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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>									
Sample Assessment Material							Paper Reference		
Time: 1 hour 40 minutes							WCH05/01		
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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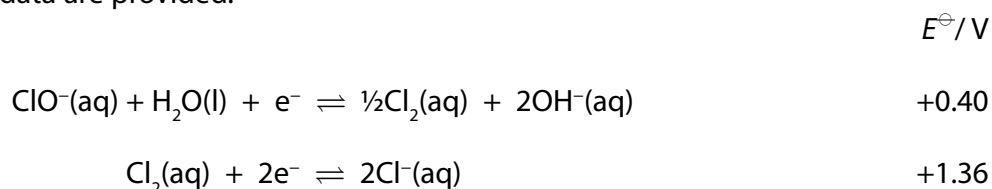
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SECTION A

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 The following data are provided.



What is the value of $E_{\text{cell}}^{\ominus}$ in which the following disproportionation reaction occurs?



- A $+\frac{1.36}{2} - 0.40 \text{ V}$
- B $+\frac{1.36}{2} + 0.40 \text{ V}$
- C $+ 1.36 - 0.40 \text{ V}$
- D $+ 1.36 + 0.40 \text{ V}$

(Total for Question 1 = 1 mark)

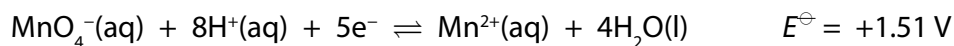
2 Which of the following is always proportional to $E_{\text{cell}}^{\ominus}$ for a chemical reaction?

- A $\Delta H_{\text{reaction}}$
- B ΔS_{system}
- C $\Delta S_{\text{surroundings}}$
- D ΔS_{total}

(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 electrode system based on the half-equation below has the standard electrode potential +1.51 V.

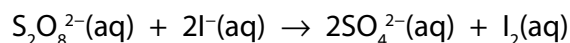


Which of the following statements about this electrode system is correct?

- A Changing the concentration of $\text{Mn}^{2+}(\text{aq})$ would cause a change in the electrode potential.
- B $\text{Mn}^{2+}(\text{aq})$ is acting as an oxidizing agent.
- C The electrode used is made of manganese.
- D When connected to a standard hydrogen electrode, the resulting cell voltage would be +0.51 V.

(Total for Question 3 = 1 mark)

- 4 Consider the following reaction.



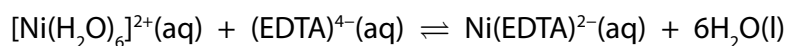
Which of the following ions could catalyse this reaction?

- A Zn^{2+}
- B Al^{3+}
- C Fe^{2+}
- D Na^+

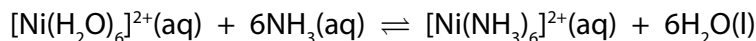
(Total for Question 4 = 1 mark)

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

5 EDTA ions form a complex with aqueous nickel(II) ions as shown by the equation



Aqueous nickel(II) ions also form a complex ion with ammonia as shown by the equation

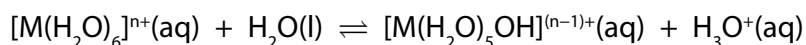


Aqueous nickel(II) ions form a more stable complex with EDTA ions than with ammonia because

- A six ammonia ligands cause steric hindrance around the central nickel(II) ion.
- B EDTA ions carry a negative charge whereas ammonia molecules do not.
- C there is a large increase in entropy when aqueous nickel(II) ions react with EDTA ions, but not when aqueous nickel(II) ions react with ammonia.
- D ammonia molecules tend to evaporate from the solution of the complex whereas EDTA ions do not.

(Total for Question 5 = 1 mark)

6 The hydrolysis of a transition metal cation can be represented by the following equation



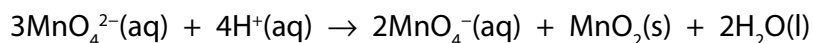
In this reaction

- A the solvent H_2O is acting as an acid by donating a proton to the metal cation.
- B the pH of the solution will be lower if the value of n is 2 instead of 3.
- C the equilibrium position lies further to the right if the value of n is 3 instead of 2.
- D the oxidation state of the metal in the cation has decreased from n to $(n - 1)$.

(Total for Question 6 = 1 mark)

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

- 7 In aqueous solution, manganate(VI) ions disproportionate into manganate(VII) ions and manganese(IV) oxide when carbon dioxide is bubbled through the solution. The ionic equation for the reaction is



The role of the carbon dioxide is to

- A lower the pH of the solution.
- B raise the pH of the solution.
- C oxidize the manganate(VI) ions.
- D reduce the manganate(VI) ions.

(Total for Question 7 = 1 mark)

- 8 Which of the following shows the correct oxidation states of **chromium** in the ions given?

	$[\text{Cr}(\text{OH})_6]^{3-}$	CrO_4^{2-}	$[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$
<input type="checkbox"/> A	-3	-2	+2
<input type="checkbox"/> B	-3	+10	+2
<input type="checkbox"/> C	+3	+8	+6
<input type="checkbox"/> D	+3	+6	+2

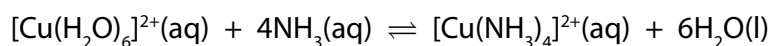
(Total for Question 8 = 1 mark)

- 9 Transition metals are often used as heterogeneous catalysts. Which of the following processes does **not** occur during such a catalysed reaction?

- A Adsorption of reactant molecules on the surface of the metal.
- B Bond breaking in the reactant molecules.
- C Desorption of product molecules from the surface of the metal.
- D An overall change in the oxidation number of the metal.

(Total for Question 9 = 1 mark)

10 Consider the equation below.



This reaction is best described as

- A acid-base.
- B redox.
- C addition.
- D ligand exchange.

(Total for Question 10 = 1 mark)

11 Which of the following will **not** reduce an acidified solution of potassium dichromate(VI)?

- A $(\text{CH}_3)_2\text{C}(\text{OH})\text{CH}_3$
- B FeSO_4
- C $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$
- D Zn

(Total for Question 11 = 1 mark)

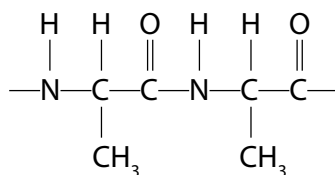
12 The total number of isomers of dibromobenzene, $\text{C}_6\text{H}_4\text{Br}_2$, containing a benzene ring is

- A 2
- B 3
- C 4
- D 5

(Total for Question 12 = 1 mark)

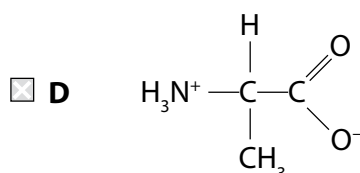
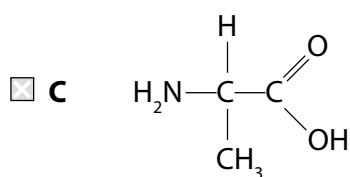
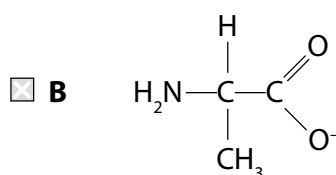
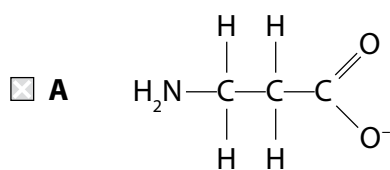
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13 A section of the polypeptide made from a single amino acid is shown below.



The polypeptide was heated with excess dilute sodium hydroxide solution until no further change took place.

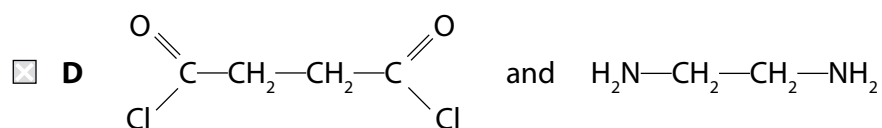
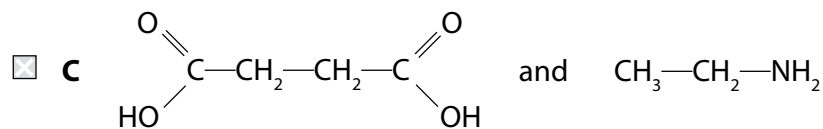
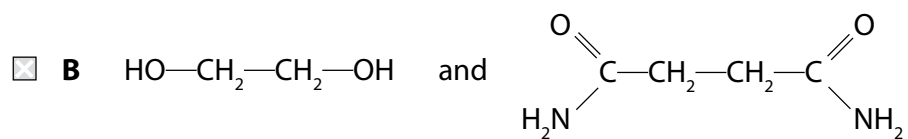
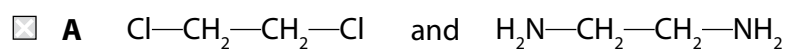
Which of the following products is formed?



(Total for Question 13 = 1 mark)

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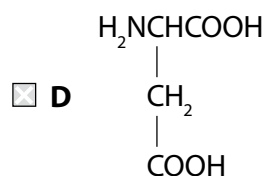
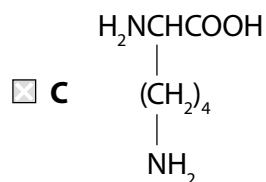
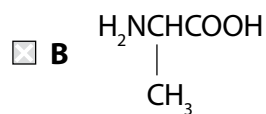
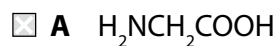
14 Which of the following pairs of compounds could form a polyamide?



(Total for Question 14 = 1 mark)

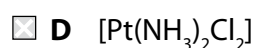
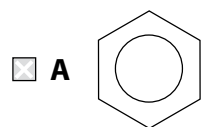
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15 Which of the following amino acids is optically active and produces an approximately neutral solution when dissolved in water?



(Total for Question 15 = 1 mark)

16 Which of the following is **not** planar?



(Total for Question 16 = 1 mark)

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

17 A 50 cm³ sample of a gaseous hydrocarbon required exactly 250 cm³ of oxygen for complete combustion. A volume of 150 cm³ of carbon dioxide was produced.

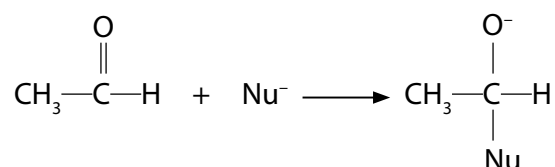
[All volume measurements were made at the same temperature and pressure.]

Which of the following is the correct formula of the hydrocarbon?

- A C₃H₄
- B C₃H₈
- C C₅H₁₀
- D C₅H₁₂

(Total for Question 17 = 1 mark)

18 The first step of a nucleophilic addition reaction to a carbonyl group by a nucleophile, Nu⁻, is shown below.



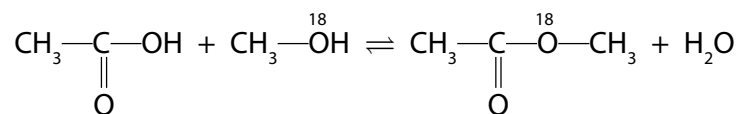
The above step is possible because the

- A nucleophile bonds to the δ⁺ carbon atom and the carbonyl oxygen accepts an electron pair from the double bond.
- B nucleophile bonds to the δ⁺ carbon atom and the carbonyl oxygen accepts one electron from the double bond.
- C methyl group donates electrons to the carbonyl carbon atom.
- D C=O bond is weak.

(Total for Question 18 = 1 mark)

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

- 19 In a reaction carried out between ethanoic acid and methanol, the methanol was labelled with the ^{18}O isotope. The ^{18}O was found to be in the organic product of the reaction



From the above information it can be deduced that the mechanism involves

- A free radical substitution.
- B breaking the C—O bond in the ethanoic acid.
- C nucleophilic attack by ethanoic acid on methanol.
- D breaking the C— ^{18}O bond in methanol.

(Total for Question 19 = 1 mark)

- 20 The hydride ion, H^- , is a strong reducing agent, a good nucleophile and a strong base.

Which of the following changes could **not** be brought about by the hydride ion?

- A CH_3CHO to $\text{CH}_3\text{CH}_2\text{OH}$
- B $\text{C}_2\text{H}_5\text{Br}$ to C_2H_6
- C $\text{CH}_2=\text{CH}_2$ to C_2H_6
- D CH_3COOH to CH_3COO^-

(Total for Question 20 = 1 mark)

TOTAL FOR SECTION A = 20 MARKS

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SECTION B

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

21 Hydrogen-oxygen fuel cells can operate in acidic or alkaline conditions. One such commercial cell uses porous platinum electrodes in contact with concentrated aqueous potassium hydroxide solution, KOH(aq).

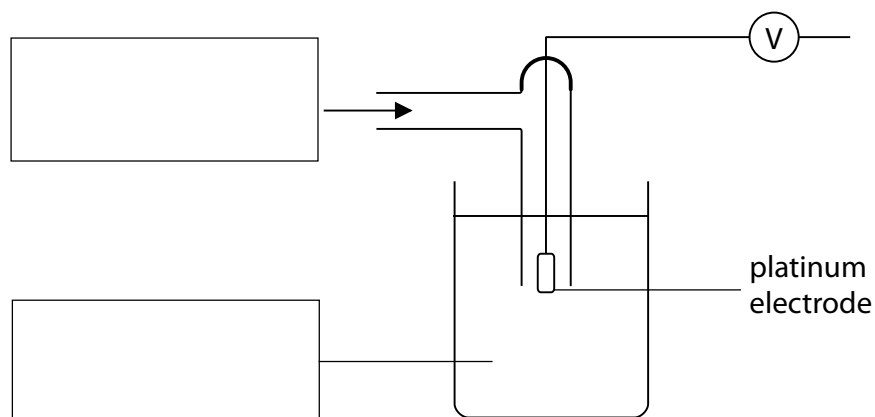
(a) Use relevant standard electrode potential values, on pages 15 and 17 of the Data Booklet, to complete the table below in which two E^\ominus values are missing.

(2)

Half-equation	E^\ominus / V
$2\text{H}_2\text{O}(\text{l}) + 2\text{e}^- \rightleftharpoons 2\text{OH}^-(\text{aq}) + \text{H}_2(\text{g})$	-0.83
$2\text{H}^+(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{H}_2(\text{g})$	0.00
$\text{O}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) + 4\text{e}^- \rightleftharpoons 4\text{OH}^-(\text{aq})$	
$\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^- \rightleftharpoons 2\text{H}_2\text{O}(\text{l})$	

(b) (i) Fill in the boxes to identify, by name or formula, the substances used in the **standard** hydrogen electrode.

(2)



(ii) State **three** conditions that are necessary for a standard hydrogen electrode.

(2)

- 1.....
- 2.....
- 3.....

(c) Write appropriate half-equations and use them to derive an overall equation for the reaction which occurs when an **alkaline** hydrogen-oxygen fuel cell operates.

(2)

(d) Use the E^\ominus values from the table in part (a) to calculate the E^\ominus_{cell} for a hydrogen-oxygen fuel cell operating in alkaline conditions.

(1)

(e) Suggest why the E^\ominus_{cell} for a hydrogen-oxygen fuel cell, operating in **acidic** conditions, is identical to that of an alkaline fuel cell.

(1)

(f) Give **one** reason (other than cost implications) why the platinum electrodes are made by coating porous material with platinum rather than by using platinum rods.

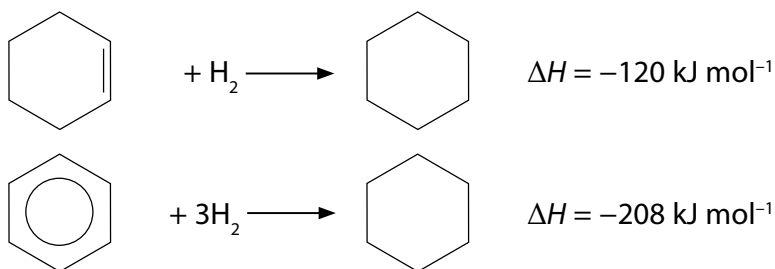
(1)

(g) Suggest **one** disadvantage of using a hydrogen-oxygen fuel cell compared with a rechargeable battery when providing electrical energy for a motor vehicle.

(1)

(Total for Question 21 = 12 marks)

- 22 (a) Equations for the catalytic hydrogenation of cyclohexene and of benzene are shown below.



- (i) What is the type of reaction in both of these hydrogenations?

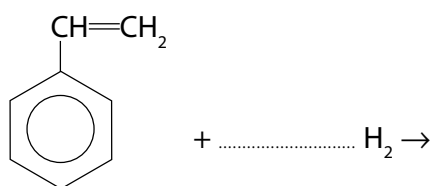
(1)

- *(ii) The enthalpy of hydrogenation of benzene might be expected to be -360 kJ mol^{-1} . Explain why this is **not** the actual value.

(2)

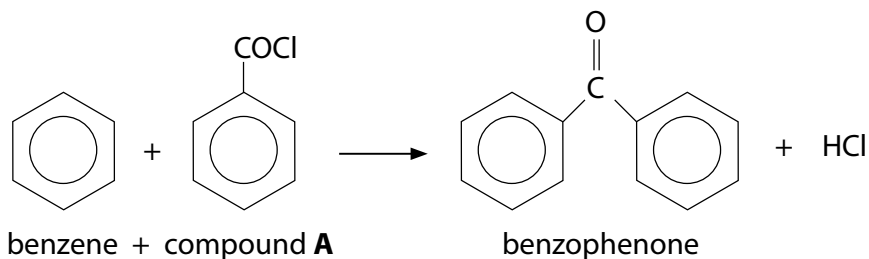
- (iii) Complete the following equation for the total hydrogenation of phenylethene. Suggest a value for the enthalpy change of this reaction.

(3)



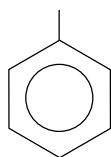
$\Delta H = \dots\dots\dots \text{ kJ mol}^{-1}$

- (b) The compound benzophenone is used as a sunscreen. It can be prepared from benzene, in the presence of aluminium chloride by the following reaction.



- (i) Complete the diagram below by showing the **displayed** formula of the -COCl group in compound **A**.

(1)



- (ii) Classify the type and mechanism of the reaction between benzene and compound **A**.

(1)

- (iii) Give the names of the two chemists associated with the type of reaction described in (b)(ii).

(1)

..... and

- (iv) Give the mechanism for the reaction between benzene and compound **A** in the presence of an aluminium chloride catalyst.

Start by showing the equation for the generation of the species which then attacks the benzene ring.

(4)

Equation to show generation of species attacking the benzene ring:

Rest of the mechanism:

- (v) Suggest the essential property of a substance that will be used as a sunscreen.

(1)

.....

.....

- (c) (i) The identity of a sample of benzophenone can be confirmed by recording its infrared and proton nmr spectra.

Identify **two** different bonds that would produce an absorption in the infrared spectrum of benzophenone. Use the Data Booklet to suggest the wavenumber of each of these absorptions.

(4)

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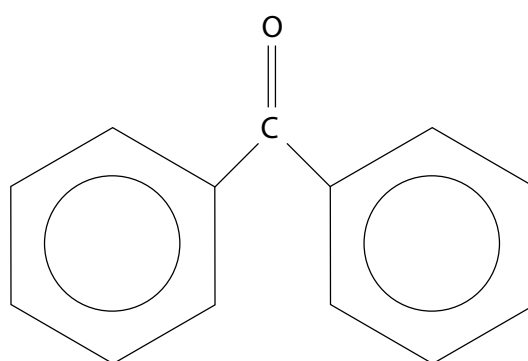
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- (ii) In benzophenone there are three different hydrogen environments, X, Y and Z, that produce signals in the ratio 2:2:1 respectively in the proton nmr spectrum.

Identify, **on the structure drawn below**, the positions of all the hydrogen atoms in each environment, labelling the different environments **X, Y and Z**.

(2)



benzophenone

(Total for Question 22 = 20 marks)

23 A scientist investigated the typical behaviour of primary amines.

(a) Amines such as butylamine, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$, and phenylamine, $\text{C}_6\text{H}_5\text{NH}_2$, both behave as bases.

(i) Which feature of an amine molecule allows it to act as a base?

(1)

(ii) The scientist reacted butylamine with two different acids.

Give the **formulae** of the salts that are formed when butylamine reacts with

(2)

sulfuric acid, H_2SO_4

ethanoic acid, CH_3COOH

(b) Phenylamine, $\text{C}_6\text{H}_5\text{NH}_2$, is formed by the reduction of nitrobenzene, $\text{C}_6\text{H}_5\text{NO}_2$.

Give the reagents that are used for this reduction.

(2)

(c) Phenylamine was reacted with a mixture of sodium nitrite, NaNO_2 , and hydrochloric acid at a temperature between 0°C and 5°C . A diazonium ion was formed. In a second step, the scientist reacted the diazonium ion with phenol, under suitable conditions. A precipitate of 4-hydroxyazobenzene (4-hydroxyphenylazobenzene) was formed.

(i) Draw the structure of the diazonium ion, clearly displaying the functional group present in the ion.

(1)

(ii) Draw the structural formula of 4-hydroxyazobenzene.

(1)

(iii) State a condition, other than a suitable temperature, required for the reaction of the diazonium ion with phenol and give a use for 4-hydroxyazobenzene.

(2)

Condition required:

.....

Use for 4-hydroxyazobenzene:

.....

- (d) The scientist repeated the first step in experiment (c), but the temperature was allowed to rise above 10 °C. Under these conditions, the diazonium ion reacted with water to produce phenol. An unreactive gas, of molar mass 28.0 g mol⁻¹, was also formed along with one other product.

Use this information to write the equation for the reaction of the diazonium ion with water.

(2)

- (e) The impure sample of 4-hydroxyazobenzene formed in part (c) may be purified by recrystallization. During this process

- the solid is dissolved in the minimum volume of hot solvent
- the mixture is then filtered whilst still hot
- the filtrate is cooled in an ice bath to produce crystals of 4-hydroxyazobenzene
- the crystals are removed by filtration and dried.

- (i) Why is the “minimum volume of hot solvent” used?

(1)

- (ii) The impure 4-hydroxyazobenzene may contain both insoluble and soluble impurities. Describe how

(2)

I. insoluble impurities are removed during recrystallization

II. soluble impurities are removed during recrystallization

(iii) How would you check the purity of 4-hydroxyazobenzene after recrystallization, other than by using spectroscopy?

(1)

.....

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(Total for Question 23 = 15 marks)

TOTAL FOR SECTION B = 47 MARKS

SECTION C

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

24

Titanium is the seventh most abundant metal in the Earth's crust and occurs principally as rutile (impure titanium(IV) oxide, TiO_2).

Early attempts to extract the metal from its oxide by reduction with heated carbon failed because the compound titanium carbide is formed. In 1910, however, pure titanium was made by heating titanium(IV) chloride with sodium.

Titanium has a high melting temperature and a density of 4.50 g cm^{-3} . Titanium is as strong as steel, but is about 40% less dense and is therefore suitable for use in the aircraft industry. Titanium metal resists corrosion as it has an impervious coating of titanium(IV) oxide. The metal adheres well to bone, is not rejected by the body and is in demand for the manufacture of replacement joints.

Titanium has two common oxidation states, +3 and +4. Solutions containing the $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}(\text{aq})$ ion, such as titanium(III) chloride, are purple in colour and are readily oxidized by the oxygen in air to colourless titanium(IV) ions. An aqueous solution of titanium(III) chloride is a strong reducing agent. Titanium(IV) chloride, TiCl_4 , is a colourless liquid with a boiling temperature of 136°C . This compound is used, in conjunction with organic compounds of aluminium, as a catalyst for the polymerization of propene to poly(propene). Titanium(IV) chloride is hydrolysed by water to give titanium(IV) oxide, TiO_2 and hydrogen chloride gas.

Titanium(IV) oxide is a white, non-toxic solid at room temperature. It is used as a white pigment in paint, largely replacing toxic lead compounds which were used previously. Titanium(IV) oxide reacts with concentrated sulfuric acid to form a salt and water. Titanium(IV) oxide also reacts with aqueous potassium hydroxide solution, under suitable conditions, to form a compound with formula $\text{K}_2\text{Ti}(\text{OH})_6$.

- (a) (i) Write the equation for the reaction which occurs during the manufacture of titanium from titanium(IV) chloride as described in the article above. State symbols are not required.

(1)

(ii) Explain, by stating the changes of oxidation numbers, why the reaction in (i) is classified as a redox reaction.

(2)

.....

.....

.....

(b) Complete the electronic configurations of

(2)

Ti [Ar]

Ti³⁺ [Ar]

Ti⁴⁺ [Ar]

(c) Use your answer to (b) to explain why titanium is

(i) a *d*-block element

(1)

.....

.....

(ii) a transition element

(1)

.....

.....

*(d) (i) Explain why the hexaaquatitanium(III) ion, $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$, is coloured.

(3)

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(ii) Explain briefly why titanium(IV) compounds are colourless.

(1)

.....

.....

*(e)(i) Titanium(IV) oxide has a melting temperature of 1830 °C. Use this data, plus information in the article at the start of the question, to compare the structure and bonding in titanium(IV) oxide with that in titanium(IV) chloride. Hence explain why these two compounds change state at very different temperatures.

(4)

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(ii) Give the term used to describe an oxide, such as titanium(IV) oxide, which can react with both acids and bases.

(1)

(iii) Using information in the article, write the equation for the reaction between titanium(IV) oxide and aqueous potassium hydroxide solution. State symbols are not required.

(1)

(iv) Titanium(IV) chloride is one of the catalysts used in the polymerization of propene to form poly(propene).

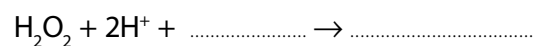
Give the displayed formula of the repeat unit of poly(propene).

(1)

(f) The concentration of a solution of titanium(III) chloride can be determined by titration with a solution of hydrogen peroxide, H_2O_2 , in acidic conditions. The end-point of the reaction is when the solution of titanium(III) chloride in the flask goes colourless.

(i) Complete the ionic half-equation to show the reduction of hydrogen peroxide.

(1)



- * (ii) One mole of hydrogen peroxide reacts with two moles of titanium(III) chloride.

In an experiment, 5.00 cm^3 of a sample of titanium(III) chloride solution was transferred to a volumetric flask and made up to 250 cm^3 of an aqueous solution. A 25.0 cm^3 portion of this diluted solution was acidified and titrated with a $0.0200 \text{ mol dm}^{-3}$ solution of hydrogen peroxide, H_2O_2 . The mean titre was 22.50 cm^3 .

Calculate the concentration of the **original** titanium(III) chloride solution, in mol dm^{-3} .

(3)

- (iii) Use information in the article to suggest why this titration gives a value that is lower than the true value for the concentration of titanium(III) chloride solutions.

(1)

(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

1	2							3	4	5	6	7	0 (8)		
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	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	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	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	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	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	[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	[277] Hs hassium 108	[268] Mt meitnerium 109	[271] Ds darmstadtium 110	[272] Rg roentgenium 111						
* 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

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

1.0	H
hydrogen	1

Key

relative atomic mass
atomic symbol
name
atomic (proton) number

