

X273/13/02

NATIONAL
QUALIFICATIONS
2014

MONDAY, 12 MAY
1.00 PM – 3.30 PM

CHEMISTRY
ADVANCED HIGHER
(REVISED)

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

SECTION A – 30 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 – 70 marks

All questions should be attempted.

Answers must be written clearly and legibly in ink.



SECTION A

Read carefully

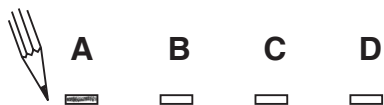
- 1 Check that the answer sheet provided is for **Chemistry Advanced Higher (Revised) (Section A)**.
- 2 For this section of the examination you must use an **HB pencil** and, where necessary, an eraser.
- 3 Check that the answer sheet you have been given has **your name, date of birth, SCN** (Scottish 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**.



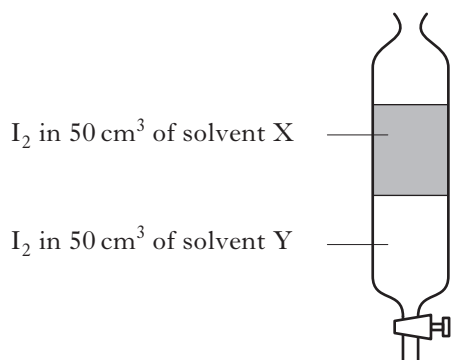
- The quantum number which specifies the shape of an orbital is the
 - principal quantum number
 - angular momentum quantum number
 - magnetic quantum number
 - spin quantum number.
- Element number 104 in the Periodic Table is
 - an s-block element
 - a p-block element
 - a d-block element
 - an f-block element.
- Which of the following statements is **incorrect** about electronic configurations of all first row transition metal atoms in their ground states?
 - The five 3d orbitals are degenerate.
 - They all have at least one electron in the 4s orbital.
 - Electrons begin to fill the 3d orbitals only after the 4s orbital is full.
 - When transition metal atoms form ions, the 4s electrons are lost first.
- The colour of a highly concentrated ionic solution which absorbs light only in the ultra-violet region of the electromagnetic spectrum is
 - red
 - black
 - violet
 - colourless.
- The Pauli Exclusion Principle states that
 - electrons fill degenerate orbitals singly
 - electrons fill orbitals in order of increasing energy
 - when degenerate orbitals are half filled all their electrons have parallel spins
 - no two electrons in the one atom can have the same set of four quantum numbers.
- The energy associated with a photon of electromagnetic radiation is
 - independent of the frequency
 - proportional to the frequency
 - inversely proportional to the frequency
 - proportional to the square of the frequency.
- In absorption spectroscopy, as the concentration of an ion in solution increases, there is an increase in the
 - wavelength of radiation absorbed
 - frequency of radiation absorbed
 - intensity of radiation absorbed
 - intensity of radiation transmitted.
- Which of the following has bond angles equal to 90° ?
 - SF_6
 - NH_4^+
 - SiCl_4
 - BeF_4^{2-}
- Which of the following does **not** have a pyramidal structure?
 - BF_3
 - NH_3
 - OH_3^+
 - PH_3
- The electronic configuration of a vanadium atom in its ground state is
 - $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$
 - $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 4p^3$
 - $1s^2 2s^2 2p^6 3s^2 3p^6 3d^3 4s^2$
 - $1s^2 2s^2 2p^6 3s^2 3p^6 3d^4 4s^1$.

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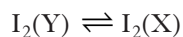
11. The highest oxidation state of chlorine is present in

- A HClO
- B HClO₂
- C HClO₃
- D HClO₄.

12.



Iodine was added to 50 cm³ of two immiscible solvents X and Y as shown. After shaking, the following equilibrium was established.



An extra 10 cm³ of solvent X was added, the mixture shaken and equilibrium re-established.

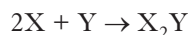
Which of the following statements is correct?

- A The concentration of I₂ in Y increases.
- B The concentration of I₂ in Y decreases.
- C The equilibrium constant increases.
- D The equilibrium constant decreases.

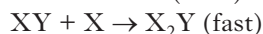
13. The order of a reaction

- A can only be obtained by experiment
- B determines the speed of the overall reaction
- C is determined by the stoichiometry involved
- D is the sequence of steps in the reaction mechanism.

14. A suggested mechanism for the reaction



is a two-step process



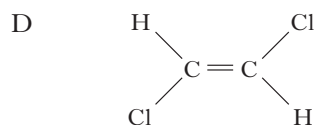
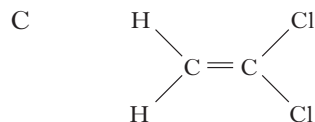
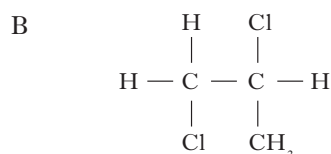
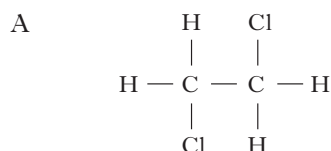
This mechanism is consistent with the rate equation,

- A rate = k[XY]
- B rate = k[X][Y]
- C rate = k[X]²[Y]
- D rate = k[X][XY].

15. The end-on overlap of two atomic orbitals lying along the axis of a bond leads to

- A hybridisation
- B a sigma bond
- C a pi bond
- D a double bond.

16. Which of the following compounds has a geometric isomer?



17. Mandelic acid has two optical isomers **X** and **Y**. The table shows the rotation of plane polarised light caused by various solutions of **X** and **Y**.

Volume of 0.1 mol l^{-1} X /cm ³	Volume of 0.1 mol l^{-1} Y /cm ³	Volume of water/cm ³	Observed rotation/°
100	0	0	+158
50	0	50	+79
50	50	0	0
0	100	0	-158

What would be the observed rotation for a solution containing 25 cm³ 0.1 mol l^{-1} **X** and 75 cm³ of 0.1 mol l^{-1} **Y**?

- A -79°
 B -39.5°
 C +39.5°
 D +79°
18. Which of the following is the formula for a tertiary haloalkane?
- A CHBr_3
 B $(\text{CH}_3)_3\text{CBr}$
 C $(\text{CH}_2\text{Br})_3\text{CH}$
 D $\text{BrCH}_2\text{C}(\text{CH}_3)_3$

19. Propene can be produced by heating 1-bromopropane with ethanolic potassium hydroxide.

This reaction is an example of

- A reduction
 B hydrolysis
 C elimination
 D condensation.

20. The formula $\text{C}_4\text{H}_{10}\text{O}$ could represent an alcohol ($\text{C}_4\text{H}_9\text{OH}$) or an ether ($\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$).

Which of the following statements would **not** be true about **both** compounds?

- A They can be made by nucleophilic substitution from a haloalkane.
 B They have hydrogen bonds between their molecules.
 C They are used as solvents.
 D They are flammable.

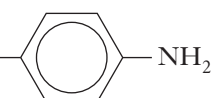
21. Which of the following will react to form $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_3$?

- A $\text{CH}_3\text{CH}_2\text{OH}$ and $\text{CH}_3\text{CH}_2\text{COONa}$
 B $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ and CH_3COONa
 C $\text{CH}_3\text{CH}_2\text{ONa}$ and $\text{CH}_3\text{CH}_2\text{CH}_2\text{I}$
 D $\text{CH}_3\text{CH}_2\text{ONa}$ and $\text{CH}_3\text{CHICH}_3$

22. Which of the following statements is true about the carboxyl group?

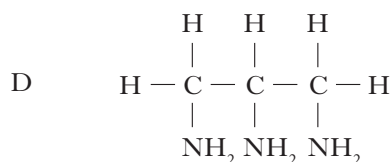
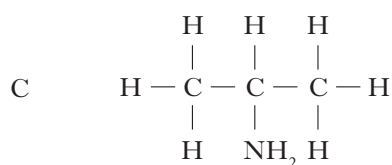
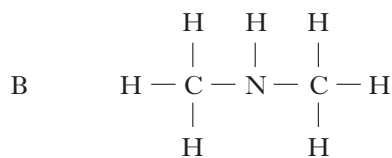
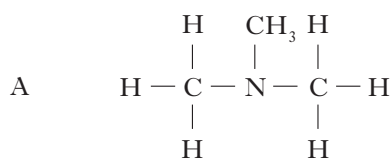
- A $\text{C}=\text{O}$ and $-\text{OH}$ each retain their own properties, unaffected by the other.
 B The properties of the $\text{C}=\text{O}$ are changed but the $-\text{OH}$ is unaffected.
 C The properties of the $-\text{OH}$ are changed but the $\text{C}=\text{O}$ is unaffected.
 D The properties of the $\text{C}=\text{O}$ and the $-\text{OH}$ are each affected by the other.

23. One mole of which of the following compounds will react with the largest volume of 1 mol l^{-1} hydrochloric acid?

- A CH_3NHCH_3
 B $\text{H}_2\text{NCH}_2\text{NH}_2$
 C $\text{HOOCCH}_2\text{NH}_2$
 D 

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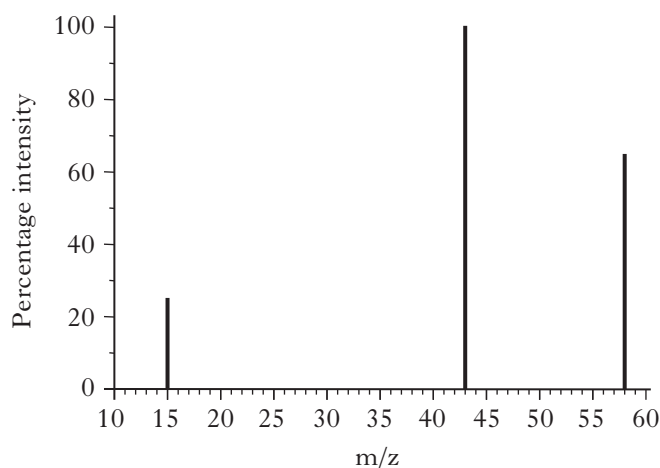
24. Which of the following structures represents a tertiary amine?



25. Which of the following is **not** an example of a hydrolysis reaction?

- A $\text{C}_2\text{H}_4 + \text{H}_2\text{O} \rightarrow \text{C}_2\text{H}_5\text{OH}$
 B $\text{CH}_3\text{CN} + 2\text{H}_2\text{O} \rightarrow \text{CH}_3\text{COOH} + \text{NH}_3$
 C $\text{CH}_3\text{COOCH}_3 + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{COOH} + \text{CH}_3\text{OH}$
 D $\text{C}_6\text{H}_5\text{COOCH}_3 + \text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_5\text{COOH} + \text{CH}_3\text{OH}$

26. A simplified mass spectrum of an organic compound is shown below.



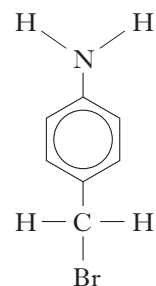
Which of the following compounds produces this spectrum?

- A Propane
 B Propan-1-ol
 C Propan-2-ol
 D Propanone

27. Which of the following analytical techniques depends on the vibrations within molecules?

- A Nuclear magnetic resonance spectroscopy
 B Atomic emission spectroscopy
 C Infra-red spectroscopy
 D Mass spectrometry

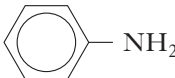
28. The two isotopes of bromine have mass numbers of 79 and 81. In the mass spectrum of



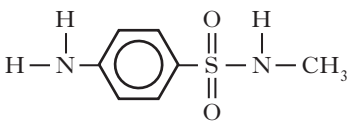
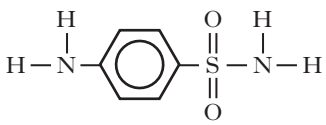
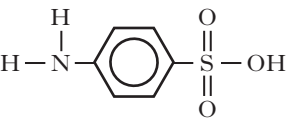
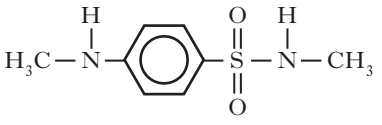
the ion fragment with a mass/charge ratio of 92 could be caused by

- A $[\text{CHBr}]^-$
 B $[\text{CH}_2\text{Br}]^+$
 C $[\text{C}_6\text{H}_4\text{NH}_2]^-$
 D $[\text{C}_6\text{H}_4\text{NH}_2]^+$

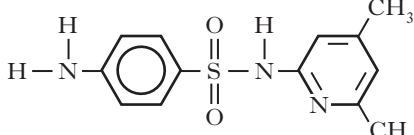
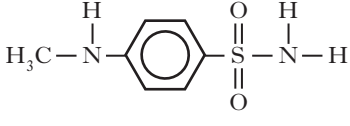
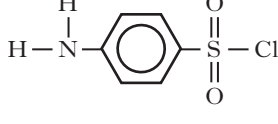
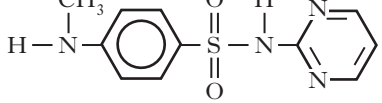
29. Which of the following amines shows no infra-red absorption between 3300cm^{-1} and 3500cm^{-1} ?

- A $(\text{CH}_3)_3\text{N}$
 B CH_3NHCH_3
 C $\text{H}_2\text{NCH}_2\text{NH}_2$
 D 

30. The table shows the structural formulae of some sulfonamides and their antibacterial activity.

Sulfonamide	Antibacterial activity
	active
	active
	inactive
	inactive

Which of the following would be an active antibacterial agent?

- A 
- B 
- C 
- D 

[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.

[Turn over for SECTION B on Page eight

SECTION B

Marks

70 marks are available in this section of the paper.

All answers must be written clearly and legibly in ink.

1. Atomic spectroscopy is a useful analytical tool for identifying and quantifying the elements present in a sample. It also provides information about atomic structure.

(a) When a high voltage is applied to a lamp filled with helium gas, a line of red light, wavelength 706 nm, is observed through a spectroscope.

(i) Explain how the line of red light is produced. 2

(ii) Calculate the energy, in kJ mol^{-1} , associated with this wavelength. 2

(b) A helium atom has two electrons in its ground state. One of the electrons can be described by the four quantum numbers 1, 0, 0, $+\frac{1}{2}$.

What four quantum numbers describe the other electron? 1

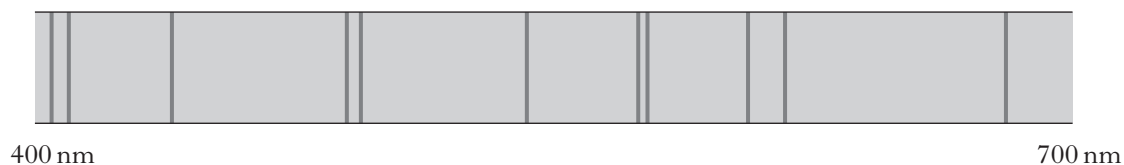
(c) (i) Using orbital box notation, write the electronic configuration for a phosphorus atom in its ground state. 1

(ii) Explain how your answer is consistent with Hund's rule. 1

(iii) When a phosphorus atom becomes excited an electron can move to the 4s orbital.

What four quantum numbers describe the excited electron? 1

(d) Mercury atoms are much larger than those of helium or phosphorus. A small section of the atomic emission spectrum for mercury is shown below.



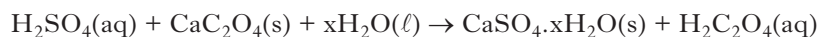
Why does this spectrum have multiple lines? 1

(e) Sir Isaac Newton was thought to have suffered from mercury poisoning and when his hair was analysed the level of mercury was found to be 73 ppm. The unit ppm stands for parts per million and refers to 1 mg per kg.

Calculate the number of moles of mercury in a 1.0×10^{-6} g sample of Newton's hair. 2

(11)

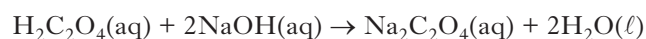
2. The dicarboxylic acid, oxalic acid, has molecular formula $\text{H}_2\text{C}_2\text{O}_4$.
It can be prepared by reacting calcium oxalate with sulfuric acid.



- (a) Draw a structural formula for oxalic acid. 1

- (b) 4.94 g of $\text{CaSO}_4 \cdot x\text{H}_2\text{O}$ was dehydrated to produce 3.89 g of CaSO_4 .
Determine the value of x . 2

- (c) The equation for the reaction between oxalic acid solution and sodium hydroxide solution is



A student used a standard solution of $0.0563 \text{ mol l}^{-1}$ oxalic acid to standardise 20.0 cm^3 of approximately 0.1 mol l^{-1} sodium hydroxide solution.

The raw results for the titration are given in the table.

	1st attempt	2nd attempt	3rd attempt
Final burette reading/ cm^3	17.2	33.8	16.6
Initial burette reading/ cm^3	0.0	17.2	0.1
Titre/ cm^3	17.2	16.6	16.5

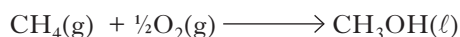
Calculate the accurate concentration of the sodium hydroxide solution. 2

- (d) Oxalic acid is a primary standard but sodium hydroxide is not. State **one** characteristic of sodium hydroxide that makes it unsuitable as a primary standard. 1
- (6)**

[Turn over

3. Methane gas can be converted into methanol in a series of steps.

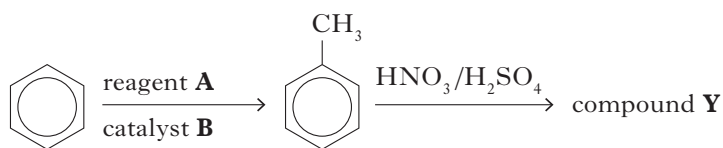
The overall equation for the reaction is



Substance	$\Delta H_f^\circ/\text{kJ mol}^{-1}$	$S^\circ/\text{J K}^{-1} \text{mol}^{-1}$
$\text{CH}_4(\text{g})$	-75	187
$\text{O}_2(\text{g})$	-	205
$\text{CH}_3\text{OH}(\ell)$	-239	127

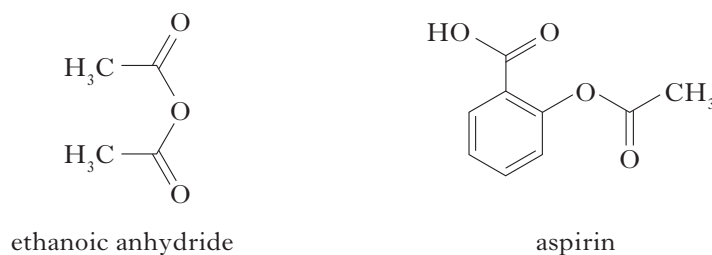
- (a) For the conversion of methane into methanol, calculate
- (i) the standard enthalpy change, ΔH° 1
- (ii) the standard entropy change, ΔS° . 1
- (b) Calculate the maximum temperature above which the reaction becomes no longer feasible. 2
- (4)**
4. During an Advanced Higher Chemistry Investigation in inorganic chemistry, a student deviates from the planned procedure and produces a pale yellow powder that the teacher suspects might be a new chemical.
- Using your knowledge of chemistry** suggest what the student might do to determine if it was a brand new substance. (3)
5. An organic acid can be extracted from a reaction mixture using ethoxyethane. 100 cm^3 of ethoxyethane were added to 500 cm^3 of an aqueous organic acid and the mixture shaken. After being allowed to settle, two immiscible layers formed.
- (a) Draw a structural formula for ethoxyethane. 1
- (b) What piece of apparatus would be used to separate both layers? 1
- (c) The following equilibrium was established.
- $$\text{organic acid(aqueous)} \rightleftharpoons \text{organic acid(ethoxyethane)}$$
- 25.0 cm^3 of the ethoxyethane layer required 22.7 cm^3 of 1.10 mol l^{-1} NaOH solution to neutralise it.
- 25.0 cm^3 of the aqueous layer was neutralised by 8.25 cm^3 of 0.10 mol l^{-1} NaOH solution.
- Calculate the equilibrium constant for the system. 3
- (5)**

6. Aromatic compounds are widely used in the production of pigments, antioxidants and agrochemicals. The reaction sequence below starts with benzene.



The first step in the sequence produces methyl benzene.

- (a) Name reagent **A**. 1
- (b) Identify catalyst **B**. 1
- (c) What name is given to the type of reaction taking place in both steps? 1
- (3)**
7. Aspirin is one of the most widely used drugs in our society. Aspirin works as a pain killer by binding to a specific enzyme and blocking its use in biological pathways which lead to the production of pain.
- (a) What name is given to drugs that behave in this way? 1
- (b) Aspirin can be prepared by reacting 2-hydroxybenzoic acid ($\text{C}_7\text{H}_6\text{O}_3$), with ethanoic anhydride in acidic conditions.



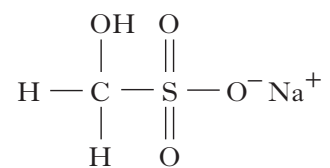
- (i) Draw a structural formula for 2-hydroxybenzoic acid. 1
- (ii) The percentage yield for this reaction is 67%.
 Calculate the minimum mass of 2-hydroxybenzoic acid required to produce 5.00 g of aspirin? 3

(5)

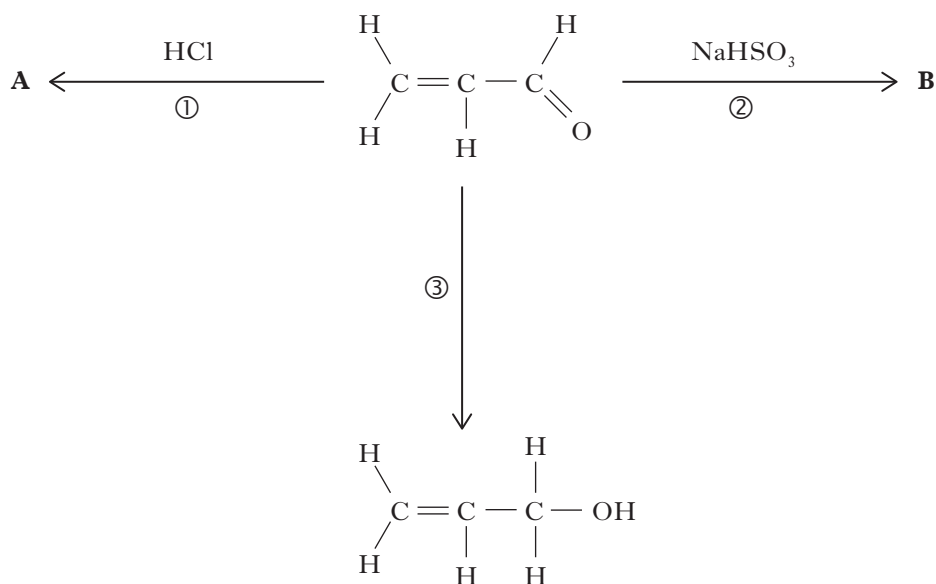
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8. Methanal is the simplest aldehyde and propenal is the simplest unsaturated aldehyde.

- (a) When methanal is reacted with a saturated solution of sodium hydrogensulfite the following product is formed.

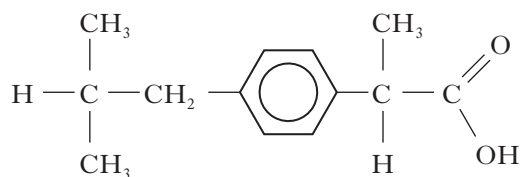


- (i) Suggest the type of chemical reaction which has taken place. 1
- (ii) State **one** way in which the identity of the product could be confirmed. 1
- (b) Some possible reactions of propenal are shown below.



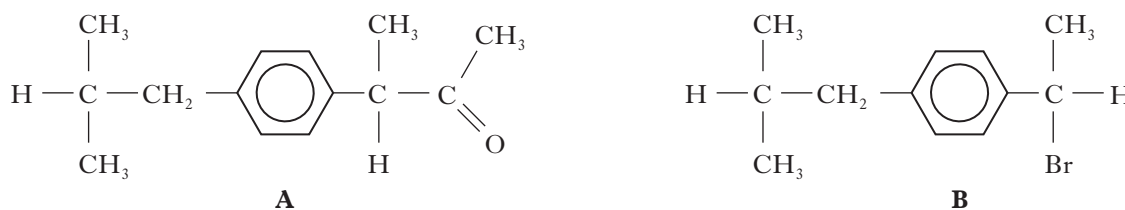
- (i) Draw a structural formula for compound **A**. 1
- (ii) Draw a structural formula for compound **B** assuming that propenal reacts with sodium hydrogensulfite in the same way as methanal. 1
- (iii) Which reagent could be used to carry out reaction ③? 1
- (5)**

9. Ibuprofen is one of the most commonly used non-steroidal anti-inflammatory drugs (NSAIDs).
The structure of ibuprofen is shown.



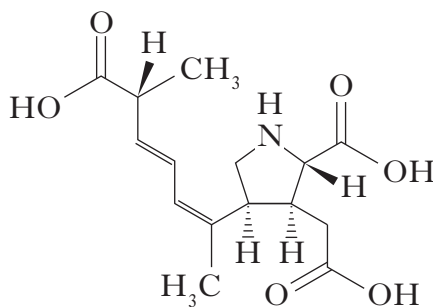
ibuprofen

- (a) Copy the relevant part of the structure of ibuprofen and circle the carbon which makes ibuprofen chiral. 1
- (b) Compounds **A** and **B**, shown below, can be used to manufacture ibuprofen.



An impure sample of ibuprofen known to be contaminated with **one** of these compounds, was subjected to IR analysis and the major peaks were identified at wavenumbers 1600, 1690, 1720 and 3300 cm^{-1} .

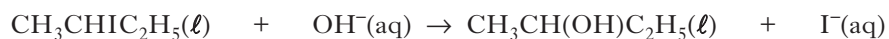
- (i) Explain which compound is present as an impurity. 1
- (ii) The percentage yield of the final purified product is 57%.
Suggest a reason why the yield is less than 100% 1
- (iii) Suggest how compound **B** could be converted into ibuprofen. 2
- (5)**
10. In the winter of 1987 over a hundred people became extremely ill within hours after dining on cultured blue mussels in restaurants around Prince Edward Island in Canada. After much research, chemists eventually isolated and identified the toxin to be domoic acid, a structural formula of which is shown below.



Using your knowledge of chemistry suggest how domoic acid could be isolated and identified from contaminated mussels. (3)

11. The results of experiments on the alkaline hydrolysis of 2-iodobutane, $\text{CH}_3\text{CHIC}_2\text{H}_5$, are shown in the table below.

The equation for the hydrolysis is



Experiment	$[\text{CH}_3\text{CHIC}_2\text{H}_5]/\text{mol l}^{-1}$	$[\text{OH}^-]/\text{mol l}^{-1}$	Initial Rate/ $\text{mol l}^{-1}\text{s}^{-1}$
1	0.10	0.10	1.4×10^{-4}
2	0.20	0.20	2.9×10^{-4}
3	0.30	0.10	4.1×10^{-4}

- (a) Determine the order of reaction with respect to
- (i) $\text{CH}_3\text{CHIC}_2\text{H}_5$ 1
- (ii) OH^- . 1
- (b) Using your answers to part (a):
- (i) write the rate equation for the reaction; 1
- (ii) calculate a value for the rate constant, k , including the appropriate units. 2
- (c) Using curly arrow notation and your answers to part (a), outline the mechanism for the above reaction. 3
- (d) If the sample of 2-iodobutane contained molecules of only one optical isomer, the product would have no effect on plane-polarised light. 1
- Explain this in terms of the mechanism. 1
- (9)**

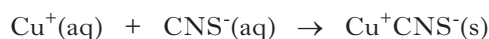
12. To determine the composition of an old coin containing silver, copper and nickel, a student dissolved the coin of mass 10.04 g in nitric acid. The resulting solution was diluted with deionised water to 1000 cm³ in a standard flask.

(a) 0.2 mol l⁻¹ hydrochloric acid was added to 100 cm³ of this solution until precipitation of silver(I) chloride was complete. After filtration, the precipitate was washed and dried and found to have a mass of 0.620 g.

(i) Calculate the percentage, by mass, of silver in the coin. 2

(ii) Suggest how the student would test that no silver(I) ions remained in the solution. 1

(b) The filtrate was treated to reduce the copper(II) ions to copper(I) ions. Ammonium thiocyanate solution was added to precipitate the copper as copper(I) thiocyanate.



After filtration, drying and weighing, the precipitate was found to weigh 0.320 g. Calculate the percentage, by mass, of copper in the coin. 2

(5)

13. An acidic buffer consists of a solution of a weak acid and one of its salts. This can be prepared by reacting a weak acid with an alkali.

20.0 cm³ of 1.00 mol l⁻¹ potassium hydroxide solution was added to 40.0 cm³ of 1.00 mol l⁻¹ aqueous ethanoic acid forming a buffer solution.

(a) Calculate the concentration of

(i) K⁺(aq) 1

(ii) H⁺(aq) 3

in the buffer solution.

(b) Explain how this solution would resist change in pH if a few more drops of the potassium hydroxide solution were added. 2

(6)

[END OF QUESTION PAPER]

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