimate the concentration of ethanol in an aqueous solution, **Q**, prepared by the fermentation of sucrose.

25 cm³ of **Q** was measured using a pipette and transferred to a 250 cm³ volumetric flask; the flask was made up to the mark with distilled water and mixed thoroughly, forming a diluted solution, **R**.

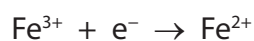
25 cm³ samples of **R** were mixed with an equal volume of a 0.200 mol dm⁻³ potassium dichromate(VI) solution and excess dilute sulfuric acid.

The mixture was allowed to stand for several hours and then the amount of unreacted potassium dichromate(VI) was determined by titration against a 0.255 mol dm⁻³ iron(II) ammonium sulfate solution. The mean titre was 23.85 cm³.

- (i) Use the ionic half-equations below to write the full ionic equation for the reaction between potassium dichromate(VI) and iron(II) ammonium sulfate.

State symbols are not required.

(1)



- (ii) Calculate the number of moles of potassium dichromate(VI) that remained **unreacted** after standing for several hours with solution **R**.

(2)



(iii) Calculate the number of moles of potassium dichromate(VI) that reacted with the ethanol while standing for several hours with solution **R**.

(2)

(iv) Write an ionic half-equation for the oxidation of ethanol to ethanoic acid.

Use your equation, and the half-equation for the reduction of dichromate(VI) ions, to show that 3 mol of ethanol are oxidized by 2 mol of potassium dichromate(VI).

(2)

(v) Calculate the concentration of ethanol (in mol dm⁻³) in solution **Q**.

(3)



*(b) The indicator used in this titration was barium diphenylamine sulfonate, which turns from deep purple to colourless at the end-point.

Identify the ion responsible for turning the indicator from deep purple to colourless at the end-point.

By considering the type of reaction involved when this ion reacts with barium diphenylamine sulfonate, suggest how barium diphenylamine sulfonate acts as an indicator in this titration. Note that complex formation does **not** occur. The detailed reactions of this particular indicator are **not** required.

(3)

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*(c) This method of determining ethanol concentration does not give very reliable results, although the titration is very accurate.

Suggest **one** reason why this might be the case, explaining how the measured concentration would differ from the actual concentration of the ethanol.

(3)

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(Total for Question 21 = 16 marks)

TOTAL FOR SECTION B = 50 MARKS



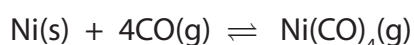
SECTION C

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

22

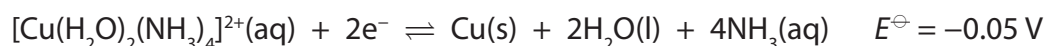
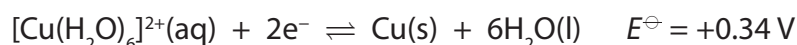
Metal Complexes

Complexes involve ligands forming dative covalent bonds with a central cation; the number of dative covalent bonds is the coordination number of the cation in the complex. Complexes may be positive, negative or neutral. The ligands may be neutral or negatively charged, but are never positively charged. The ligands must have a lone pair of electrons. In some complexes the central atom is neutral, as is the case with nickel carbonyl which is used in the Mond process for the purification of nickel:



The formation of complexes is typical of transition metals but other elements also form complexes. Zinc, which is a d block element but not a transition metal, and aluminium, which is a Group 3 element, both form complexes. Transition metal complexes are usually coloured, but if the interaction between the ligand and the central ion is very strong, then the resulting complex may well be colourless. This is the case with the complex $[\text{FeF}_6]^{3-}$.

The ligand in a complex affects its redox properties and this is apparent from considering the relevant standard electrode potentials. For example, with copper(II) species:



Complexes are industrially important, for example in the purification of nickel mentioned above and in the extraction of gold which involves the complex $[\text{Au(CN)}_2]^-$.

Complex formation is used in estimating the concentrations of metal ions in solution. Examples of this are the use of EDTA in titration and dimethylglyoxime in gravimetric analysis. Complexes are also used in qualitative analysis, for example, in Tollens' reagent. This reagent is usually prepared by the addition of sodium hydroxide solution to an aqueous solution of silver nitrate followed by aqueous ammonia. The resulting solution contains diamminesilver(I) ions.



(a) The hydrated copper(II) ion is classed as a complex but the hydrated sodium ion is not. By considering the interaction between the water molecules and the sodium ion, explain why the hydrated sodium ion is **not** considered to be a complex.

(2)

(b) Suggest how the aluminium ion is able to form dative covalent bonds in its complexes such as $[\text{AlF}_6]^{3-}$.

(1)

*(c) (i) Transition metal complexes are usually coloured. Explain how the colours occur.

(4)

(ii) Why are zinc complexes such as $[\text{Zn}(\text{NH}_3)_4]^{2+}$ colourless?

(1)



(iii) Suggest why the strong interactions between the F^- ligands and Fe^{3+} ion result in the complex $[FeF_6]^{3-}$ being colourless.

(2)

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(d) Use the standard electrode potentials given in the passage to predict whether it is feasible for thiosulfate ions, $S_2O_3^{2-}$, to reduce copper(II) ions to copper. Consider the case when the copper(II) ions are dissolved in water, and when they are dissolved in aqueous ammonia. Give chemical equations to support your answer.

(3)

The relevant redox reaction for thiosulfate ions is



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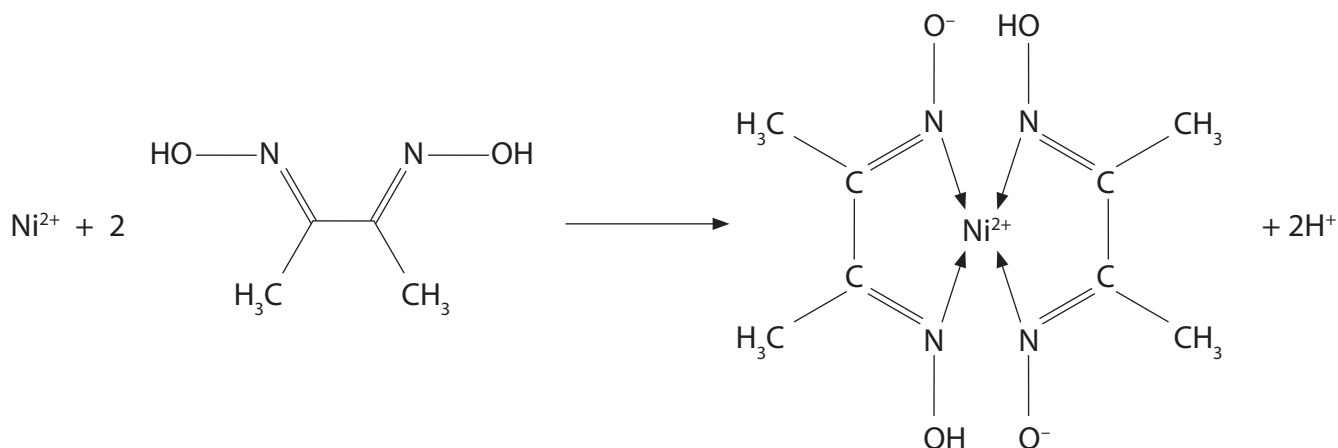
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- (e) The proportion of nickel in nisil, an alloy of nickel and silicon used in thermocouples, may be determined by the following gravimetric analysis.

Finely ground nisil is dissolved in concentrated hydrochloric acid and, after neutralization, excess dimethylglyoxime dissolved in ethanol is added to the solution formed. The resulting red precipitate is filtered, washed, dried and weighed. The equation for the formation of the precipitate is



- (i) State the coordination number of the nickel in the complex ion. (1)

- (ii) In an experiment, 1.02 g of nisil formed 4.82 g of the complex. Calculate the percentage by mass of nickel in the alloy. The molar mass of the complex is 288.7 g mol⁻¹. (2)



(f) Suggest why the nickel carbonyl complex is used to purify nickel ores.

(1)

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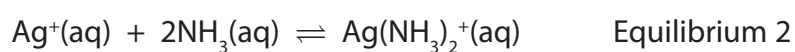
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(g) Use the equilibria below to explain why ammonia is used to prepare Tollens' reagent, as described in the passage.

(3)



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(Total for Question 22 = 20 marks)

TOTAL FOR SECTION C = 20 MARKS

TOTAL FOR PAPER = 90 MARKS



The Periodic Table of Elements

	1	2	Key										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)	
				relative atomic mass atomic symbol name atomic (proton) number															
	6.9 Li lithium 3	9.0 Be beryllium 4		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	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	4.0 He helium 2	
	23.0 Na sodium 11	24.3 Mg magnesium 12		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	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		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	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	
	132.9 Cs caesium 55	137.3 Ba barium 56		178.5 La* lanthanum 57	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	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	
	[223] Fr francium 87	[226] Ra radium 88		[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							
				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		
				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		

* Lanthanide series
* Actinide series

