

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.



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

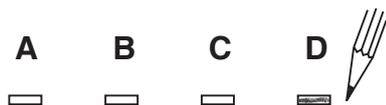
- A chromatography
- B fractional distillation
- C fractional crystallisation
- D filtration.

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



Changing an answer

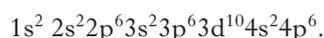
If you decide to change your answer, carefully erase your first answer and using your pencil, fill in the answer you want. The answer below has been changed to **D**.



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

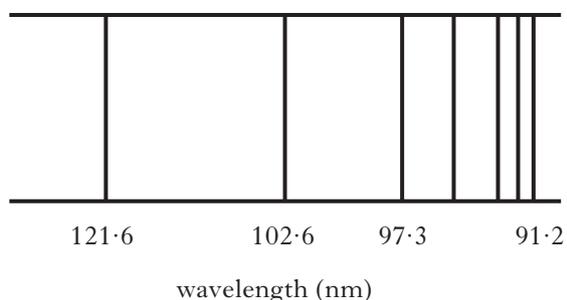
- A shorter wavelength and higher frequency
- B longer wavelength and lower velocity
- C longer wavelength and lower frequency
- D shorter wavelength and higher velocity.

2. The electronic configuration of a krypton atom is



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

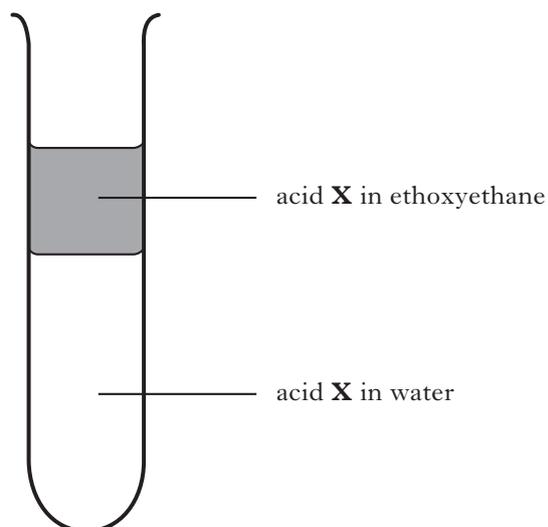
- A $[\text{Cu}(\text{NH}_3)_4\text{Cl}_2]^{2-}$
- B $[\text{Cu}(\text{NH}_3)_4\text{Cl}_2]$
- C $[\text{Cu}(\text{NH}_3)_4\text{Cl}_2]^{2+}$
- D $[\text{Cu}(\text{NH}_3)_4\text{Cl}_2]^{4+}$.

10. $\text{ClO}_3^-(\text{aq}) + 6\text{H}^+(\text{aq}) + n\text{e}^- \rightarrow \text{Cl}^-(\text{aq}) + 3\text{H}_2\text{O}(\ell)$

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

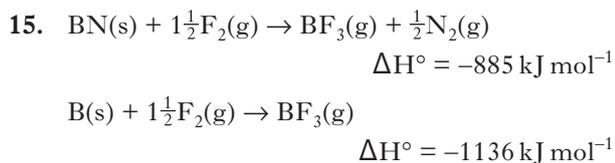
13. Which of the following would **not** be suitable as a buffer solution?

- 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.



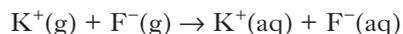
From the above data, it can be deduced that the enthalpy of formation, in kJ mol^{-1} , of boron nitride, BN(s) , is

- 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 $\text{NH}_3(\text{g}) \rightarrow \text{N}(\text{g}) + 3\text{H}(\text{g})$
- B $2\text{NH}_3(\text{g}) \rightarrow \text{N}_2(\text{g}) + 3\text{H}_2(\text{g})$
- C $\text{NH}_3(\text{g}) \rightarrow \frac{1}{2}\text{N}_2(\text{g}) + \frac{3}{2}\text{H}_2(\text{g})$
- D $2\text{NH}_3(\text{g}) + 1\frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{N}_2(\text{g}) + 3\text{H}_2\text{O}(\text{g})$

17. The enthalpy change for the reaction



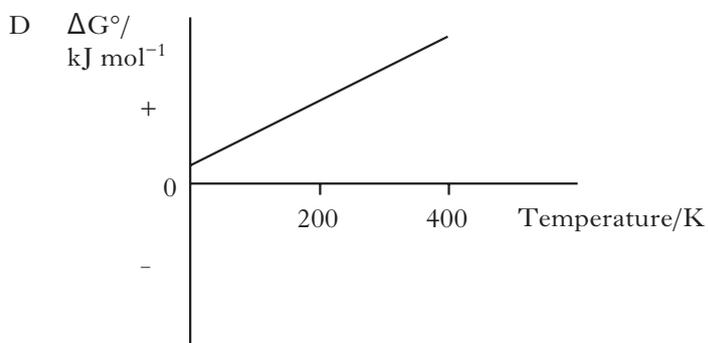
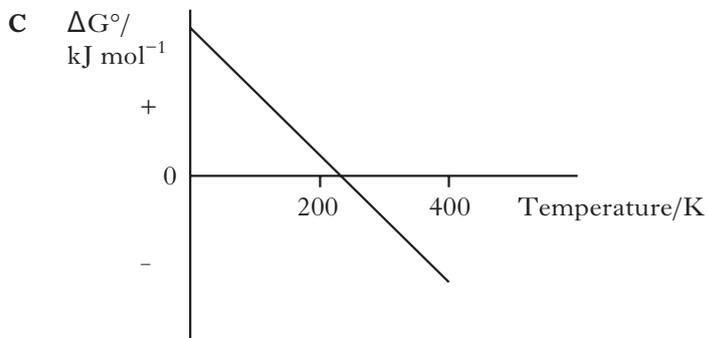
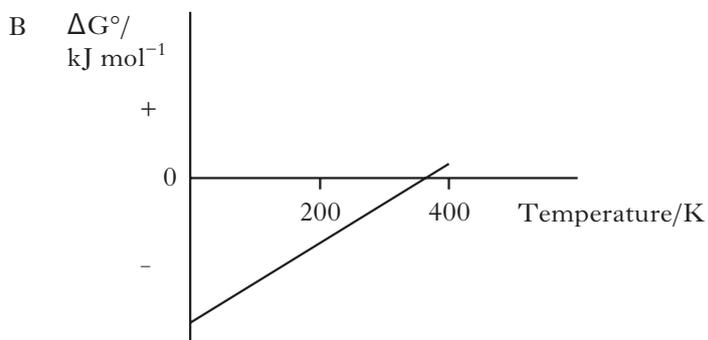
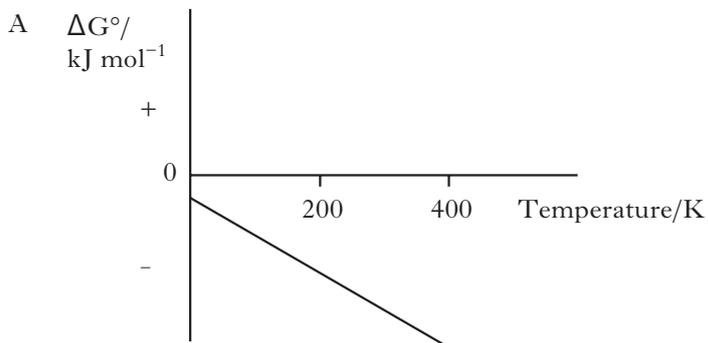
is

- 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?



20. The reaction



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 $\Delta G^\circ > 0$
- B $K > 1$ and $\Delta G^\circ < 0$
- C $K < 1$ and $\Delta G^\circ > 0$
- D $K < 1$ and $\Delta G^\circ < 0$

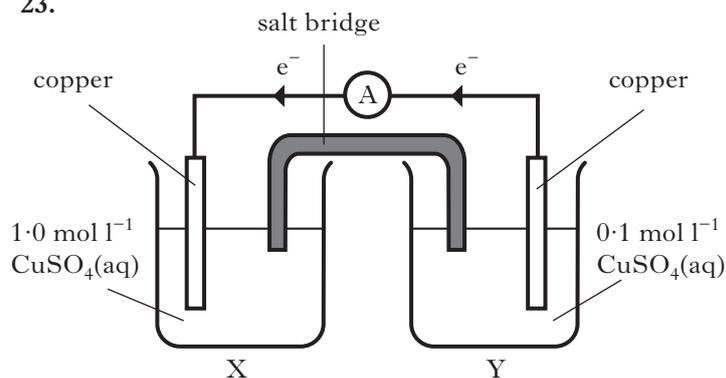
21. For which of the following reactions would the value of $\Delta G^\circ - \Delta H^\circ$ be approximately zero?

- A $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$
- B $\text{C}(\text{s}) + \text{H}_2\text{O}(\text{g}) \rightarrow \text{CO}(\text{g}) + \text{H}_2(\text{g})$
- C $\text{Zn}(\text{s}) + 2\text{H}^+(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{H}_2(\text{g})$
- D $\text{Cu}^{2+}(\text{aq}) + \text{Mg}(\text{s}) \rightarrow \text{Mg}^{2+}(\text{aq}) + \text{Cu}(\text{s})$

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.

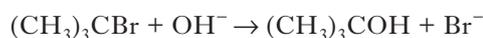


Which of the following will occur in the above cell?

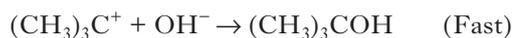
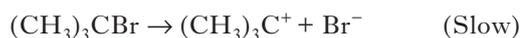
- A The blue colour in Y will become less intense.
- B The mass of the electrode in Y will decrease.
- C The concentration of the solution in X will increase.
- D Electrons will flow from X to Y through the salt bridge.

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

One of these has only one step



The other has two steps



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

- A $\text{rate} = k[(\text{CH}_3)_3\text{CBr}]$
- B $\text{rate} = k[(\text{CH}_3)_3\text{CBr}][\text{OH}^-]$
- C $\text{rate} = k[(\text{CH}_3)_3\text{C}^+]$
- D $\text{rate} = k[(\text{CH}_3)_3\text{C}^+][\text{OH}^-]$.



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

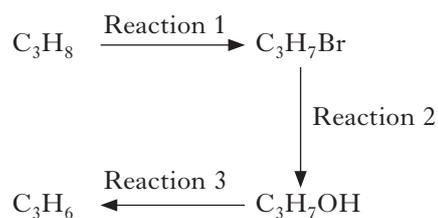
26. In a chemical reaction the rate is doubled for every 10°C rise in temperature. When the temperature is increased from 20°C to 60°C , the rate of the reaction will become faster by a factor of

- A 3
- B 4
- C 8
- D 16.

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

- A $\text{Cl}\cdot + \text{Cl}\cdot \rightarrow \text{Cl}_2$
- B $\text{Cl}\cdot + \text{CH}_4 \rightarrow \text{CH}_3\cdot + \text{HCl}$
- C $\text{CH}_3\cdot + \text{Cl}\cdot \rightarrow \text{CH}_3\text{Cl}$
- D $\text{Cl}_2 \rightarrow \text{Cl}\cdot + \text{Cl}\cdot$

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



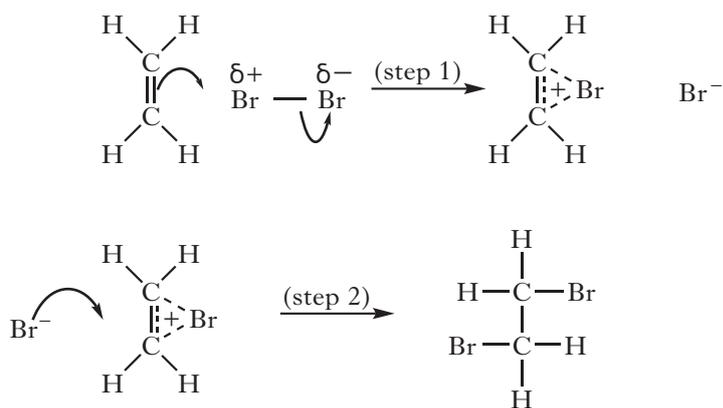
	Reaction 1	Reaction 2	Reaction 3
A	addition	substitution	elimination
B	addition	addition	condensation
C	substitution	substitution	elimination
D	substitution	addition	condensation

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

- A $\text{C}_3\text{H}_7\text{Br} + \text{KOH} \xrightarrow{\text{ethanol}} \text{C}_3\text{H}_6 + \text{KBr} + \text{H}_2\text{O}$
- B $\text{C}_3\text{H}_7\text{Br} + \text{KCN} \xrightarrow{\text{ethanol}} \text{C}_3\text{H}_7\text{CN} + \text{KBr}$
- C $\text{C}_2\text{H}_5\text{Cl} + \text{C}_2\text{H}_5\text{ONa} \xrightarrow{\text{ethanol}} \text{C}_2\text{H}_5\text{OC}_2\text{H}_5 + \text{NaCl}$
- D $\text{C}_2\text{H}_5\text{Br} + \text{NaOH} \xrightarrow{\text{water}} \text{C}_2\text{H}_5\text{OH} + \text{NaBr}$

[Turn over

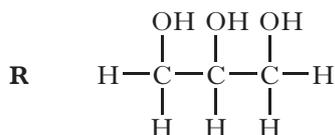
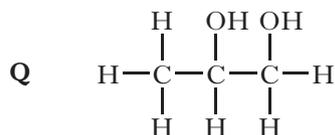
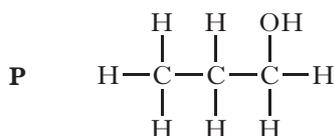
30.



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.



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?

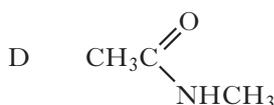
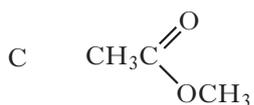
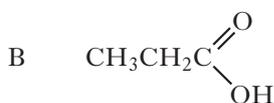
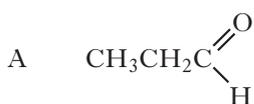
- A Aqueous sodium hydroxide followed by oxidation
- B Potassium cyanide followed by hydrolysis
- C Sodium hydroxide in ethanol
- D Sodium in ethanol

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?



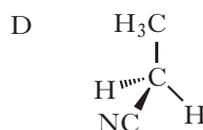
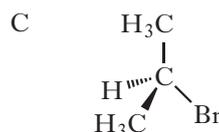
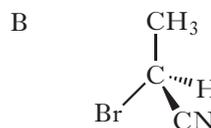
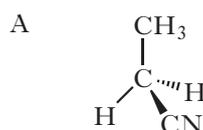
35. To help in the identification of an organic compound, a crystalline derivative **must**

- 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.

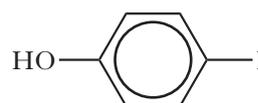
36. Which of the following compounds will react with both dilute hydrochloric acid and sodium hydroxide solution?

- 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?



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

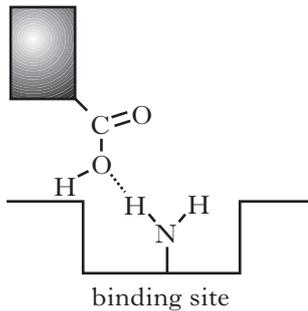
39. Sulphonamides are synthetic compounds that block the production of folic acid in bacterial cells.

Sulphonamides are best described as

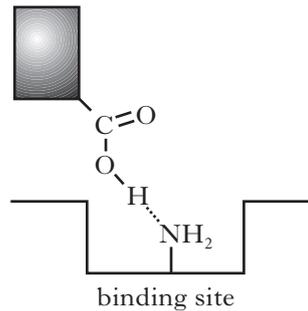
- A agonists
- B receptors
- C antagonists
- D pharmacophores.

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

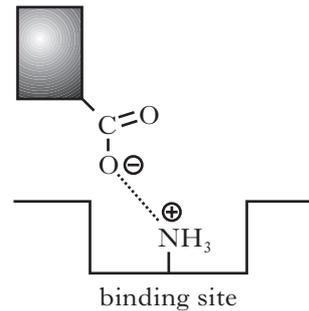
Hydrogen-bond acceptor



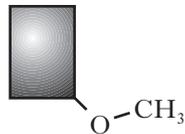
Hydrogen-bond donor



Ionic interaction



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.

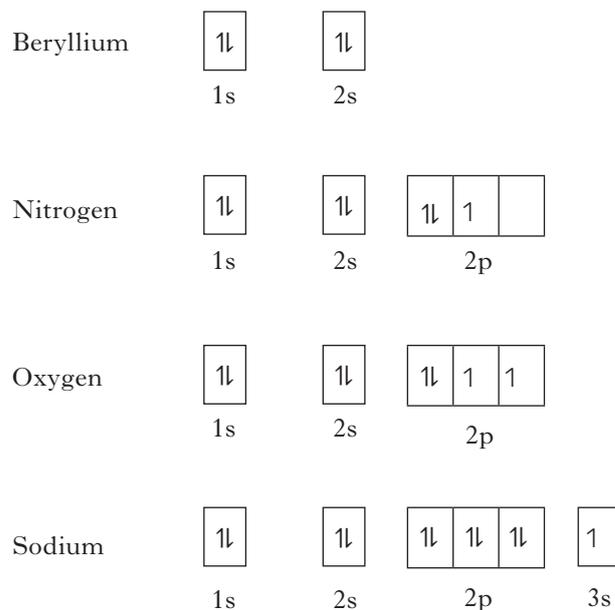
SECTION B

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 1 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)

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

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



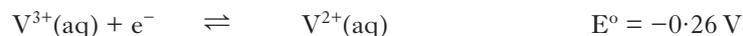
Substance	Standard enthalpy of formation, $\Delta H_f^\circ / \text{kJ mol}^{-1}$	Standard entropy, $S^\circ / \text{J K}^{-1} \text{mol}^{-1}$
ZnO(s)	-348	44
CO(g)	-110	198
Zn(g)	+130	161
CO ₂ (g)	-394	214

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 $\text{J K}^{-1} \text{mol}^{-1}$; 1
- (c) the theoretical temperature above which the reaction becomes feasible. 2
- (4)**

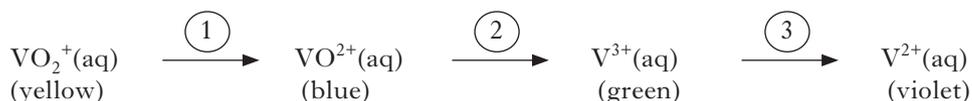
3. Vanadium is a transition metal which exhibits different oxidation states. This property allows it to be used in electrochemical cells and also gives rise to different coloured solutions.

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



- (i) Calculate the standard emf, E° , 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, $\text{VO}_2^{+}(\text{aq})$. 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.



- (i) Determine the oxidation number of vanadium in the blue $\text{VO}^{2+}(\text{aq})$ ion. 1
- (ii) It was observed during the demonstration that the yellow solution turned green before turning blue in reaction $\textcircled{1}$.
Suggest a reason for this. 1
- (iii) In reaction $\textcircled{3}$ $\text{V}^{2+}(\text{aq})$ ions are produced.
How many d electrons does a $\text{V}^{2+}(\text{aq})$ ion have? 1
- (iv) When the cotton wool stopper is removed the violet solution slowly changes back to blue.
Suggest why this happens. 1

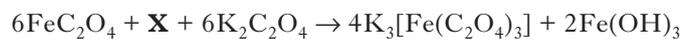
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4. In a **PPA**, potassium trioxalatoferrate(III) crystals are prepared from ammonium iron(II) sulphate in a series of steps.

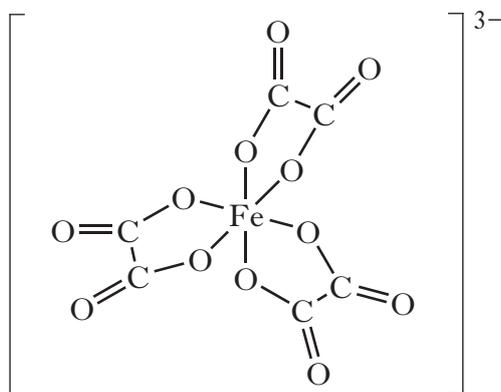
Step 1 A precipitate of iron(II) oxalate is produced.

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



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.

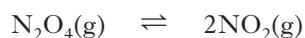


Name the shape given to the arrangement of bonds around the iron.

1
(3)

5. Nitrogen forms a variety of oxides.

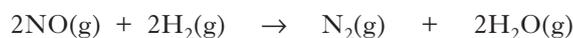
- (a) Dinitrogen tetroxide, $\text{N}_2\text{O}_4(\text{g})$, dissociates to form nitrogen dioxide, $\text{NO}_2(\text{g})$, according to the equation.



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.



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

Experiment	Initial $[\text{NO}] / \text{mol l}^{-1}$	Initial $[\text{H}_2] / \text{mol l}^{-1}$	Initial rate / $\text{mol l}^{-1}\text{s}^{-1}$
1	2.00×10^{-3}	1.20×10^{-3}	7.40×10^{-4}
2	2.00×10^{-3}	2.40×10^{-3}	x
3	4.00×10^{-3}	2.40×10^{-3}	y

The following rate equation was deduced.

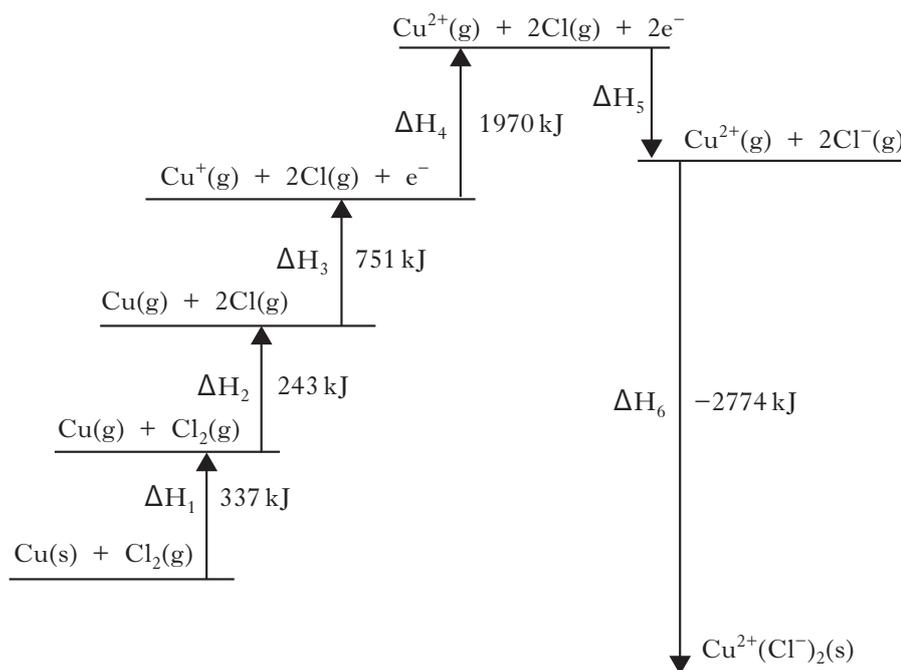
$$\text{Rate} = k[\text{NO}]^2$$

- (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

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° , in kJ mol^{-1} , for $\text{Cu}^{2+}(\text{Cl}^{-})_2(\text{s})$. 2
- (b) Using selected information from the thermochemical cycle above and the equation below calculate the standard enthalpy of formation, ΔH_f° , in kJ mol^{-1} , of $\text{Cu}^{+}\text{Cl}^{-}(\text{s})$.

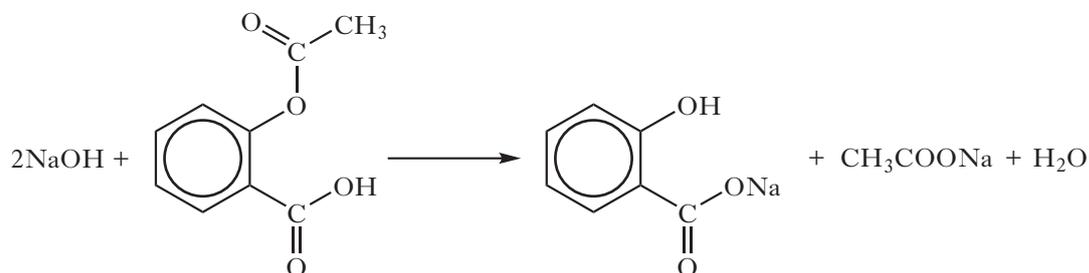


- (c) **Explain** which of the two chlorides of copper will be more stable at 298 K. 1

(5)

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.



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)

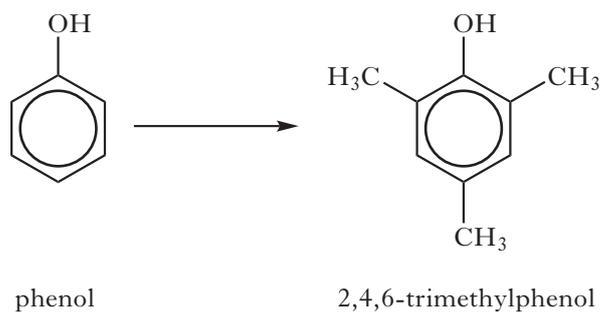
[Turn over

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.



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

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

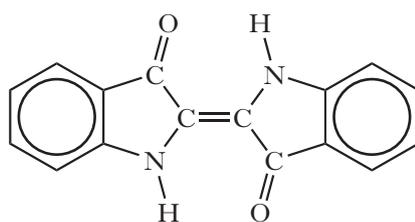
(c) Phenol can be converted into 2,4,6-trinitrophenol using a mixture of concentrated nitric acid and concentrated sulphuric acid.

(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)

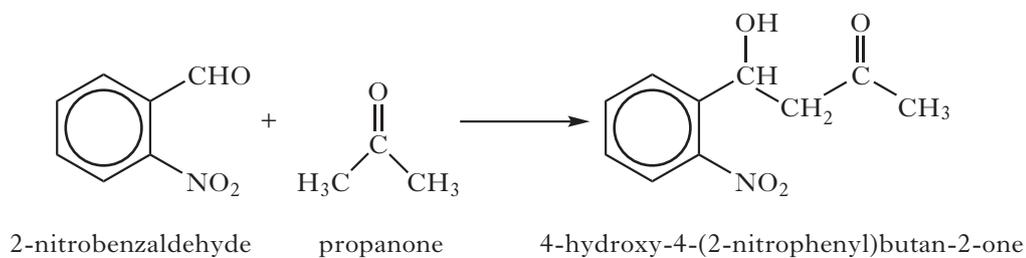
9. The blue colour of denim jeans comes from a dye known as indigo.



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.



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

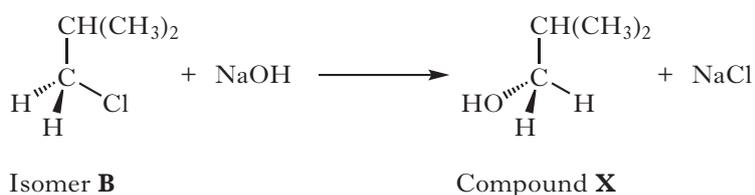
1
(3)

[Turn over

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

**A****B****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.



- (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)

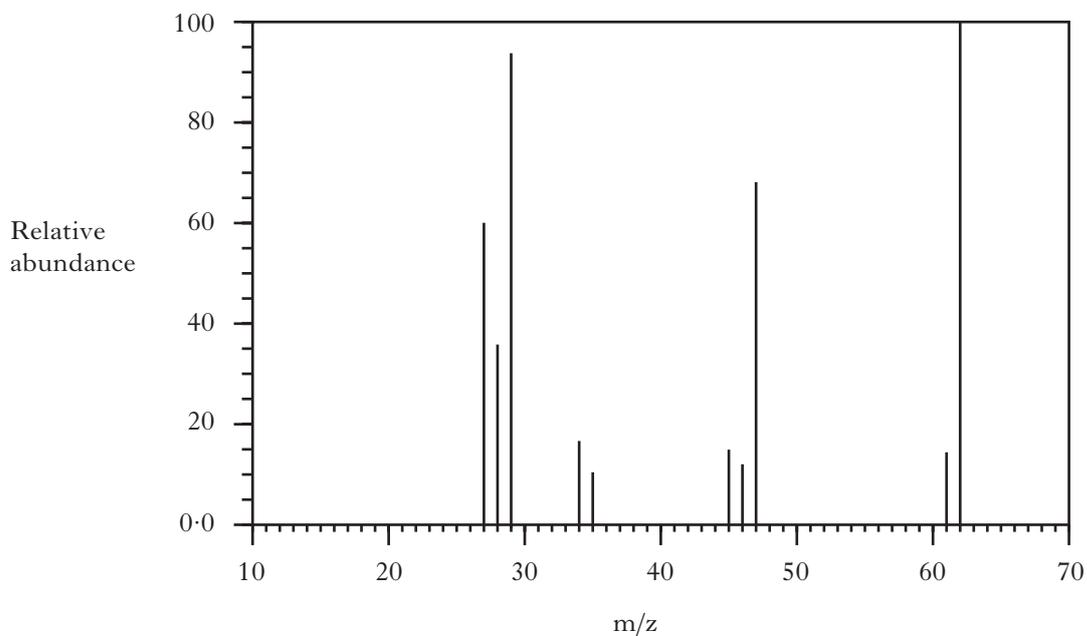
11. Compound **X** contains only carbon, hydrogen and sulphur.

(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)

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