X012/13/02

NATIONAL QUALIFICATIONS 2015

THURSDAY, 28 MAY
1.00 PM – 3.30 PM

CHEMISTRY
ADVANCED HIGHER

Reference may be made to the Chemistry Higher and Advanced Higher Data Booklet.

SECTION A – 40 marks

Instructions for completion of **SECTION A** are given on page two.

For this section of the examination you must use an **HB pencil.**

SECTION B – 60 marks

All questions should be attempted.

Answers must be written clearly and legibly in ink.

PB

SECTION A

Read carefully

1 Check that the answer sheet provided is for **Chemistry Advanced Higher (Section A)**.

2 For this section of the examination you must use an **HB pencil** and, where necessary, an eraser.

3 Check that the answer sheet you have been given has **your name**, **date of birth**, **SCN** (Scottish Candidate Number) and **Centre Name** printed on it.

Do not change any of these details.

4 If any of this information is wrong, tell the Invigilator immediately.

5 If this information is correct, **print** your name and seat number in the boxes provided.

6 The answer to each question is **either** A, B, C or D. Decide what your answer is, then, using your pencil, put a horizontal line in the space provided (see sample question below).

7 There is **only one correct** answer to each question.

8 Any rough working should be done on the question paper or the rough working sheet, **not** on your answer sheet.

9 At the end of the exam, put the **answer sheet for Section A inside the front cover of your answer book**.

Sample Question

To show that the ink in a ball-pen consists of a mixture of dyes, the method of separation would be

A chromatography

B fractional distillation

C fractional crystallisation

D filtration.

The correct answer is **A**—chromatography. The answer **A** has been clearly marked in **pencil** with a horizontal line (see below).

Changing an answer

If you decide to change your answer, carefully erase your first answer and using your pencil, fill in the answer you want. The answer below has been changed to **D**.

1. Infrared radiation can be used in the analysis and identification of organic compounds. Compared to visible radiation, infrared radiation has a

A shorter wavelength and higher frequency

B longer wavelength and lower velocity

C longer wavelength and lower frequency

D shorter wavelength and higher velocity.

2. The electronic configuration of a krypton atom is

$1s^2\ 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$.

Which of the following ions does **not** have this configuration?

A Sr^{2+}

B Se^{2-}

C As^{3-}

D Zr^{3+}

3. The diagram shows one of the series of lines in the hydrogen emission spectrum.

Each line

A represents an energy level within a hydrogen atom

B results from an electron moving to a higher energy level

C lies within the visible part of the electromagnetic spectrum

D results from an excited electron dropping to a lower energy level.

4. Which of the following compounds is likely to show the most ionic character?

A KCl

B NaI

C BH_3

D PH_3

5. A Lewis base may be regarded as a substance which is capable of donating an unshared pair of electrons to form a covalent bond.

Which of the following could act as a Lewis base?

A Co^{3+}

B PH_3

C BCl_3

D NH_4^+

6. Which of the following species has the same shape as an ammonia molecule?

A BH_3

B CH_3^+

C CH_3^-

D CO_3^{2-}

7. Silicon can be converted into an n-type semiconductor by doping with

A boron

B carbon

C arsenic

D aluminium.

8. A white solid gives a lilac flame colour. It reacts with water releasing hydrogen gas and forming a strongly alkaline solution.

The solid could be

A calcium oxide

B potassium oxide

C calcium hydride

D potassium hydride.

9. The formula for the tetraamminedichlorocopper(II) complex is

A $[Cu(NH_3)_4Cl_2]^{2-}$

B $[Cu(NH_3)_4Cl_2]$

C $[Cu(NH_3)_4Cl_2]^{2+}$

D $[Cu(NH_3)_4Cl_2]^{4+}$.

10. $ClO_3^-(aq) + 6H^+(aq) + \mathbf{n}e^- \rightarrow Cl^-(aq) + 3H_2O(\ell)$

What value of **n** is required to balance the above equation?

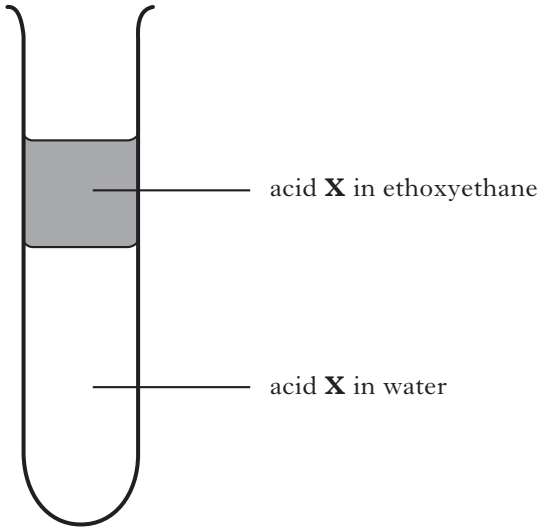
A 4

B 5

C 6

D 7

11. An organic acid, **X**, was dissolved in water and then shaken with ethoxyethane until equilibrium was established.



The value of the partition coefficient for this system will be altered by changing the

A temperature

B volume of water

C original mass of acid **X**

D original concentration of acid **X**.

12. Gas liquid chromatography could be used to separate a mixture of hydrocarbons. The mixture is passed through a column packed with silica particles coated in a non-polar liquid. Helium can be used to carry the mixture through the column.

Which line in the table identifies correctly the stationary and mobile phases in this chromatographic separation?

	Stationary phase	**Mobile phase**
A	silica	non-polar liquid
B	silica	helium
C	non-polar liquid	helium
D	non-polar liquid	hydrocarbon mixture

13. Which of the following would **not** be suitable as a buffer solution?

A Boric acid and sodium borate

B Nitric acid and sodium nitrate

C Benzoic acid and sodium benzoate

D Propanoic acid and sodium propanoate

14. Solution **X** has a pH of 4·38. When it is diluted tenfold the pH changes to 4·88.

X is likely to be

A a partly soluble acid

B a buffered acid

C a strong acid

D a weak acid.

15. $BN(s) + 1\frac{1}{2}F_2(g) \rightarrow BF_3(g) + \frac{1}{2}N_2(g)$

$\Delta H^\circ = -885\,kJ\,mol^{-1}$

$B(s) + 1\frac{1}{2}F_2(g) \rightarrow BF_3(g)$

$\Delta H^\circ = -1136\,kJ\,mol^{-1}$

From the above data, it can be deduced that the enthalpy of formation, in $kJ\,mol^{-1}$, of boron nitride, BN(s), is

A −2021

B −251

C +251

D +2021.

16. The mean bond enthalpy of the N−H bond is equal to one third of the value of ΔH for which of the following changes?

A $NH_3(g) \rightarrow N(g) + 3H(g)$

B $2NH_3(g) \rightarrow N_2(g) + 3H_2(g)$

C $NH_3(g) \rightarrow \frac{1}{2}N_2(g) + 1\frac{1}{2}H_2(g)$

D $2NH_3(g) + 1\frac{1}{2}O_2(g) \rightarrow N_2(g) + 3H_2O(g)$

17. The enthalpy change for the reaction

$K^+(g) + F^-(g) \rightarrow K^+(aq) + F^-(aq)$

is

A the enthalpy of solution of potassium fluoride

B the enthalpy of formation of potassium fluoride

C the sum of the hydration energies of potassium and fluoride ions

D the sum of the first ionisation energy of potassium and the electron affinity of fluorine.

18. The standard entropy of a perfect crystal is zero at

A 0 K

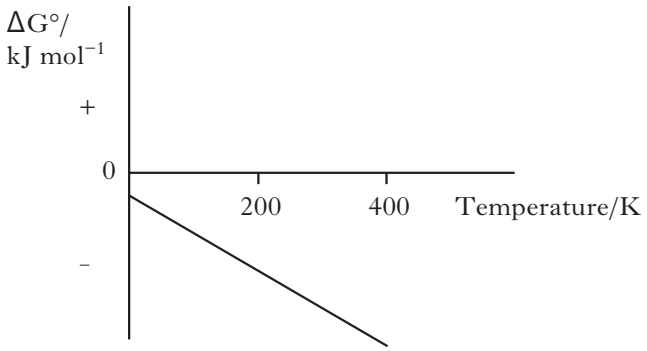
B 25 K

C 273 K

D 298 K.

19. Which of the following graphs shows the variation in ΔG° with temperature for a reaction which is always feasible?

A



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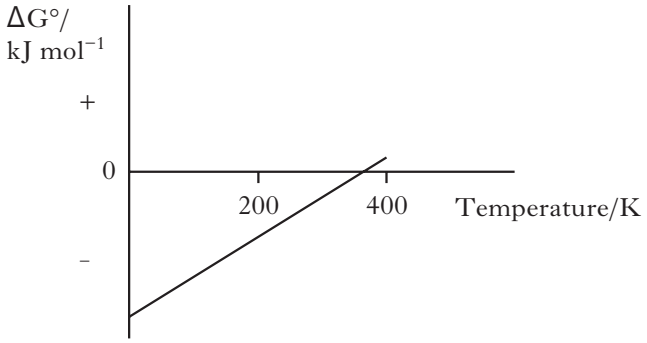
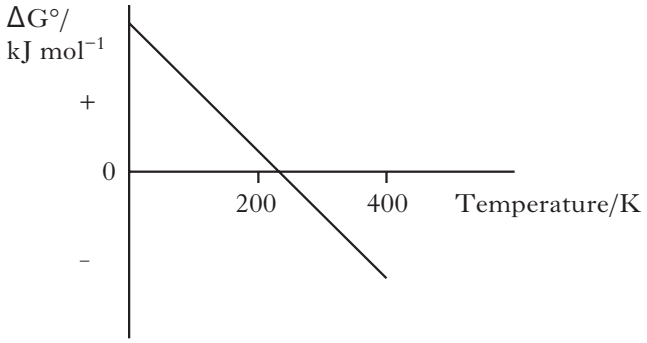
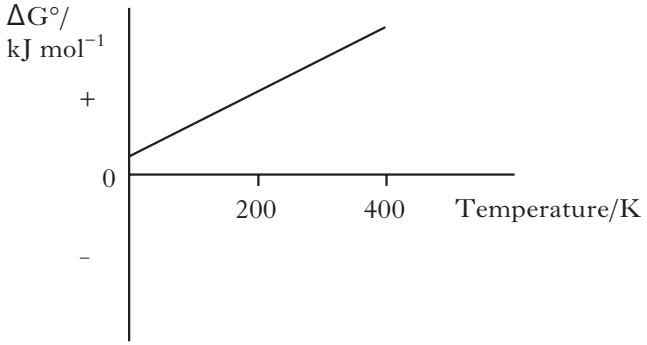


C



D



20. The reaction

$2SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons 2SO_3(g)$

is reversible. After equilibrium has been established the reaction mixture was found to contain 0·2 moles of SO_2, 0·2 moles of O_2 and 16 moles of SO_3.

Which of the following is correct?

A $K > 1$ and $\Delta G° > 0$

B $K > 1$ and $\Delta G° < 0$

C $K < 1$ and $\Delta G° > 0$

D $K < 1$ and $\Delta G° < 0$

21. For which of the following reactions would the value of $\Delta G° - \Delta H°$ be approximately zero?

A $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$

B $C(s) + H_2O(g) \rightarrow CO(g) + H_2(g)$

C $Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$

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

22. Which of the following is **not** a required condition for measuring standard electrode potentials?

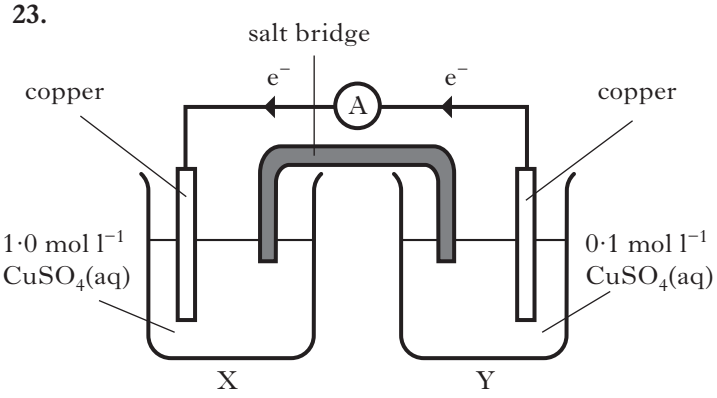
A Volume of 1 litre

B Temperature of 298 K

C Concentration of 1·0 mol l^{-1}

D Pressure of 1 atmosphere

23.



Which of the following will occur in the above cell?

A The blue colour in Y will become less intense.

B The mass of the electrode in Y will decrease.

C The concentration of the solution in X will increase.

D Electrons will flow from X to Y through the salt bridge.

24. Two mechanisms have been proposed for the hydrolysis of 2-bromo-2-methylpropane.

One of these has only one step

$(CH_3)_3CBr + OH^- \rightarrow (CH_3)_3COH + Br^-$

The other has two steps

$(CH_3)_3CBr \rightarrow (CH_3)_3C^+ + Br^-$ (Slow)

$(CH_3)_3C^+ + OH^- \rightarrow (CH_3)_3COH$ (Fast)

The reaction is observed to follow first order kinetics. The rate equation for the overall reaction is

A rate = $k[(CH_3)_3CBr]$

B rate = $k[(CH_3)_3CBr][OH^-]$

C rate = $k[(CH_3)_3C^+]$

D rate = $k[(CH_3)_3C^+][OH^-]$.

25. $2P + Q \rightleftharpoons R + S \quad \Delta G^\circ = +40\,kJ\,mol^{-1}$

Which of the following **cannot** be deduced from the above information?

A The feasibility of the reaction

B The order of the reaction

C The stoichiometry of the reaction

D The position of equilibrium

26. In a chemical reaction the rate is doubled for every 10 °C rise in temperature. When the temperature is increased from 20 °C to 60 °C, the rate of the reaction will become faster by a factor of

A 3

B 4

C 8

D 16.

27. Which of the following represents a propagation step in a chain reaction?

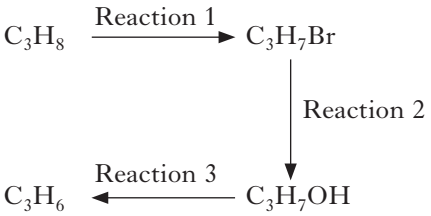
A $Cl\bullet + Cl\bullet \rightarrow Cl_2$

B $Cl\bullet + CH_4 \rightarrow CH_3\bullet + HCl$

C $CH_3\bullet + Cl\bullet \rightarrow CH_3Cl$

D $Cl_2 \rightarrow Cl\bullet + Cl\bullet$

28. Which line in the table correctly describes the types of reaction in the following sequence?



	Reaction 1	**Reaction 2**	**Reaction 3**
A	addition	substitution	elimination
B	addition	addition	condensation
C	substitution	substitution	elimination
D	substitution	addition	condensation

29. Which of the following equations does **not** involve a nucleophilic substitution?

A $C_3H_7Br + KOH \xrightarrow{\text{ethanol}} C_3H_6 + KBr + H_2O$

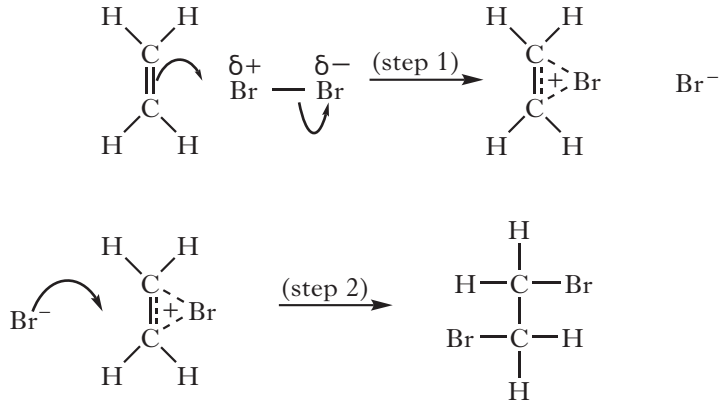
B $C_3H_7Br + KCN \xrightarrow{\text{ethanol}} C_3H_7CN + KBr$

C $C_2H_5Cl + C_2H_5ONa \xrightarrow{\text{ethanol}} C_2H_5OC_2H_5 + NaCl$

D $C_2H_5Br + NaOH \xrightarrow{\text{water}} C_2H_5OH + NaBr$

[Turn over

30.



The two steps in the reaction mechanism shown can be described as

A ethene acting as a nucleophile and Br^- acting as a nucleophile

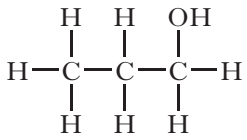
B ethene acting as a nucleophile and Br^- acting as an electrophile

C ethene acting as an electrophile and Br^- acting as a nucleophile

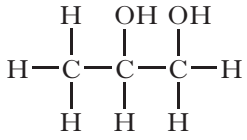
D ethene acting as an electrophile and Br^- acting as an electrophile.

31. The structures of three alcohols, **P**, **Q** and **R** are shown.

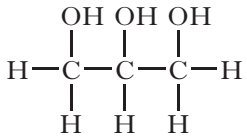
P



Q



R



Which line in the table describes correctly the trends in boiling points and viscosities from **P** to **Q** to **R**?

	Boiling point	**Viscosity**
A	increases	increases
B	increases	decreases
C	decreases	increases
D	decreases	decreases

32. Which of the following would be required to convert a halogenoalkane into an ether?

A Aqueous sodium hydroxide followed by oxidation

B Potassium cyanide followed by hydrolysis

C Sodium hydroxide in ethanol

D Sodium in ethanol

33. A compound, **X**, reacts with the product of its own oxidation to form an ester.

X could be

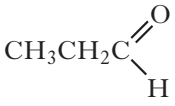
A propanal

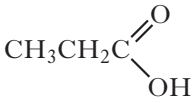
B propan-1-ol

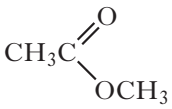
C propan-2-ol

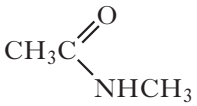
D propanoic acid.

34. Which of the following will form a derivative with 2,4-dinitrophenylhydrazine?

A 

B 

C 

D 

35. To help in the identification of an organic compound, a crystalline derivative **must**

A have a sharp boiling point

B have a sharp melting point

C decompose at its melting point

D have a low relative molecular mass.

36. Which of the following compounds will react with both dilute hydrochloric acid and sodium hydroxide solution?

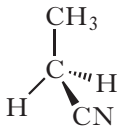
A C_6H_5OH

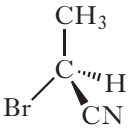
B $C_6H_5NH_2$

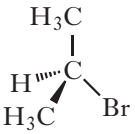
C HOC_6H_4COOH

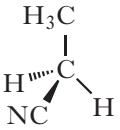
D $H_2NC_6H_4COOH$

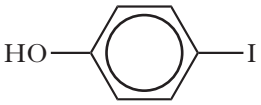
37. Which of the following compounds will have an optical isomer?

A 

B 

C 

D 

38. 

Which atom in the above structure would be located **most** readily using X-ray crystallography?

A Carbon

B Hydrogen

C Iodine

D Oxygen

[Turn over

39. Sulphonamides are synthetic compounds that block the production of folic acid in bacterial cells.

Sulphonamides are best described as

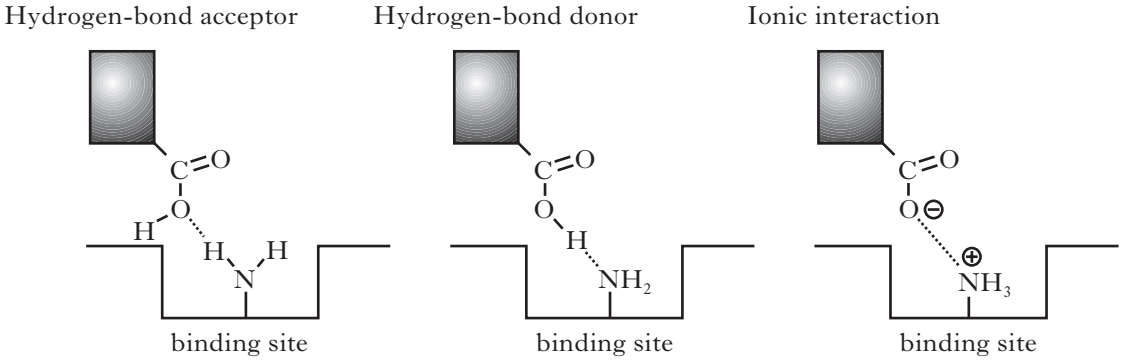
A agonists

B receptors

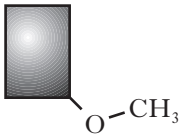
C antagonists

D pharmacophores.

40. A drug containing a carboxyl group can bind to an amino group on a receptor site in three different ways.



The drug with the following structure



could bind to the same site

A only by ionic interaction

B only as a hydrogen-bond donor

C only as a hydrogen-bond acceptor

D both as a hydrogen-bond donor and acceptor.

[*END OF SECTION A*]

Candidates are reminded that the answer sheet for Section A MUST be placed INSIDE the front cover of your answer book.

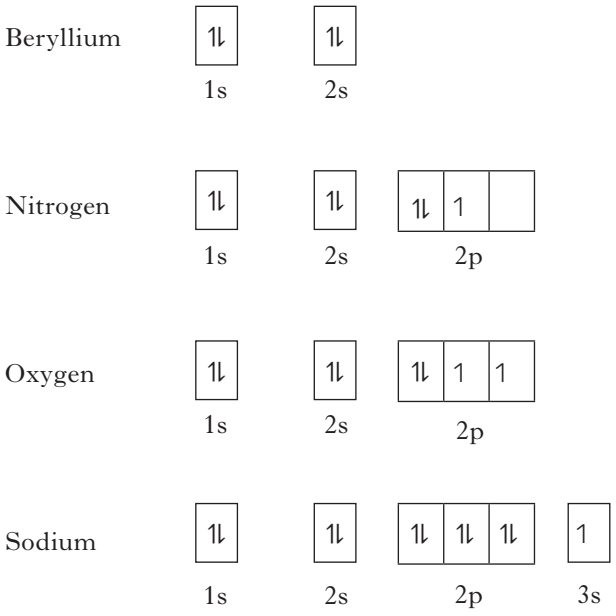
SECTION B

Marks

60 marks are available in this section of the paper.

All answers must be written clearly and legibly in ink.

1. (*a*) A student wrote the following ground state electronic configurations for atoms of beryllium, nitrogen, oxygen and sodium, where ↿ denotes an electron.



(i) The three atomic orbitals in the 2p subshell are said to be degenerate.

What is meant by the term degenerate? **1**

(ii) Explain why the electronic configuration for nitrogen shown above is incorrect. **1**

(*b*) The first ionisation energy of sodium is 502 kJ mol^{-1}.

(i) Calculate the wavelength of light corresponding to this ionisation energy. **3**

(ii) Explain whether visible light would provide sufficient energy to ionise gaseous sodium atoms. **1**

(6)

[Turn over

Marks

2. Zinc oxide can be reduced to zinc in a blast furnace.

One of the reactions taking place in the furnace is shown.

$$ZnO(s) + CO(g) \rightarrow Zn(g) + CO_2(g)$$

Substance	**Standard enthalpy of formation, ΔH_f°/ kJ mol^{-1}**	**Standard entropy, S°/ J K^{-1} mol^{-1}**
ZnO(s)	−348	44
CO(g)	−110	198
Zn(g)	+130	161
CO_2(g)	−394	214

For the reduction of zinc oxide with carbon monoxide, use the data in the table to calculate:

(*a*) the standard enthalpy change, ΔH°, in kJ mol^{-1}; **1**

(*b*) the standard entropy change, ΔS°, in J K^{-1} mol^{-1}; **1**

(*c*) the theoretical temperature above which the reaction becomes feasible. **2**

(4)

Marks

3. Vanadium is a transition metal which exhibits different oxidation states. This property allows it to be used in electrochemical cells and also gives rise to different coloured solutions.

(*a*) Two ion-electron equations for vanadium in an electrochemical cell are

$$V^{3+}(aq) + e^- \rightleftharpoons V^{2+}(aq) \qquad E^o = -0{\cdot}26\ V$$

$$VO_2^+(aq) + 2H^+(aq) + e^- \rightleftharpoons VO^{2+}(aq) + H_2O(\ell) \qquad E^o = 1{\cdot}00\ V$$

(i) Calculate the standard emf, E^o, of this cell. **1**

(ii) Calculate the standard free energy change, ΔG°, in kJ mol^{-1}, for the cell reaction. **2**

(*b*) A classic chemistry demonstration involves vanadium changing oxidation states.

Some zinc metal is added to a flask containing an acidified solution of the dioxovanadium(V) ion, $VO_2^+(aq)$. The flask is stoppered with some cotton wool and gently swirled. The colour of the solution turns from yellow to blue. Further swirling turns the solution from blue to green. Finally, the flask is shaken vigorously and a violet colour is produced.

$$\underset{\text{(yellow)}}{VO_2^+(aq)} \xrightarrow{(1)} \underset{\text{(blue)}}{VO^{2+}(aq)} \xrightarrow{(2)} \underset{\text{(green)}}{V^{3+}(aq)} \xrightarrow{(3)} \underset{\text{(violet)}}{V^{2+}(aq)}$$

(i) Determine the oxidation number of vanadium in the blue $VO^{2+}(aq)$ ion. **1**

(ii) It was observed during the demonstration that the yellow solution turned green before turning blue in reaction (1).

Suggest a reason for this. **1**

(iii) In reaction (3) $V^{2+}(aq)$ ions are produced.

How many d electrons does a $V^{2+}(aq)$ ion have? **1**

(iv) When the cotton wool stopper is removed the violet solution slowly changes back to blue.

Suggest why this happens. **1**

(7)

[Turn over

4. In a **PPA**, potassium trioxalatoferrate(III) crystals are prepared from ammonium iron(II) sulphate in a series of steps.

Step 1 A precipitate of iron(II) oxalate is produced.

Step 2 The precipitate of iron(II) oxalate is oxidised and heated with a solution of potassium oxalate.

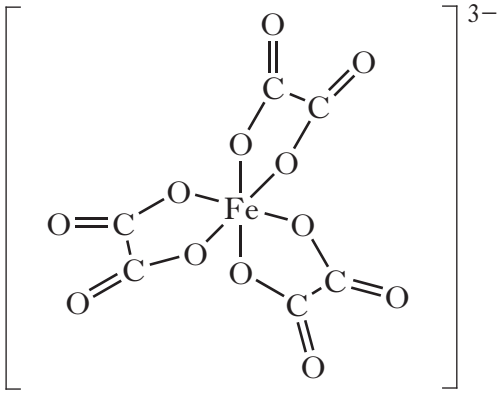
$$6FeC_2O_4 + \mathbf{X} + 6K_2C_2O_4 \rightarrow 4K_3[Fe(C_2O_4)_3] + 2Fe(OH)_3$$

Step 3 Additional oxalic acid is added to convert the iron(III) hydroxide into more potassium trioxalatoferrate(III).

(*a*) What colour are the crystals which form in this PPA? **1**

(*b*) Name the oxidising agent **X** used in Step 2. **1**

(*c*) The diagram shows how the oxalate ions are arranged in the complex ion.



Name the shape given to the arrangement of bonds around the iron. **1**

(3)

Marks

5. Nitrogen forms a variety of oxides.

(*a*) Dinitrogen tetroxide, $N_2O_4(g)$, dissociates to form nitrogen dioxide, $NO_2(g)$, according to the equation.

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

0·28 mol of N_2O_4 gas is placed in an empty 1·00 litre flask and heated to 127 °C. When the system reaches equilibrium, 0·24 mol of NO_2 gas is present in the flask.

(i) Calculate the equilibrium constant, K, for the reaction at 127 °C. **3**

(ii) At 25 °C, the numerical value of the equilibrium constant for this reaction is 0·12.

Explain whether the forward reaction is endothermic or exothermic. **1**

(*b*) Nitrogen monoxide reacts with hydrogen as shown.

$$2NO(g) + 2H_2(g) \rightarrow N_2(g) + 2H_2O(g)$$

In a series of experiments, at a fixed temperature, the initial rates of this reaction were measured.

Experiment	**Initial [NO]/ mol l^{-1}**	**Initial [H_2]/ mol l^{-1}**	**Initial rate/ mol $l^{-1}s^{-1}$**
1	$2{\cdot}00 \times 10^{-3}$	$1{\cdot}20 \times 10^{-3}$	$7{\cdot}40 \times 10^{-4}$
2	$2{\cdot}00 \times 10^{-3}$	$2{\cdot}40 \times 10^{-3}$	**x**
3	$4{\cdot}00 \times 10^{-3}$	$2{\cdot}40 \times 10^{-3}$	**y**

The following rate equation was deduced.

$$\text{Rate} = k[NO]^2$$

(i) Using the information above, determine the numerical values for **x** and **y**. **2**

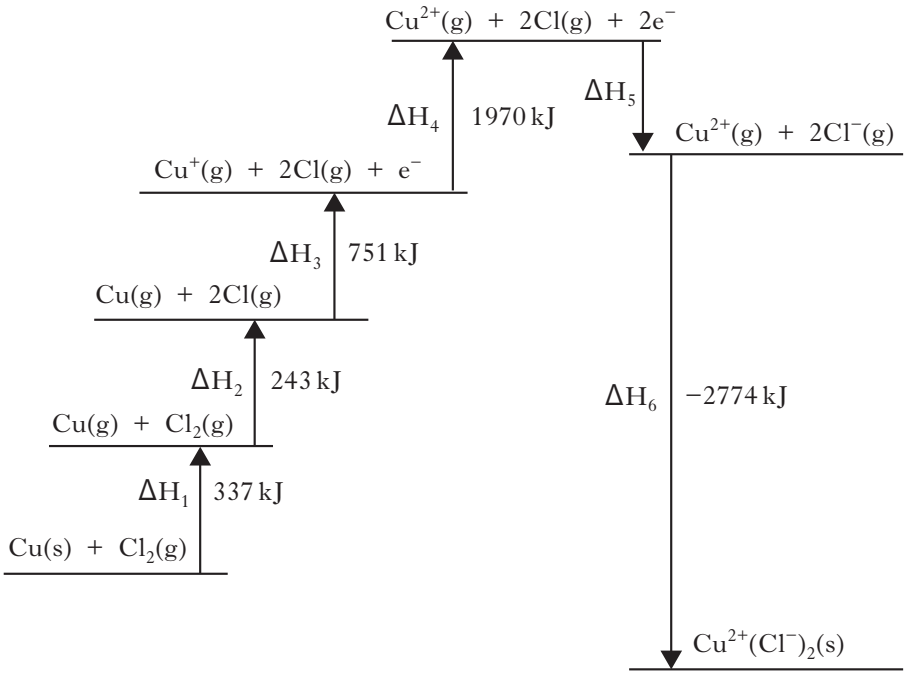
(ii) For experiment 1, calculate the value of the rate constant, k, including the appropriate units. **2**

(8)

[Turn over

Marks

6. The thermochemical cycle below is not drawn to scale.



(*a*) Using information from the Data Booklet and the above thermochemical cycle calculate the standard enthalpy of formation, ΔH_f^o, in kJ mol^{-1}, for $Cu^{2+}(Cl^-)_2(s)$. **2**

(*b*) Using selected information from the thermochemical cycle above and the equation below calculate the standard enthalpy of formation, ΔH_f^o, in kJ mol^{-1}, of $Cu^+Cl^-(s)$.

$$Cu^+(g) + Cl^-(g) \longrightarrow Cu^+Cl^-(s) \qquad \Delta H^o = -921 \text{ kJ mol}^{-1}$$ **2**

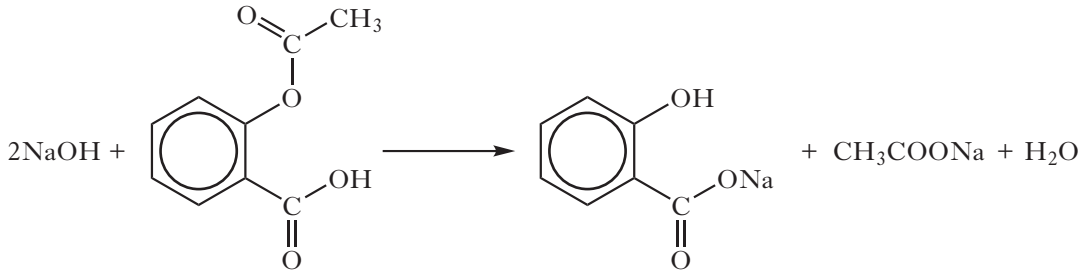
(*c*) **Explain** which of the two chlorides of copper will be more stable at 298 K. **1**

(5)

Marks

7. In a **PPA**, the acetylsalicylic acid ($C_9H_8O_4$) content of an aspirin tablet was determined using a back titration.

Five aspirin tablets were crushed and added to 25·0 cm^3 of 1·00 mol l^{-1} sodium hydroxide solution. The mixture was heated and allowed to simmer for 30 minutes.



The resulting mixture was allowed to cool before being transferred to a 250 cm^3 standard flask and made up to the mark with deionised water.

25·0 cm^3 samples of this solution were titrated with 0·050 mol l^{-1} sulphuric acid.

$$2NaOH + H_2SO_4 \longrightarrow Na_2SO_4 + 2H_2O$$

The results of the titration are shown in the table.

	Rough titration	**1st titration**	**2nd titration**
Initial burette reading/cm^3	0·0	9·0	17·7
Final burette reading/cm^3	9·0	17·7	26·3
Volume used/cm^3	9·0	8·7	8·6

(*a*) Which indicator is used in the back titration? **1**

(*b*) (i) Calculate the number of moles of sulphuric acid in the average titre. **1**

(ii) Calculate the number of moles of excess sodium hydroxide in the **standard flask**. **1**

(iii) Calculate the number of moles of sodium hydroxide which reacted with the acetylsalicylic acid. **1**

(iv) The mass of one mole of acetylsalicylic acid is 180 g.

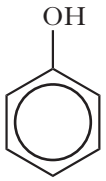
Use this and your answer to part (*b*)(iii) to calculate the mass of acetylsalicylic acid in one aspirin tablet. **2**

(6)

[Turn over

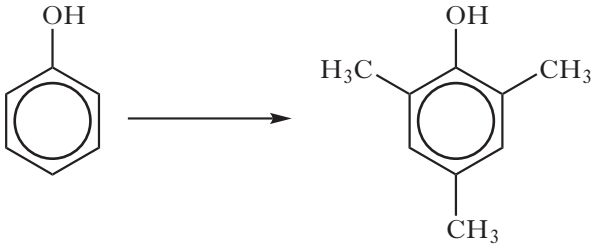
Marks

8. Phenol is an aromatic compound with the following structure.



(*a*) What type of hybridisation do the carbon atoms exhibit in phenol? **1**

(*b*) Phenol takes part in the following reaction.



phenol 2,4,6-trimethylphenol

(i) Suggest a suitable reagent and catalyst for this reaction. **1**

(ii) What type of reaction is taking place? **1**

(*c*) Phenol can be converted into 2,4,6-trinitrophenol using a mixture of concentrated nitric acid and concentrated sulphuric acid.

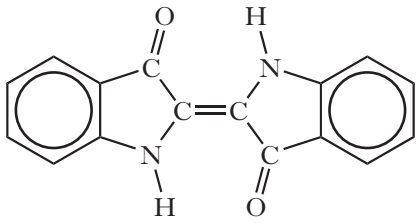
(i) Draw a structural formula for 2,4,6-trinitrophenol. **1**

(ii) Write the formula of the reactive species acting on phenol in this reaction. **1**

(5)

Marks

9. The blue colour of denim jeans comes from a dye known as indigo.



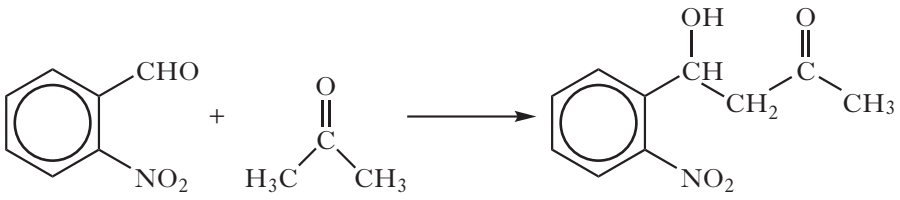
indigo

The synthesis of this dye involves a series of complex chemical reactions.

(*a*) Why does a dye, such as indigo, appear blue when viewed in daylight? **1**

(*b*) Draw a structural formula for the geometric isomer of indigo. **1**

(*c*) The first step in the synthesis of indigo is the reaction of 2-nitrobenzaldehyde with propanone.



2-nitrobenzaldehyde propanone 4-hydroxy-4-(2-nitrophenyl)butan-2-one

Suggest the type of chemical reaction taking place during this step of the synthesis. **1**

(3)

[Turn over

Marks

10. There are four isomers with the molecular formula C_4H_9Cl. Structural formulae for three of these isomers are

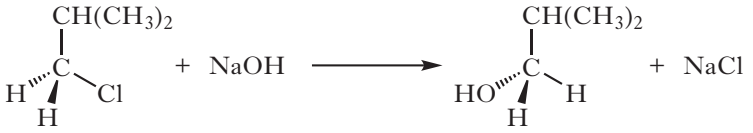
$CH_3CHClCH_2CH_3$ **A** $(CH_3)_2CHCH_2Cl$ **B** $(CH_3)_3CCl$ **C**

(*a*) What is the systematic name of isomer **C**? **1**

(*b*) When refluxed with a solution of potassium hydroxide in ethanol, compound **A** undergoes an elimination reaction. Two structural isomers are produced.

Draw a structural formula for each of these two isomers. **2**

(*c*) Isomer **B** reacts with aqueous sodium hydroxide in an S_N2 reaction.



Isomer **B** Compound **X**

(i) Name compound **X**. **1**

(ii) Draw a structure for the transition state in this reaction. **1**

(*d*) Draw a structural formula for the fourth isomer of C_4H_9Cl. **1**

(*e*) Proton NMR spectroscopy can be used to distinguish between isomers **A, B** and **C** simply by counting the different numbers of peaks in each spectrum.

How many peaks would be seen in the spectrum of isomer **B**? **1**

(*f*) Separate solutions of isomers **A** and **B** were analysed using plane polarised light. Neither solution showed optical rotation.

For **each isomer** explain why no optical rotation occurred. **2**

(9)

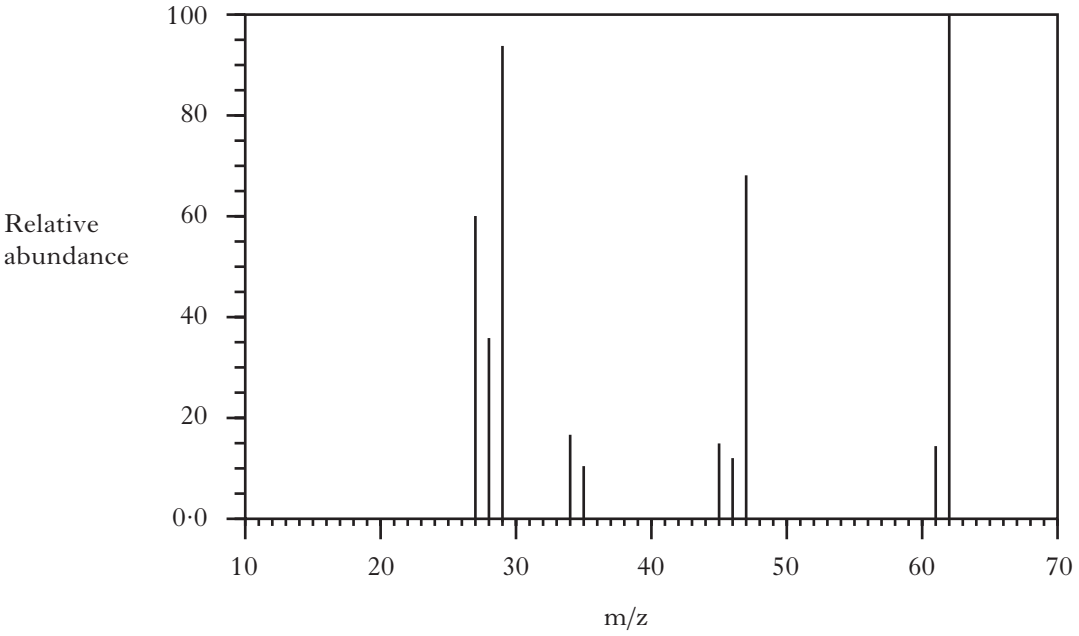
Marks

11. Compound **X** contains only carbon, hydrogen and sulphur.

(*a*) Complete combustion of **X** gave 3·52 g of carbon dioxide, 2·16 g of water and 2·56 g of sulphur dioxide.

Show, by calculation, that the empirical formula of compound **X** is C_2H_6S **2**

(*b*) The mass spectrum for compound **X** is shown below.



Suggest a possible ion fragment which may be responsible for the peak at m/z 47 in the mass spectrum. **1**

(*c*) The results of the analysis of the proton NMR spectrum of **X** are shown in the table below.

Peak	Chemical shift/ppm	Relative area under the peak
1	1·2	97
2	1·5	32
3	2·4	65

Considering all the evidence above, draw a structural formula for compound **X**. **1**

(4)

[*END OF QUESTION PAPER*]

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2015 Chemistry

Advanced Higher

Finalised Marking Instructions

Part One: General Marking Principles for: Chemistry Advanced Higher

This information is provided to help you understand the general principles you must apply when marking candidate responses to questions in this Paper. These principles must be read in conjunction with the specific Marking Instructions for each question.

(a) Marks for each candidate response must always be assigned in line with these general marking principles and the specific Marking Instructions for the relevant question. If a specific candidate response does not seem to be covered by either the principles or detailed Marking Instructions, and you are uncertain how to assess it, you must seek guidance from your Team Leader/Principal Assessor.

(b) Marking should always be positive ie, marks should be awarded for what is correct and not deducted for errors or omissions.

GENERAL MARKING ADVICE: Chemistry Advanced Higher

The marking schemes are written to assist in determining the "minimal acceptable answer" rather than listing every possible correct and incorrect answer. The following notes are offered to support Markers in making judgements on candidates' evidence, and apply to marking both end of unit assessments and course assessments.

General information for markers

The general comments given below should be considered during all marking.

1 Marks should **not** be deducted for incorrect spelling or loose language as long as the meaning of the word(s) is conveyed.

Example: Answers like 'distilling' (for 'distillation') and 'it gets hotter' (for 'the temperature rises') should be accepted.

2 A right answer followed by a wrong answer should be treated as a cancelling error and no marks should be given.

Example: What is the colour of universal indicator in acid solution?

The answer 'red, blue' gains no marks.

3 If a right answer is followed by additional information which does not conflict, the additional information should be ignored, whether correct or not.

Example: Why can the tube not be made of copper?

If the correct answer is related to a low melting point, and the candidate's answer is 'It has a low melting point and is coloured grey' this would **not** be treated as a cancelling error.

4 Full marks should be awarded for the correct answer to a calculation on its own whether or not the various steps are shown **unless the question is structured or working is specifically asked for.**

5 A mark should be deducted in a calculation for each arithmetic slip **unless stated otherwise in the marking scheme.** No marks should be deducted for incorrect or missing units at intermediate stages in a calculation

6 A mark should be deducted for incorrect or missing units **unless stated otherwise in the marking scheme**. Please note, for example, that KJ mol^{-1} is not acceptable for kJ mol^{-1} and a mark should be deducted.

7 Where a wrong numerical answer (already penalised) is carried forward to another step, no further penalty is incurred provided the result is used correctly.

8 No mark is given for the solution of an equation which is based on a wrong principle.

Example: Use the information in the table to calculate the standard entropy change for the reaction:

$$C_2H_2 + 2HCl \longrightarrow CH_2ClCH_2Cl$$

Compound	**S^o/J K^{-1} mol^{-1}**
C_2H_2	201
HCl	187
CH_2ClCH_2Cl	208

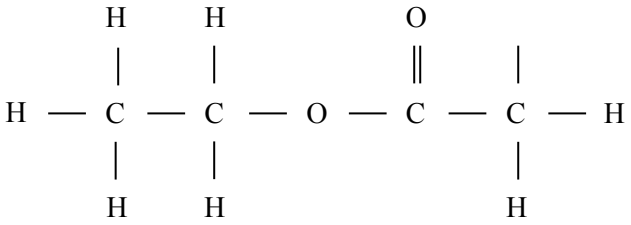
Using $\Delta S^o = S^o_{\text{reactants}} - S^o_{\text{products}}$ would gain zero marks.

9 No marks are given for the description of the wrong experiment.

10 Full marks should be given for correct information conveyed by a sketch or diagram in place of a written description or explanation.

11 In a structural formula, if one hydrogen atom is missing but the bond is shown, no marks are deducted.

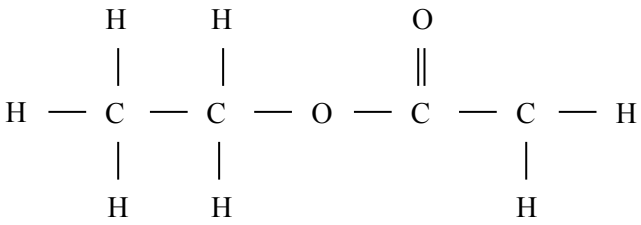
Examples:



Would not be penalised as the structural formula for ethyl ethanoate.

If the bond is also missing, then zero marks should be awarded.

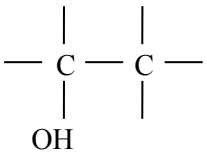
Example:



12 If a structural formula is asked for, CH_3- and CH_3CH_2- are acceptable as methyl and ethyl groups respectively.

13 With structures involving an –OH or an $–NH_2$ group, no mark should be awarded if the 'O' or 'N' are not bonded to a carbon, ie $OH–CH_2$ and $NH_2–CH_2$.

14 When drawing structural formulae, no mark should be awarded if the bond points to the 'wrong' atom, eg



15 A symbol or correct formula should be accepted in place of a name **unless stated otherwise in the marking scheme**.

16 When formulae of ionic compounds are given as answers it will only be necessary to show ion charges if these have been specifically asked for. However, if ion charges are shown, they must be correct. If incorrect charges are shown, no marks should be awarded.

17 If an answer comes directly from the text of the question, no marks should be given.

Example: A student found that 0·05 mol of propane, C_3H_8 burned to give 82·4 kJ of energy.

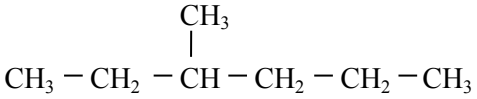
$$C_3H_8(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(\ell)$$

Name the kind of enthalpy change which the student measured.

No marks should be given for 'burning' since the word 'burned' appears in the text.

18 A guiding principle in marking is to give credit for (partially) correct chemistry rather than to look for reasons not to give marks.

Example 1: The structure of a hydrocarbon found in petrol is shown below.



Name the hydrocarbon.

Although not completely correct, the answer, '3, methyl-hexane' would gain the full mark ie wrong use of commas and dashes.

Example 2: A student measured the pH of four carboxylic acids to find out how their strength is related to the number of chlorine atoms in the molecule. The results are shown.

Structural formula	**pH**
CH_3COOH	1·65
$CH_2ClCOOH$	1·27
$CHCl_2COOH$	0·90
CCl_3COOH	0·51

How is the strength of the acids related to the number of chlorine atoms in the molecule?

Again, although not completely correct, an answer like 'the more Cl_2, the stronger the acid' should gain the full mark.

Example 3: Why does the (catalytic) converter have a honeycomb structure?

A response like 'to make it work' may be correct but it is not a chemical answer and the mark should not be given.

2015 Chemistry Advanced Higher
Part Two: Marking Instructions for each Question
Section A

Question	Expected Answer(s)	Max Mark
1.	C	**1**
2.	D	**1**
3.	D	**1**
4.	A	**1**
5.	B	**1**
6.	C	**1**
7.	C	**1**
8.	D	**1**
9.	B	**1**
10.	C	**1**
11.	A	**1**
12.	C	**1**
13.	B	**1**
14.	D	**1**
15.	B	**1**
16.	A	**1**
17.	C	**1**
18.	A	**1**
19.	A	**1**
20.	B	**1**

Question	Expected Answer(s)	Max Mark
21.	D	**1**
22.	A	**1**
23.	B	**1**
24.	A	**1**
25.	B	**1**
26.	D	**1**
27.	B	**1**
28.	C	**1**
29.	A	**1**
30.	A	**1**
31.	A	**1**
32.	D	**1**
33.	B	**1**
34.	A	**1**
35.	B	**1**
36.	D	**1**
37.	B	**1**
38.	C	**1**
39.	C	**1**
40.	C	**1**

Section B

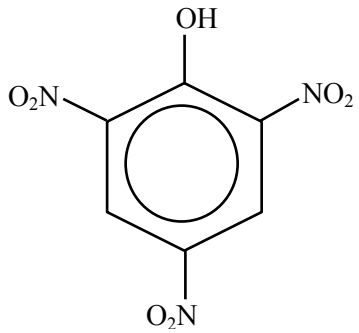
Question			Acceptable Answer	Max Mark	Unacceptable
1	**a**	**i**	Equal energy/same energy/contains the same energy	**1**	Same energy level/same energy subshell/
1	**a**	**ii**	Correct statement of Hund's Rule. Each orbital should be filled singly before spin pairing takes place The 2p should be filled singly (before spin pairing takes place) The 2p should be filled singly (before they double up) Orbital box diagram showing **correct** representation	**1**	"**They**" should be filled singly ….. Each orbital should be filled singly Breaks Hund's rule
1	**b**	**i**	$E = Lhc/\lambda$ **(1)** $\lambda = 6{\cdot}02\times10^{23}\times6{\cdot}63\times10^{-34}\times3\times10^{8}/502000$ **(1)** $\lambda = 238{\cdot}5\text{nm} = 239\text{nm}$ or $2{\cdot}39\times10^{-7}$m or $2{\cdot}385\times10^{-7}$m **(1)** Correct = 3 sig figs – accept 2 sig figs to 5 sig figs (240nm and 238·52nm are also acceptable) 238nm = (2) Not using L = (2) if units correct So $3{\cdot}96\times10^{-31}$ m or 3.9622×10^{-31} m or $3{\cdot}962\times10^{-31}$ m or $3{\cdot}96\times10^{-22}$ nm or $4{\cdot}0\times10^{-31}$ m would all get (2) marks If don't convert J to kJ and get $2{\cdot}39\times10^{-4}$m / $2{\cdot}385\times10^{-4}$ m / 23852 nm / 24000 nm then **(2)** Correct answer with no working = **(3)**	**3**	E = Lhf (and nothing else) **(0)** **or** f = c/λ (and nothing else) **(0)** Correct figures but in wrong place and no equation given = **(0)** No units = −1 Mistake in a number = −1 Two errors in one line = −1 Wrong answer with no working = 0 (unless the answers are one of those mentioned here)
1	**b**	**i**	No – wavelength required is too short. Wavelength required is outside visible range. UV light required / visible light too long wavelength / frequency of visible light too low / visible light is between 400-700nm / 239nm is not in the visible region If calculated waveength in part (i) is in the range 400-700nm then follow through answer " yes" with correct explanation = **(1)**	**1**	No with no explanation. Visible light (energy) not enough No with wrong range of visible light = **(0)** No because visible light is not correct wavelength / energy. Any mention of energy with no explanation = **(0)**
				(6)	

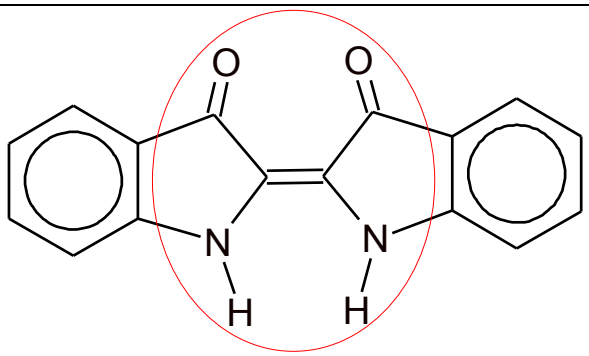
Question			Acceptable Answer	Max Mark	Unacceptable
2	**a**		$\Delta H° = (-394 + 130) - (-110 - 348)$ $= 194$	**1**	−194
2	**b**		$\Delta S° = (214 + 161) - (44 + 198)$ $= 133$		−133 / 0·133
2	**c**		$\Delta G^o = \Delta H^o - T\Delta S^o = 0$ **or** $T = \frac{\Delta H^o}{\Delta S^o}$ **(1)** $= \frac{194000}{133} = 1458 \cdot 6\,K$ **or** $1459\,K$ or 1460 K Allow 3 to 5 sig figs Follow through from incorrect (a) and (b) 194/133 = **(1)** Standard symbols not needed for first mark	**2**	Deduct 1 mark for ^oK or for −ve value for temp 1458 K, 1458, 1500 K, 1458.65 K are only worth 1 mark if correct relationship given
				(4)	

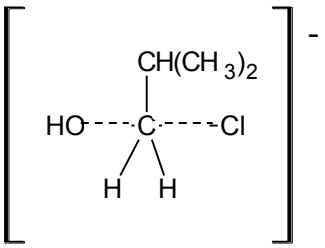
Question			Acceptable Answer	Max Mark	Unacceptable
3	**a**	**i**	1·26 V	**1**	No units (0)
3	**a**	**ii**	$\Delta G^o = -\ n\ F\ E^o$ / $\Delta G = -nFE$ **(1)** $-\ 121{\cdot}59$ (kJ mol^{-1})/ $-\ 121{\cdot}6$ (kJ/mol^{-1}) **or** −122 would get (2) marks 121·59 gets (1) only unless correct follow through from (i) −71·41 follow through from 0·74 in (i) = **(2)**	**2**	Incorrect follow through = **(1)** If use +nFE = maximum of **(1)**
3	**b**	**i**	(IV), 4, +4, IV, 4+, four	**1**	−4 / 4−
3	**b**	**ii**	Both the blue / VO^{2+} and yellow / VO_2^+ coloured (ions) are present (and will produce the green colour) / yellow and blue gives green	**1**	Green is an intermediate colour between blue and yellow
3	**b**	**iii**	3 / three	**1**	
3	**b**	**iv**	(Oxygen) oxidises the vanadium ions / reacts with oxygen / oxygen turns it back / oxygen effects the mixture / oxidation of V^{2+} ion / reacts with air to oxidised form/it has been oxidised	**1**	Reacts with the air / oxygen reduces the vanadium ions / oxide ions / oxygen reacts with zinc / due to something escaping
				(7)	
4	**a**		Green / lime green / light green	**1**	Green − blue or blue – green, cyan, turquoise, aqua marine
4	**b**		Hydrogen peroxide / H_2O_2 / O_2H_2	**1**	
4	**c**		Octahedral (incorrect spelling is OK)	**1**	Octagonal / octahedron / octagon
				(3)	

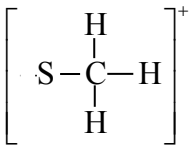
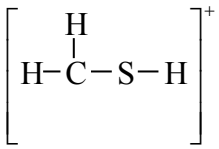
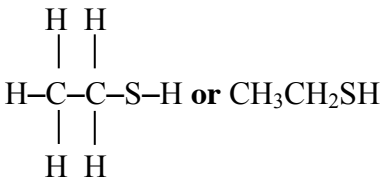
Question			Acceptable Answer	Max Mark	Unacceptable
5	a	i	At equilibrium $[NO_2] = 0{\cdot}24$ mol l^{-1} N_2O_4 reacted → $0{\cdot}24/2 = 0{\cdot}12$ $[N_2O_4]$ at equilibrium → $0{\cdot}28 - 0{\cdot}12 = 0{\cdot}16$ **(1)** $K = [NO_2]^2/[N_2O_4]$ **or** $= (0{\cdot}24)^2/(0{\cdot}16)$ **(1)** $= 0{\cdot}36$ **(1)** Correct FT from incorrect (or missing 0·16) For example $0{\cdot}24^2 / 0{\cdot}28 = 0{\cdot}206 / 0{\cdot}21 / 0{\cdot}2$ **(2)** $0{\cdot}24^2 / 0{\cdot}12 = 0{\cdot}48$ **(2)**	**3**	$0{\cdot}24^2/0{\cdot}28 \times 127 = 0$ marks 1 mark deducted if units given
5	a	ii	The forward reaction is endothermic since decreasing the temp has favoured the reverse reaction. The forward reaction is endothermic with an acceptable reason that shows an understanding of degree of dissociation (eg more product forms at higher temperatures / as temp decreases the yield decreases). **Or** There is bond breaking taking place therefore the reaction is endothermic. Correct FT from (i)	**1**	Reaction is endothermic because as temperature decreases K decreases
5	b	i	$x = 7{\cdot}40 \times 10^{-4} / 7{\cdot}4 \times 10^{-4}$ **(1)** $y = 2{\cdot}96 \times 10^{-3} / 3{\cdot}0 \times 10^{-3}$ **(1)**	**2**	3×10^{-3}
5	b	ii	Rate = $k\,[NO]^2$ $k = \dfrac{7{\cdot}40 \times 10^{-4}}{\left(2{\cdot}00 \times 10^{-3}\right)^2} = 185$ **(1)** $l\ mol^{-1}s^{-1}$ **(1)** (units in any order eg $mol^{-1}ls^{-1}$) − if unit is incorrect lose one mark	**2**	
				(8)	

Question			Acceptable Answer	Max Mark	Unacceptable
6	a		$\Delta H_5 = -698$ **(1)** 337 + 243 + 751 + 1970 + (−698) + (−2774) = −171 allow follow through from incorrect ΔH_5	**2**	
6	b		337 + 121·5 + 751 + (−349) + (−921) = −60·5 −1 for each incorrect number 2nd mark for correct calculation with follow through from wrong numbers	**2**	If only use 3 numbers for example – wrong principle
6	c		$CuCl_2$ – more negative ΔH_f value FT from a) and b) so whichever is more negative Negative formation energy means reverse reaction is less likely than CuCl	**1**	More energy to break Greater / smaller (but not cancelling) Negative formation energy means reverse reaction is less likely
				(5)	
7	a		Phenolphthalein (including incorrect spellings – provided it sounds correct when spoken) / phenylphthalein	**1**	phenylalanine
7	b	i	mol H_2SO_4 = 8·65/1000 × 0·050 = $4·325 \times 10^{-4}$ (mol) $4·3 \times 10^{-4}$ or $4·33 \times 10^{-4}$ (8·6 /1000 × 0·050 = (**1**))	**1**	$4·0 \times 10^{-4}$
7	b	ii	Mol NaOH in 25 cm^3 sample = $4·325 \times 10^{-4} \times 2 = 8·65 \times 10^{-4}$ mol mol NaOH in 250 cm^3 standard flask = $8·65 \times 10^{-3}$ (0·00865 mol) / $8·7 \times 10^{-3}$ Follow on = 20 × answer to part (i)	**1**	
7	b	iii	Initial moles of NaOH = 25/1000 × 1 = 0·025 mol Moles of NaOH reacting with ASA = 0·025 – 0·00865 = 0·01635 / 0·016 / 0·0164 Accept 0·0163 as follow on from 8·7	**1**	

Question			Acceptable Answer	Max Mark	Unacceptable
7	**b**	**iv**	Moles of ASA = 0·01635/2 = 0·008175 Mass of ASA 0·008175 × 180 = 1·4715 g **(1)** Mass of ASA in one tablet = 0·2943 g **(1)** **0·29 / 0·294 / 0·2952 / 0·295 / 0·3 or converted to mg** Allow follow through from any answer in (iii) 1 mark for 90 × answer to part (iii) 2 marks for 18 x answer to part (iii)	**2**	
				(6)	
8	**a**		sp^2	**1**	
8	**b**	**i**	Chloromethane / bromomethane and $FeCl_3$ / $FeBr_3$ / $AlCl_3$ / $AlBr_3$ Reagent and catalyst needed for mark	**1**	
8	**b**	**ii**	Electrophilic substitution / alkylation / Friedel Crafts	**1**	Nucleophilic is cancelling substitution
8	**c**	**i**	 Kekule structure is fine Must have correct placing of bonds to nitro groups	**1**	Bonds from benzene ring going to O of the nitro group
8	**c**	**ii**	NO_2^+	**1**	NO^{2+} H_2SO_4 / HNO_3
				(5)	

Question			Acceptable Answer	Max Mark	Unacceptable
9	**a**		An answer such as red and green being absorbed (and blue being transmitted) / absorbs all colours except blue / orange absorbed/red and yellow absorbed	**1**	Reflects – cancelling Blue light emitted - cancelling General answer in terms of absorption and transmittance
9	**b**		 Non – skeletal Circled part most important – NH on same side with C=O on opposite.	**1**	
9	**c**		Addition Ignore electrophilic and nucleophilic	**1**	
				(3)	

Question			Acceptable Answer	Max Mark	Unacceptable
10	**a**		2-chloro-2-methylpropane 2-chloromethylpropane	**1**	2,2-chloromethylpropane methyl-2-chloropropane 2-methylchloropropane
10	**b**		$CH_3CH = CHCH_3$ **(1)** and $CH_2 = CHCH_2CH_3$ **(1)** Or full structural formulae Ignore incorrect names	**2**	Names only
10	**c**	**i**	2-methylpropan-1-ol Methylpropan-1-ol 1-hydroxy-2-methylpropane Methyl-1-propanol	**1**	
10	**c**	**ii**	Five membered transition state with negative charge  Needs dotted bonds as above Wedges and dotted 3D bonds are OK.	**1**	OH---- (dotted bond going – to H of OH)
10	**d**		$CH_3CH_2CH_2CH_2Cl$ Or full structural / skeletal	**1**	
10	**e**		3 / three	**1**	
10	**f**		A= (has an asymmetric carbon and so) must be a racemic mix **(1)** B = no chiral carbon / no carbon with four different groups around it **(1)**	**2**	Carbon does not have four molecules around it Carbon does not have four atoms around it B does not have an optical isomer
				(9)	

Question			Acceptable Answer	Max Mark	Unacceptable
11	**a**			**2**	
			C = 0·96g H = 0·24g S = 1·28g **(1)** C 0·96g/12 = 0·08 H 0·24g/ 1 = 0·24 S 1·28g/32·1 = 0·04 2 6 1 **(1)** (Empirical formula C_2H_6S) Alternative methods acceptable: C = 3·52/44 = 0·08; H = 2·16 /18 = 0·12; S = 2·56/64 = 0·04 **(1)** Mole ratio $CO_2 : H_2O : SO_2$ = 2: 3: 1 So 2 × C : 6 × H : 1 × S **(1)** Must use values given in question.		
11	**b**		 **or**  **SCH_3^+ or CH_2SH^+** any order of atoms with a positive charge is acceptable Round brackets OK If no brackets for full structural then charge must be on S (LHS fragment) or C (RHS fragment)	**1**	No charge / negative charge
11	**c**		 **or** CH_3CH_2SH	**1**	Alkene structure = 0 S with two methyl groups is not acceptable C_2H_5SH
				(4)	

[END OF MARKING INSTRUCTIONS]