Examiners' Report

June 2013

GCE Chemistry 6CH05 01

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Introduction

The paper proved accessible to most candidates and provided them with the opportunity to demonstrate their knowledge and understanding of the key concepts in Unit 5. There was very little evidence of candidates having insufficient time to complete the paper.

The mean score for the multiple-choice questions in Section A was 14/20. Questions 2, 8 and 10 were found to be the most straightforward, whilst Questions 6, 11 and 20 were found to be the most demanding of the multiple-choice items.

Candidates attempted the volumetric calculations with confidence and the reagents required for organic reactions were accurately recalled by the majority of candidates. The questions requiring the application of knowledge, e.g. those relating to fuel cells, were found to be the most challenging. Rather more surprisingly, Q24(e)(i) was found to be the most difficult structured question despite the fact that it covered fundamental aspects of structure and bonding.

Question 21(a)

(2)

Half-equation	$E^{\ominus}$ / V
$2H_2O(l) + 2e^- \rightleftharpoons 2OH^-(aq) + H_2(g)$	−0.83
$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$	0.00
$O_2(g) + 2H_2O(l) + 4e^- \rightleftharpoons 4OH^-(aq)$	+0.40
$O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(l)$	+1.23

+1.23

ResultsPlus
Examiner Comments

The candidate has correctly looked up the relevant data in the Data Booklet.

ResultsPlus
Examiner Tip

Be familiar with the Data Booklet before the A2 examinations so that you can easily find your way around it.

Half-equation	$E^{\ominus}$ / V
$2H_2O(l) + 2e^- \rightleftharpoons 2OH^-(aq) + H_2(g)$	-0.83
$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$	0.00
$O_2(g) + 2H_2O(l) + 4e^- \rightleftharpoons 4OH^-(aq)$	$+4.0$
$O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(l)$	$+1.23$

ResultsPlus
Examiner Comments

This answer scored one of the two marks available. The first missing voltage should have been "+0.40" V rather than "+4.0", as written.
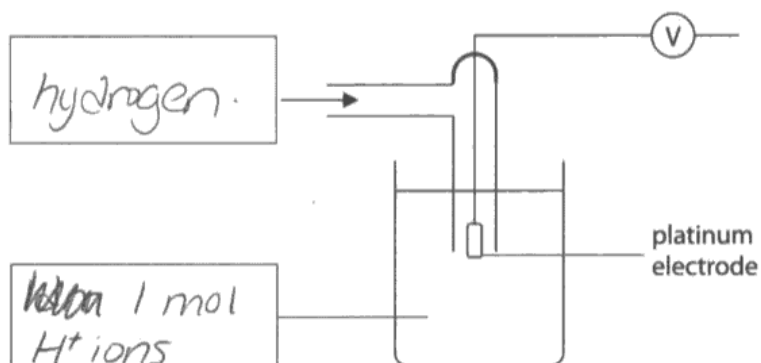
ResultsPlus
Examiner Tip

Always double-check any data that you extract from your Data Booklet!

Question 21(b)(i)

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

(2)

hydrogen.

1 mol H^+ ions

platinum electrode

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

(2)

Box 1: Hydrogen gas

Box 2: 1 M solution of test ions

platinum electrode

ResultsPlus
Examiner Comments

The candidate has identified hydrogen gas correctly, but has not given the name or formula of a suitable acid for the solution surrounding the platinum electrode.

Question 21(b)(ii)

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

(2)

1. H_2 gas bubbled through at 1 atm (101 kPa)
2. 1 mol dm^{-3} H$^+$ ions in the solution (HCl in this case)
3. Standard temperature (25°C or 273K)

ResultsPlus
Examiner Comments

There is a contradiction in this answer as 25°C equates to 298K, rather than 273K.

ResultsPlus
Examiner Tip

Be careful when converting from °C to K.

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

(2)

1. Temperature is 25°C
2. HCl is at 1 mol dm^{-3}
3. H_2 gas is at 1 atm

ResultsPlus
Examiner Comments

The conditions necessary for a standard hydrogen electrode are correctly identified.
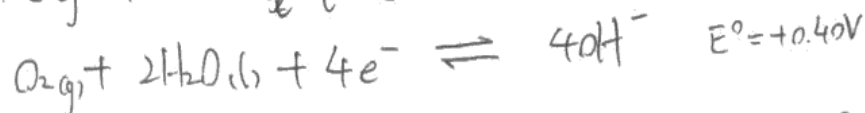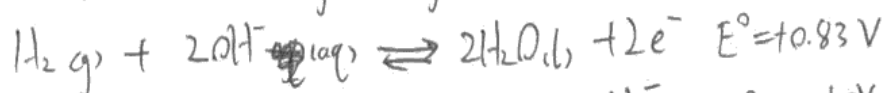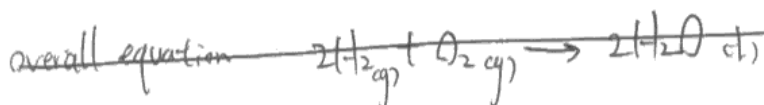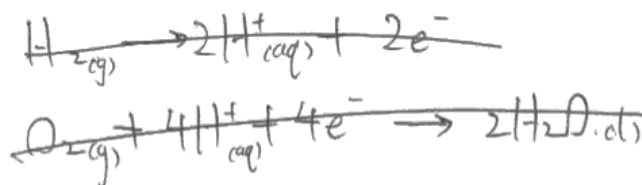
ResultsPlus
Examiner Tip

Recall the units of standard conditions accurately in this type of question.

Question 21(c)

Many candidates ignored 'alkaline' in the question and selected half-equations containing H^+ ions. A surprising number, who had selected the half-equations correctly, were then unable to add these half-equations appropriately. Often, they did not cancel out the hydroxide ions and the extra water molecules.

(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)

$$H_{2(g)} \rightarrow 2H^+_{(aq)} + 2e^-$$

$$O_{2(g)} + 4H^+_{(aq)} + 4e^- \rightarrow 2H_2O_{(l)}$$

overall equation $\quad 2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(l)}$

$$H_{2(g)} + 2OH^-_{(aq)} \rightleftharpoons 2H_2O_{(l)} + 2e^- \quad E^\circ = +0.83\ V$$

$$O_{2(g)} + 2H_2O_{(l)} + 4e^- \rightleftharpoons 4OH^- \quad E^\circ = +0.40\ V$$

overall equation $\quad 2H_2O^+ \quad 2H_{2(g)} + O_{2(g)} \rightarrow H_2O_{(l)}$

ResultsPlus
Examiner Comments

The candidate has correctly selected the two half-equations. However, the equation for the reaction between hydrogen and oxygen forming water is not balanced correctly.
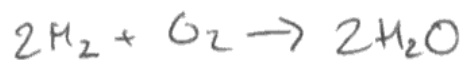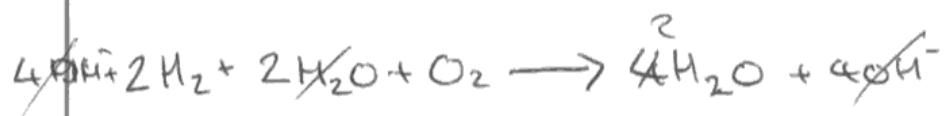
ResultsPlus
Examiner Tip

Always check that your equations are balanced!

(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)

$$4OH^- \longrightarrow O_2 + 2H_2O + 4e^-$$

$$H_2 + 2OH^- \longrightarrow 2e^- + 2H_2O \quad \times 2$$

$$2H_2O + O_2 + 4e \longrightarrow 4OH^-$$

$$4OH^- + 2H_2 + 2H_2O + O_2 \longrightarrow 4H_2O + 4OH^-$$

$$2H_2 + O_2 \longrightarrow 2H_2O$$
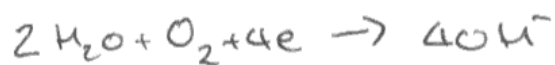
ResultsPlus
Examiner Comments

The correct half-equations have been selected and then combined together to give the equation for the reaction between hydrogen and oxygen to form water.

Question 21(d)

The majority of candidates scored the mark available, although some selected the wrong values from the table.

(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)

$$E^{\ominus}_{cell} = 0.00 - (+0.40)$$
$$= -0.4 \text{ V} \checkmark$$

ResultsPlus
Examiner Comments

The $E^{\ominus}$ value for the standard hydrogen electrode has wrongly been included in this answer.

ResultsPlus
Examiner Tip

Always check the data that you are using in any calculation. The $E^{\ominus}$ value for the cell when operating cannot have a negative value.

(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)

$$0.4 - (-0.83) = +1.23 \checkmark .$$

ResultsPlus
Examiner Comments

The working and answer are both correct here.

Question 21(e)

A large proportion of the candidates did not appreciate that the overall redox reaction was the same, regardless of the conditions. The value of +1.23 V from (d) was often quoted.

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

(1)

the overall equation is the same $(2H_2(g) + O_2(g) \rightleftharpoons 2H_2O(l))$ and $+1.23V - 0.00V = +1.23V.$

ResultsPlus
Examiner Comments

The equation for the reaction occurring in a hydrogen-oxygen fuel cell is the same, whether it operates under acidic or alkaline conditions.

ResultsPlus
Examiner Tip

Practise combining half-equations relating to fuel cells.

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

(1)

The initial reactants and final products are the same.

ResultsPlus
Examiner Comments

This answer effectively explains that the overall reaction occurring is the same, whether the cell operates under acidic or alkaline conditions.

Question 21(f)

Surprisingly few candidates mentioned the increase in surface area as a result of the coating. Answers relating to porosity, electrical conductivity, expense and inertness were common.

Platinum is a good conductor of electricity.

(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)

Poor electrical conductivity

ResultsPlus
Examiner Comments

The increase in surface area is not mentioned in this answer.

(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)

Increases surface area

ResultsPlus
Examiner Comments

This answer addresses the increase in surface area.

ResultsP
Examiner Tip

Understand all the features of a standard hydrogen electrode.

Question 21(g)

Most candidates could correctly identify a disadvantage of a hydrogen-oxygen fuel cell.

(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)

...... • Always Has to be a constant flow of

...... H_2 & O_2 supplied

(Total for Question 21 = 12 marks)

ResultsPlus
Examiner Comments

This response acknowledges the fact that constant replenishment with hydrogen and oxygen is required in such a fuel-cell.

Question 22(a)(i)

The majority of candidates could classify the hydrogenation reactions correctly.

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

$\Delta H = -120$ kJ mol^{-1}

$\Delta H = -208$ kJ mol^{-1}
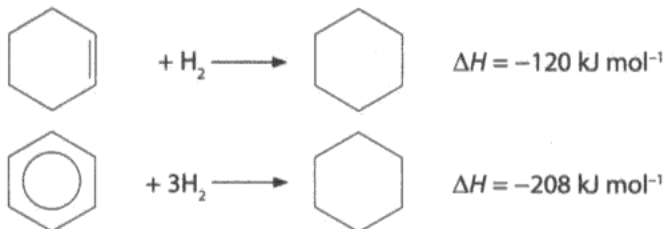
(i) What is the type of reaction in both of these hydrogenations?

(1)

Addition

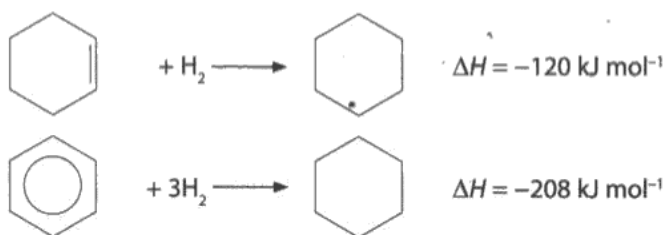### ResultsPlus
Examiner Comments

Hydrogenation is an example of an addition reaction.

ResultsPlus
Examiner Tip

Be able to classify reactions in more than one way where appropriate.

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

$+ H_2$ ⟶ $\Delta H = -120$ kJ mol^{-1}

$+ 3H_2$ ⟶ $\Delta H = -208$ kJ mol^{-1}

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

(1)

Reduction.

ResultsPlus
Examiner Comments

Gain of hydrogen is also a definition of reduction.

ResultsPlus
Examiner Tip

Be able to classify reactions in more than one way where appropriate.

Question 22(a)(ii)

Most of the candidates mentioned delocalisation and then linked this to the stability conferred by the benzene ring. There were often unnecessary references to carbon-carbon bond lengths in the benzene ring.

*(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)

The electrons in benzene are delocalized and therefore does not equate to the value of three C=C double bonds. Therefore less energy is required than expected.

ResultsPlus
Examiner Comments

This answer includes a reference to delocalisation of electrons in benzene. However, the resultant stability means that more energy is required to break the bonds in benzene rather than less.

ResultsPlus
Examiner Tip

Always check the logic of arguments in your answer.

*(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)

Due to the π system, the p-orbital overlap creating a delocalised ring. This structure is more stable and will undergo substitution reactions more readily than addition reactions to preserve this delocalised ring arrangement.
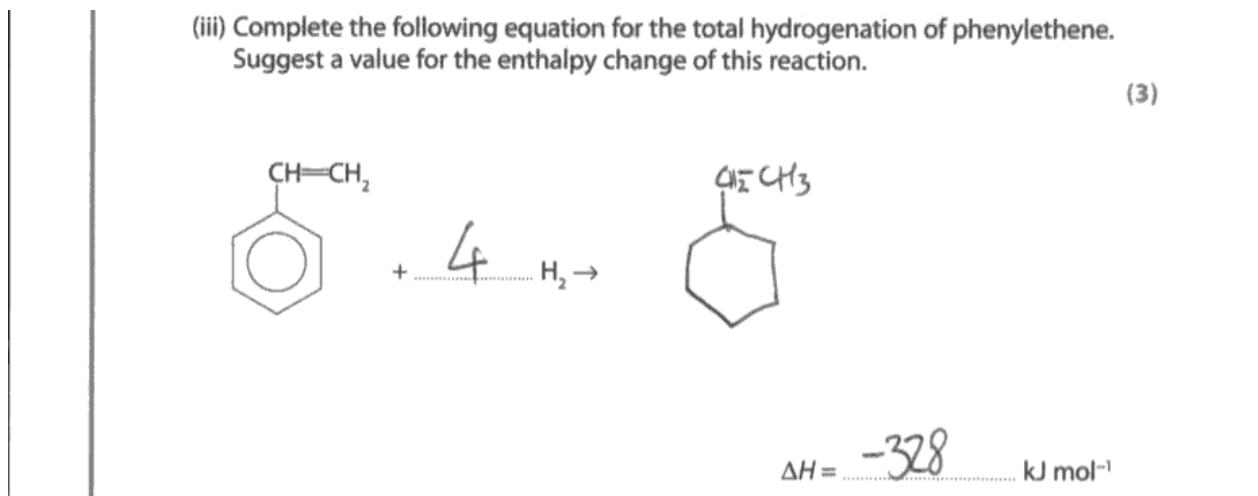
ResultsPlus
Examiner Comments

This answer addresses both the delocalisation in benzene and the resulting stability conferred on the molecule as a result.

Question 22(a)(iii)

Few candidates obtained all three available marks here. Identifying the correct number of moles of hydrogen molecules proved to be the most difficult hurdle to negotiate. Often, there was no attempt made to draw the final product of the reaction.
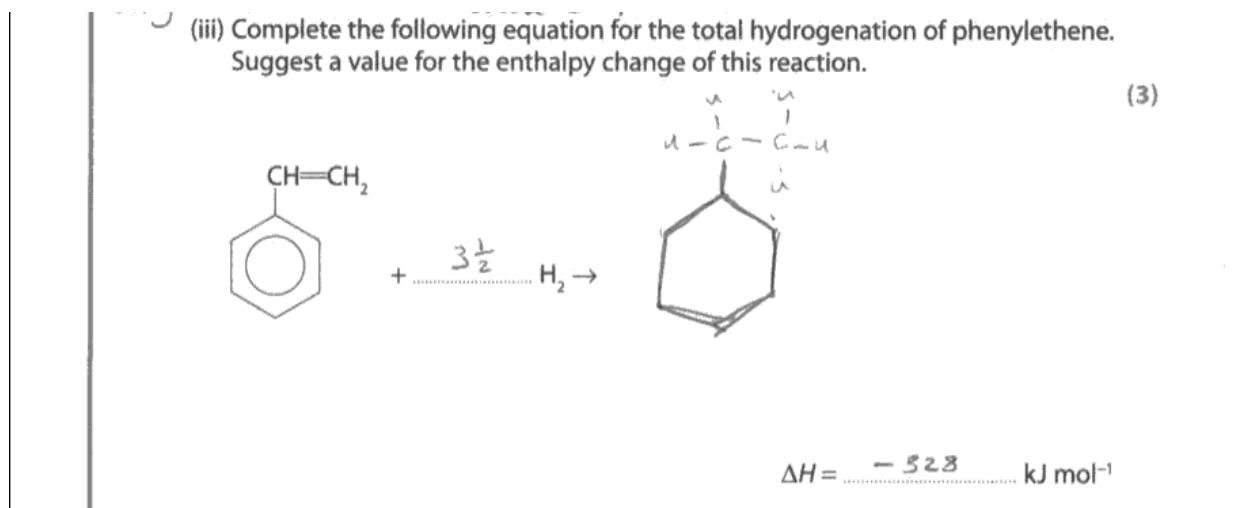
(iii) Complete the following equation for the total hydrogenation of phenylethene. Suggest a value for the enthalpy change of this reaction.

(3)

$CH=CH_2$

$+$ ...4... $H_2 \rightarrow$

$CH_2 CH_3$

$\Delta H =$ ...−328... $kJ\ mol^{-1}$

ResultsPlus
Examiner Comments

The moles of hydrogen, the structure of the product and the total enthalpy change (-208) + (-120) = -328 kJ mol⁻¹ have been correctly stated.

ResultsPlus
Examiner Tip

Check for all possible parts of the molecule that can undergo reduction with molecular hydrogen.

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

(3)

$CH=CH_2$

$+$ ...$3\frac{1}{2}$... $H_2 \rightarrow$

$H-C-C-H$

$\Delta H =$ ...− 528... $kJ\ mol^{-1}$

ResultsPlus
Examiner Comments

The correct product and enthalpy change have both been given. The number of moles of hydrogen, however, should have been given as four.
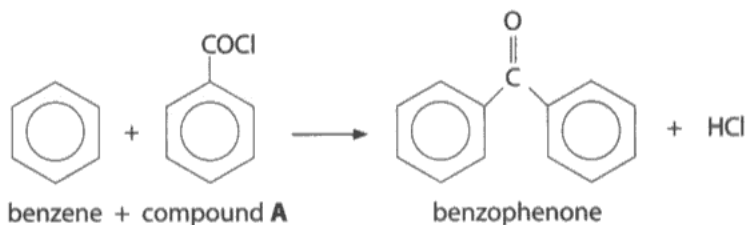
ResultsPlus
Examiner Tip

Always check the number of hydrogen atoms in the reactant and the product. There are eight hydrogen atoms in the reactant molecule and sixteen hydrogen atoms in the product molecule. Therefore, four molecules of hydrogen, H_2, will be added to each organic reactant molecule.
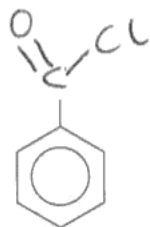
Question 22(b)(i)

Almost all candidates were able to draw out the acid chloride group correctly.

(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.

benzene + compound **A** → benzophenone + HCl

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

(1)

Question 22(b)(ii)

A high percentage of candidates were able to classify the reaction type and mechanism correctly as electrophilic substitution. Omission of the word 'electrophilic' was the most frequent reason for this mark not to be awarded.

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

electrophilic substitution (1)

electrophilic substitution

ResultsPlus
Examiner Comments

The reaction type and mechanism have both been identified correctly.

ResultsPlus
Examiner Tip

Remember to include both the words 'substitution' and 'electrophilic' when asked to classify the reaction type and mechanism.

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

(1)

electrophilic substitution / friedel crafts acylation

(iii) Give the names of the two chemists associated with the type of reaction

ResultsPlus
Examiner Comments

The word 'acylation' was ignored and the mark was awarded for the correct answer.

Question 22(b)(iii)

Friedel-Crafts reactions are mentioned in Topic 5.4 (1)(c) of the Unit 5 specification.

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

(1)

Friedel and Crafts

ResultsPlus
Examiner Comments

Both chemists have been correctly identified.

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

(1)

freidel and Craft

ResultsPlus
Examiner Comments

Slight misspellings were ignored if the names of both chemists could be recognised.
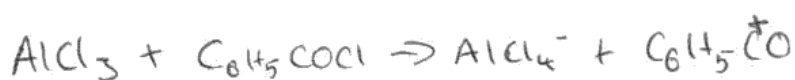
Question 22(b)(iv)

There were many clear and accurate representations of the mechanism. Some candidates, however, chose their own acid chloride instead of using benzoyl chloride. Three out of four was the typical mark for this question. Curly arrows sometimes started from, or finished at, the wrong place.

(iv) Give the mechanism for the reaction between benzene and compound **A** in the presence of an aluminium chloride catalyst.
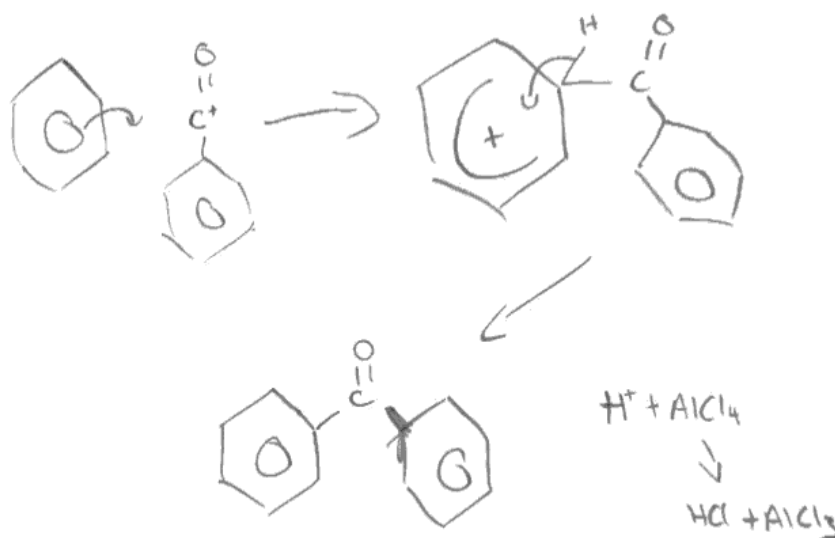
Start by showing the equation for the generation of the species which then attacks the benzene ring.

(4)

Equation to show generation of species attacking the benzene ring:

$$AlCl_3 + C_6H_5COCl \rightarrow AlCl_4^- + C_6H_5\overset{+}{C}O$$

Rest of the mechanism:

$$H^+ + AlCl_4^-$$
$$\downarrow$$
$$HCl + AlCl_3$$

ResultsPlus
Examiner Comments

All four scoring points in the Mark Scheme were awarded for this response.

ResultsPlus
Examiner Tip

Practise drawing mechanisms that include 'curly arrows' and make sure you understand what these arrows mean in terms of the movement of electron pairs.

(iv) Give the mechanism for the reaction between benzene and compound **A** in the presence of an aluminium chloride catalyst.
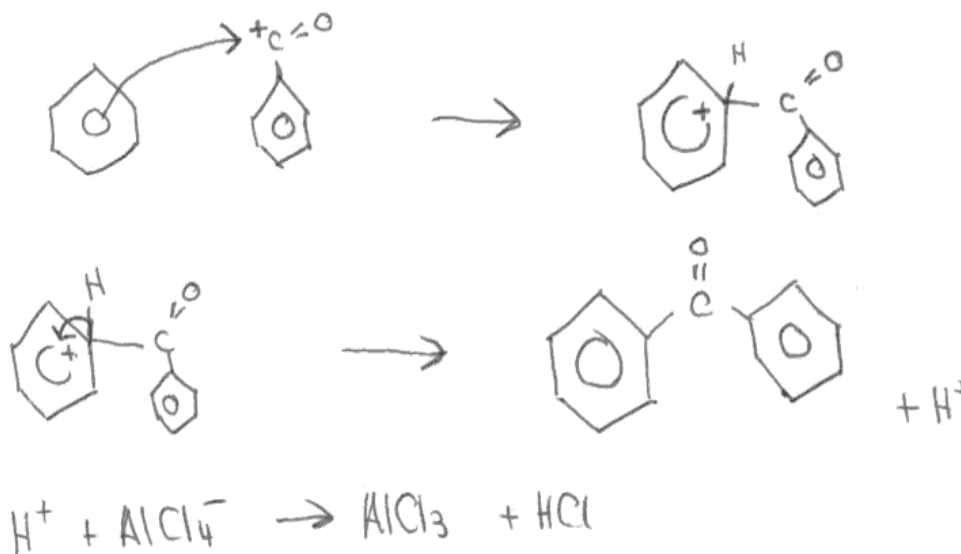
Start by showing the equation for the generation of the species which then attacks the benzene ring.

(4)

Equation to show generation of species attacking the benzene ring:

Rest of the mechanism:

$H^+ + AlCl_4^- \rightarrow AlCl_3 + HCl$

Question 22(b)(v)

Almost two-thirds of candidates were able to answer this question correctly. They suggested that the substance should either absorb or reflect UV light. Other candidates did not give a specific reason or only suggested that the substance should be non-toxic.

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

(1)

It reflects UV light.

ResultsPlus
Examiner Comments

This correct response was awarded the mark available.

Question 22(c)(i)

A significant number of candidates achieved all four marks for selecting the correct bonds and wavenumbers. Marks were lost, however, for not specifying the bond (e.g. writing just 'ketone', instead of C=O) or for selecting the wavenumber values incorrectly from the Data Booklet.

(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)

C=O, wavenumber : 1700-1680
C=C, wavenumber : 1600 - 1450

ResultsPlus
Examiner Comments

This response scored three out of the four available marks. For the C=C bond, all four specific wavenumbers 1600, 1580, 1500 and 1450 cm^{-1} had to be quoted rather than the range as given by this candidate.

ResultsPlus
Examiner Tip

Always quote data accurately from the Data Booklet.

(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)

C=O group. wavenumber of 1700-1680 cm^{-1}
C-H group in benzene ring. Wavenumber of 3030 cm^{-1}

ResultsPlus
Examiner Comments

This response was awarded all four marks.

ResultsPlus
Examiner Tip

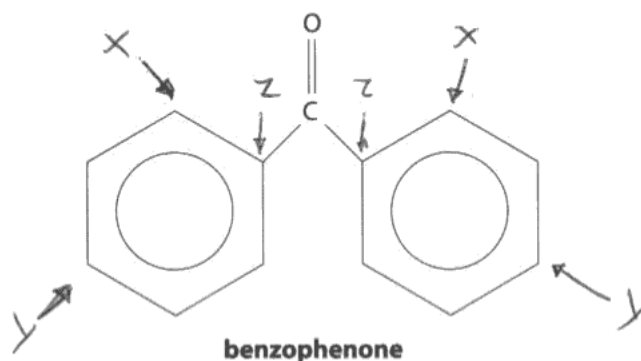Double-check any data that you quote from the Data Booklet.

Question 22(c)(ii)

This question on NMR was not answered well by the majority of candidates. A few correctly identified the three proton environments, but then used letters which did not fit the 2:2:1 ratio given. Quite often, one of the letters **X**, **Y** or **Z** was placed at a point on the ring where there is no proton.

(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)

(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)

ResultsPlus
Examiner Comments

One mark was awarded for this response. The proton environment, **Z**, has been shown correctly on each of the benzene rings. The environments **X** and **Y** have not been correctly labelled, however.

Question 23(a)(i)

The majority of candidates identified that the nitrogen atom in the -NH$_2$ group has a lone pair of electrons. However, a substantial number mentioned only that an amine group can accept a proton without stating the reason for this.

23 A scientist investigated the typical behaviour of primary amines.

(a) Amines such as butylamine, $CH_3CH_2CH_2CH_2NH_2$, and phenylamine, $C_6H_5NH_2$, both behave as bases.

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

(1)

the nitrogen atom on the NH$_2$ group can accept a Hydrogen ion (H$^+$) due to its lone pair and $\delta^{+/-}$.

Question 23ai_2001272_01.png

ResultsPlus
Examiner Comments

This response was awarded the mark as it includes the fact that the nitrogen atom has a lone pair of electrons on it.

ResultsPlus
Examiner Tip

Always read the question carefully. In this case, it was not sufficient just to define the term base (i.e. proton acceptor). The feature of the amine molecule enabling it to do this had to be mentioned in the response.

23 A scientist investigated the typical behaviour of primary amines.

(a) Amines such as butylamine, $CH_3CH_2CH_2CH_2NH_2$, and phenylamine, $C_6H_5NH_2$, both behave as bases.

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

(1)

its NH$_2$ group can accept a proton

ResultsPlus
Examiner Comments

This response was not awarded the available mark as there is no mention of the lone pair of electrons.

Question 23(a)(ii)

Many candidates found it challenging to write the formulae for the salts produced. Sulfate ions were often given a single negative charge and many answers incorrectly showed the formation of an amide from the reaction with ethanoic acid.

(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 .... $(CH_3CH_2CH_2CH_2NH_3)_2SO_4$

ethanoic acid, CH_3COOH .... $CH_3CH_2CH_2CH_2NH_3^{\oplus}$ $CH_3COO^{\ominus}$ $CH_3CH_2CH_2CH_2NH_3OOCCH_3$
$CH_3CH_2CH_2CH_2NH_3CH_3COO$
$OOCHCH_3$

(b) Phenylamine, $C_6H_5NH_2$, is formed by the reduction of nitrobenzene, $C_6H_5NO_2$

ResultsPlus
Examiner Comments

Both formulae are correct here.

ResultsPlus
Examiner Tip

Always check the charge on each cation and each anion to ensure that the formula of each salt is correctly written.

(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 .... $CH_3CH_2CH_2CH_2NH_3^{+} SO_4^{-}$

ethanoic acid, CH_3COOH .... $CH_3CH_2CH_2CH_2NH_3^{+} CH_3COO^{-}$

ResultsPlus
Examiner Comments

The formula of the salt produced with ethanoic acid has been given correctly for the second answer. However, the 'H' is missing from the hydrogensulfate ion in the first response.

ResultsPlus
Examiner Tip

Always check the ions formed as a result of the transfer of the proton from the acid to the base.

Question 23(b)

Many candidates could give both reagents, but some lost a mark by stating just 'HCl' or 'dilute hydrochloric acid', instead of concentrated hydrochloric acid.

(b) Phenylamine, $C_6H_5NH_2$, is formed by the reduction of nitrobenzene, $C_6H_5NO_2$.

Give the reagents that are used for this reduction.

(2)

Tin and concentrated HCL. Reflux.
(add NaOH in the second step to get rid of the salt).

ResultsPlus
Examiner Comments

Both reagents have been stated correctly.

ResultsPlus
Examiner Tip

Learn all reagents and conditions for the organic reactions included in the specification.

(b) Phenylamine, $C_6H_5NH_2$, is formed by the reduction of nitrobenzene, $C_6H_5NO_2$.

Give the reagents that are used for this reduction.

(2)

Tin and Hydrochloric acid

ethanoyl chloride + HCl
immi n ethanol

ResultsPlus
Examiner Comments

Although this answer was awarded both marks, the word 'concentrated' should have been included before the 'hydrochloric acid'.

Question 23(c)(i)

Many candidates could draw the correct structure, but there were a significant number of answers with the positive charge on the wrong nitrogen atom.

(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)
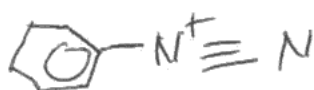
ResultsPlus
Examiner Comments

The diazonium ion has been drawn with the positive charge on the correct nitrogen atom.
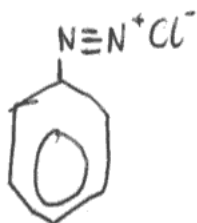
ResultsPlus
Examiner Tip

Use your knowledge of bonding to deduce the correct nitrogen atom on which to show the positive charge.

(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)

ResultsPlus
Examiner Comments

No mark was awarded here as the positive charge was shown on the wrong nitrogen atom.

Question 23(c)(ii)

Two thirds of candidates gave the correct structure. Incorrect answers often included either the -OH group on the wrong carbon or an -OH group on both benzene rings.

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

(1)
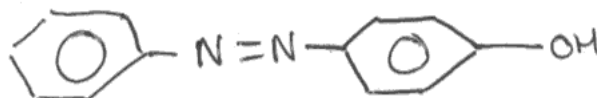
ResultsPlus
Examiner Comments

The structure of 4-hydroxyazobenzene has been drawn correctly.

ResultsPlus
Examiner Tip

Always check the number of covalent bonds attached to each atom in the molecule!

Question 23(c)(iii)

There were a substantial number of correct answers to this question. However, some answers stated incorrectly that acidic conditions would be used, whilst others included a reaction temperature despite this not being a requirement of the question.

(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:

Soo Phenol kept in sodium hydroxide solution

Use for 4-hydroxyazobenzene:

Con be used as a dye

ResultsPlus
Examiner Comments

Both scoring points were addressed correctly in this response.

Question 23(d)

Many candidates were able to identify that nitrogen, N_2, was the unreactive gas formed. However, obtaining a fully correct equation proved to be far more difficult and hydrogen, H_2, was frequently given as a product.

(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)
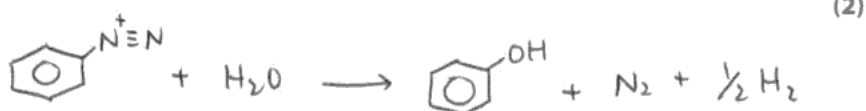
ResultsPlus
Examiner Comments

The formation of nitrogen was deduced correctly, but hydrogen ions, H⁺, rather than hydrogen gas, should have been given as a product.

(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)
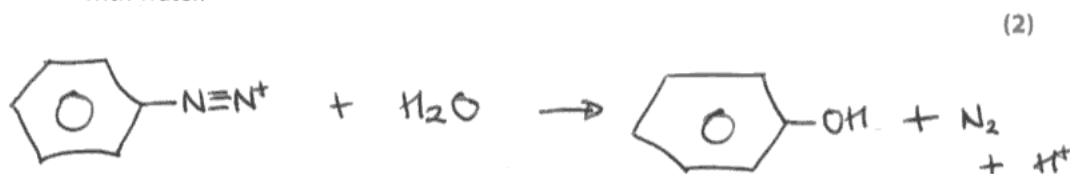

ResultsPlus
Examiner Comments

Both marks were awarded as the equation given is fully correct.

ResultsPlus
Examiner Tip

Always check that equations balance for charge as well as for species.

Question 23(e)(i)

The link between using the minimum volume of hot solvent and maximising the yield of product was not fully understood. Only a minority of candidates appreciated that when excess solvent is used the solute is more likely to remain in solution. A large number of candidates stated only that 'a saturated solution is formed'.

(i) Why is the "minimum volume of hot solvent" used?

(1)

minimise losses of product ~~through~~.

ResultsPlus
Examiner Comments

This candidate has acknowledged that the loss of product will be minimised.

(i) Why is the "minimum volume of hot solvent" used?

(1)

The minimum volume is used so that the 4-hydroxyazobenzene only just dissolves, ~~and the precipitate appears~~ and it is hot so that when cooled it will precipitate out as solubility decreases with temperature.

ResultsPlus
Examiner Comments

This response was awarded the mark available.

ResultsPlus
Examiner Tip

Make sure that you understood the techniques you encounter when doing practical work.

Question 23(e)(ii)

A large proportion of candidates understood that insoluble impurities are removed during hot filtration. Only a few candidates were able to explain where the soluble impurities would be after the second filtration.

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

(2)

I. insoluble impurities are removed during recrystallization

Filtration through filter paper and under pressure in Buchner funnel.

II. soluble impurities are removed during recrystallization

Filtrate cooled allowing crystals to reform but not soluble impurities which stay in solution.

ResultsPlus
Examiner Comments

The first mark was not awarded as there was no mention of hot filtration for removing the insoluble impurities.

ResultsPlus
Examiner Tip

Make sure you understand the principles that underpin the practical techniques encountered in the laboratory.

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

(2)

I. insoluble impurities are removed during recrystallization

Mixture is filtered whilst hot with fluted filter paper

II. soluble impurities are removed during recrystallization

The filtrate is filtered Once the filtrate is cooled in an ice bath, it is filtered under pressure using a Buchner funnel.

ResultsPlus
Examiner Comments

Hot filtration was mentioned for the award of the first mark.

Question 23(e)(iii)

A surprising number of candidates suggested finding the boiling point of the solid. Others ignored the requirements of the question and mentioned spectroscopic techniques.

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

(1)

by measuring at its boiling point + melting point if its boiling point is exactly at expected value (given room reference data) then pure

(Total for Question 23 = 15 marks)

TOTAL FOR SECTION B = 47 MARKS

ResultsPlus
Examiner Comments

The melting point, rather than the boiling point, of a solid is determined to check its purity. The melting point obtained is then compared with the literature value.
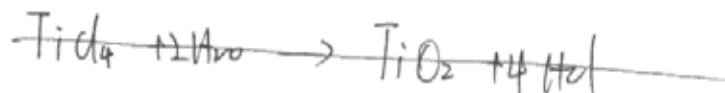
ResultsPlus
Examiner Tip

Always consider carefully the physical state of the product at room temperature.

Question 24(a)(i)

Marks were generally lost for not balancing the equation.

(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)

$$TiCl_4 + 2H_2O \longrightarrow TiO_2 + 4HCl$$

$$TiCl_4 + 4Na \longrightarrow Ti + 4NaCl$$

ResultsPlus
Examiner Comments

The required equation was correctly given.

(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.
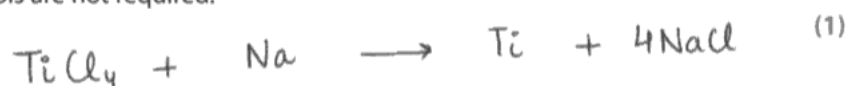
$$TiCl_4 + Na \longrightarrow Ti + 4NaCl$$

(1)

ResultsPlus
Examiner Comments

Although the species are all correct, this equation is not balanced.

ResultsPlus
Examiner Tip

Always check carefully that equations are balanced!

Question 24(a)(ii)

Many candidates identified that titanium is reduced, whilst sodium is oxidized. Some answers identified the correct oxidation numbers of these elements before and after the reaction, but did not relate the changes specifically to oxidation and reduction.

> (ii) Explain, by stating the changes of oxidation numbers, why the reaction in (i) is classified as a redox reaction.
>
> (2)
>
> Titanium is being reduced from oxidation state 4+ to 0. Meanwhile Na is being oxidised from 0 to 4+, thus creating a redox reaction.

ResultsPlus
Examiner Comments

The reduction of titanium has been correctly identified in terms of the change in oxidation number. However, the oxidation number of sodium in sodium chloride should have been given as +1, rather than +4.

ResultsPlus
Examiner Tip

Charges on ions are written as a number followed by a sign (e.g. "4+"), whereas oxidation numbers are written with a sign followed by a number (e.g. "+4").

> (ii) Explain, by stating the changes of oxidation numbers, why the reaction in (i) is classified as a redox reaction.
>
> (2)
>
> Because Titanium is reduced from +4 to 0 whilst sodium is oxidised from 0 to +1 so both oxidation and reduction occur in this reaction

ResultsPlus
Examiner Comments

A clearly set-out answer, covering both of the required scoring points.

Question 24(b)

This question was answered correctly by the vast majority of the candidates.

(b) Complete the electronic configurations of

(2)

Ti   [Ar] $4s^2, 3d^2$

Ti^{3+} [Ar] $4s^0, 3d^1$

Ti^{4+} [Ar] $4s^0, 3d^0$

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

ResultsPlus
Examiner Comments

All electronic configurations given here are correct.

ResultsPlus
Examiner Tip

Use lower-case letters (s, p, d), rather than upper-case letters (S, P, D), when writing out electronic configurations in this notation.

(b) Complete the electronic configurations of

(2)

Ti   [Ar] $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^2$

Ti^{3+} [Ar] $1s^2 2s^2 2p^6 3s^2 3p^6 3d^1$

Ti^{4+} [Ar] $1s^2 2s^2 2p^6 3s^2 3p^6$

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

ResultsPlus
Examiner Comments

Although the question requires candidates to use the noble gas 'core' of argon, credit was given for correct s,p,d electronic configurations written in full.

ResultsPlus
Examiner Tip

Check whether you are required to use a noble gas 'core' or to write out the electronic configurations in full.

Question 24(c)(i)

Many candidates stated that the 3d sub-shell is the occupied sub-shell of highest energy.

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

(i) a d-block element

(1)

Titanium has ~~its~~ electrons in its d-orbital.

Question 24(c)(ii)

Most candidates were able to identify that titanium forms one or more ions that have incompletely filled d-orbitals.

(ii) a transition element

(1)

It has more than one oxidation State.

ResultsPlus
Examiner Comments

Although this is a true statement, for the award of the mark, the response had to be a definition along the lines of that in the Unit 5 specification.

ResultsPlus
Examiner Tip

Learn all definitions thoroughly.

(ii) a transition element

(1)

forms one or more ions with incomplete d-orbitals

ResultsPlus
Examiner Comments

This is a correct definition.

+Question 24(d)(i)

Although many candidates correctly identified that d-orbitals were split in energy levels by the ligands, a significant number stated that 'the d-orbital was split'. The majority of candidates also appreciated that the absorption of light energy excited electrons from a lower to a higher energy level. A minority of candidates subsequently described the theory explaining flame colours, thereby negating much of their earlier good work.

*(d) (i) Explain why the hexaaquatitanium(III) ion, $[Ti(H_2O)_6]^{3+}$, is coloured.

(3)

> The addition of water ~~liga~~ ligands to Titanium splits the d-orbitals into two groups of different energies. The electron transitions between the split energy levels in this incomplete ~~E~~ D-subshell results in titanium ~~being~~ having coloured ~~E~~ ions in aqueous solutions. (Coloured complexes)

ResultsPlus
Examiner Comments

The first of the three scoring points was awarded for the idea of the d-orbitals being split. No mention, however, was made of promotion of the electrons from lower energy to higher energy levels or of the absorption of light. So one mark was awarded overall.

ResultsPlus
Examiner Tip

Practise structuring answers to questions requiring explanations of chemical phenomena.

*(d) (i) Explain why the hexaaquatitanium(III) ion, $[Ti(H_2O)_6]^{3+}$, is coloured.

(3)

> The ~~big~~ d orbitals of Ti^{3+} ion is splitted into a higher energy level and a lower energy level by the ligands. Electron absorbs energy from light and migrates to a higher energy level from a ~~lower~~ lower energy level.

ResultsPlus
Examiner Comments

All three scoring points in the Mark Scheme were addressed in this answer and so all three available marks were awarded.

Question 24(d)(ii)

The majority of candidates correctly identified the link between the lack of colour in titanium(IV) compounds and the empty 3d sub-shell.

(ii) Explain briefly why titanium(IV) compounds are colourless. *an energy level.*

(1)

~~It has~~ Ions of titanium (IV) have no electrons in d subshell.

ResultsPlus
Examiner Comments

This correct response was awarded the available mark.

Question 24(e)(i)

The mean mark for this question was less than one out of four. There was much confusion as to which bonds or forces are broken on melting and boiling. The most common errors were to suggest that titanium(IV) oxide had the same structure and bonding as carbon dioxide and also that titanium(IV) chloride was ionic. These statements were made despite the information given in the question that titanium(IV) oxide has a melting temperature of 1830°C and titanium(IV) chloride has a boiling temperature of 136°C.

*(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)

> $Ti O_2$ has a very high melting temperature and so must have very strong ~~intermolecular forces~~ ionic bonds betw in it's structure. Ti^{4+} has no electrons in the 3d 4s or d subshells and so it's bonding electrons must be from the 3p subshell, as this is nearer the nucleus of Ti and so the ~~covalent bond~~ bond between Ti and O would be more strongly held. The structure should be a giant ionic lattice in which the ions are in positions of maximum attraction between ~~opposite ion~~ oppositely charged ions and maximum separation (due to repulsion) of same charged ions. Oxygen is more electronegative than Cl^- and so would have a greater attraction making the ionic bond stronger in TiO_2 than $TiCl_4$.

ResultsPlus
Examiner Comments

This response scored two marks out of four. The first mark was for stating that titanium(IV) oxide has a giant ionic lattice structure and the second mark for mentioning the strong attraction between oppositely-charged ions in this substance.

*(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)

As you cannot extract Titanium from TiO_2 because this compound contains titanium Carbide, so as you made by heating totanium(IV) Chloride with sodium. TiO_2 has is a white, non toxic which is solid at room temp wheras $TiCl_4$ is a colourless liquid with Boiling temp of 186°C. You can hydrolyse $TiCl_4$ by water to give TiO_2 and $HCl(g)$. As they both have different structures. which is arranged in different manner; they both contain different temperatures.

Question 24(e)(ii)

A very straightforward item, with a large number of correct responses.

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

neutral   proton donor and proton acceptor.

(1)
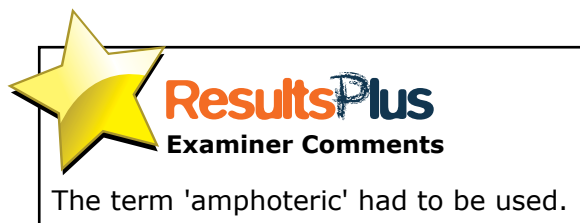
Question 24(e)(iii)

Only about one third of responses to this question were correct. The vast majority of answers were incorrect due to the omission of water molecules from the left-hand side of the equation.

(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)

$$TiO_2 + OH^- \rightarrow Ti$$

$$TiO_2 + 2KOH \rightarrow K_2Ti(OH)_6$$
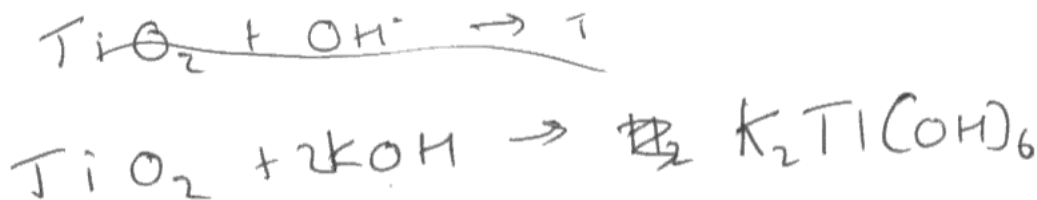
ResultsPlus
Examiner Comments

This equation was incorrect. Water molecules have not been included on the left-hand side.

(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.
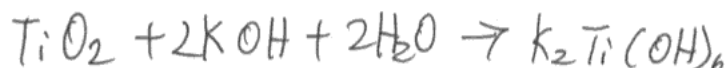
(1)

$$TiO_2 + KOH \rightarrow K_2Ti(OH)_6$$

$$TiO_2 + 2KOH + 2H_2O \rightarrow K_2Ti(OH)_6$$

ResultsPlus
Examiner Comments

This correct equation was awarded the mark available.

Question 24(f)(i)

The majority of candidates completed the half-equation correctly. Some candidates, however, did not balance the equation and 'H_4O_2', instead of '$2H_2O$', was seen on occasions.

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

(1)

$$H_2O_2 + 2H^+ + \underline{\ 2e^-\ } \rightarrow \underline{\ 2H_2O\ }$$

tick

red left

1 2 2 2
   2 2 1
1/2

ResultsPlus
Examiner Comments

Correct answer, so the mark was awarded.

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

(1)

$$H_2O_2 + 2H^+ + \underline{\ 2e^-\ } \rightarrow \underline{\ H_2O\ }$$

ResultsPlus
Examiner Comments

Species were correct, but the half-equation was not balanced. So no mark was awarded.

ResultsPlus
Examiner Tip

Check half-equations balance for both species and for charge.

Question 24(f)(ii)

The majority of candidates calculated the moles of hydrogen peroxide correctly. Some did not, however, take the mole ratio of titanium(III) ions to hydrogen peroxide into account. Others did not acknowledge that a 25.0 cm³ sample was titrated or that the 250 cm³ of dilute titanium(III) chloride solution was originally made from only 5.00 cm³ of solution. A minority of candidates mistakenly used the volume of 25.00 cm³ for the hydrogen peroxide titre, rather than 22.50 cm³.

---

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

In an experiment, 5.00 cm³ of a sample of titanium(III) chloride solution was transferred to a volumetric flask and made up to 250 cm³ of an aqueous solution. A 25.0 cm³ portion of this diluted solution was acidified and titrated with a 0.0200 mol dm⁻³ solution of hydrogen peroxide, H_2O_2. The mean titre was 22.50 cm³.

Calculate the concentration of the **original** titanium(III) chloride solution, in mol dm⁻³.

(3)

$$\text{moles of } H_2O_2 = \frac{0.02 \times 22.5}{1000} = 4.5 \times 10^{-4}$$

H_2O_2 : Titanium (III) chloride
1 : 2

therefore $4.5 \times 10^{-4} \times 2 = 9 \times 10^{-4}$ moles titanium(III) chloride in 25 cm3

$9 \times 10^{-4} \times 10 = 9 \times 10^{-3}$ moles in 250 cm3

$$\text{concentration} = \frac{9 \times 10^{-3} \times 1000}{5} = 1.8 \text{ mol dm}^{-3}$$

ResultsPlus
Examiner Comments

This well laid-out answer scored all three available marks.

ResultsPlus
Examiner Tip

Set out answers to calculation questions with a few words of explanation - as is the case with this response.

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

In an experiment, 5.00 cm³ of a sample of titanium(III) chloride solution was transferred to a volumetric flask and made up to 250 cm³ of an aqueous solution. A 25.0 cm³ portion of this diluted solution was acidified and titrated with a 0.0200 mol dm⁻³ solution of hydrogen peroxide, H_2O_2. The mean titre was 22.50 cm³.

Calculate the concentration of the **original** titanium(III) chloride solution, in mol dm⁻³.

(3)

$$1H \rightarrow 2TiCl_3$$

$$Moles\ H_2O_2 = \frac{22.5 \times 0.02}{1000} = 4.5 \times 10^{-4}$$

$$Moles\ H_2O_2\ in\ 250 = 4.5 \times 10^{-4} \times 10 = 4.5 \times 10^{-3}$$

$$Moles\ TiCl_3\ in\ 250 = 4.5 \times 10^{-3} \times 2 = \underline{9 \times 10^{-3}}$$

Question 24(f)(iii)

The majority of candidates gave the correct answer, but some did not use the information in the article as candidates were advised to do in the question.

(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)

Because the titanium(III) is readily oxidised in the air by oxygen into titanium(IV). Therefore not all of the original titanium(III) will be still be there by the ml.

(Total for Question 24 = 23 marks)

TOTAL FOR SECTION C = 23 MARKS
TOTAL FOR PAPER = 90 MARKS

ResultsPlus Examiner Comments

This response acknowledges that the titanium(III) chloride would be oxidized by oxygen in the air.

ResultsPlus Examiner Tip

Read the Section C article carefully, to extract relevant information when necessary.

(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)

$TiCl_3$ is readily oxidised in air to Ti^{4+} ions.

(Total for Question 24 = 23 marks)

TOTAL FOR SECTION C = 23 MARKS
TOTAL FOR PAPER = 90 MARKS

ResultsPlus Examiner Comments

The mark was awarded as the candidate has mentioned that the titanium(III) chloride would be oxidized by air.

Paper Summary

On the basis of their performance on this paper candidates are offered the following advice:

- Remember that AS content will be required when answering A2 question papers.

- Read questions carefully, especially those in Section C or questions set in an unfamiliar context.

- Organic reaction mechanisms need to be accurately drawn: ensure that 'curly arrows' are precisely located and that all intermediate structures are correct.

- In extended responses, make sure that the thread of an argument is maintained and that it matches the number of available marks.

- Learn how to balance half-equations and then how to add them together to produce the overall equation for a reaction.

- Practise justifying the feasibility of a redox reaction using standard electrode potentials.

- Label each step of a calculation to show clearly what you are attempting to work out.

- In multi-stage calculations, don't round numbers up or down until the final step.

Grade Boundaries

Grade boundaries for this, and all other papers, can be found on the website on this link:

http://www.edexcel.com/iwantto/Pages/grade-boundaries.aspx