X012/13/02

NATIONAL QUALIFICATIONS 2014

MONDAY, 12 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

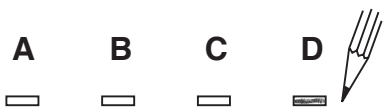
C fractional crystallisation

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. The energy associated with a photon of electromagnetic radiation is

A independent of the frequency

B proportional to the frequency

C inversely proportional to the frequency

D proportional to the square of the frequency.

2. The energy, in $kJ\,mol^{-1}$, corresponding to light of wavelength 501 nm is

A $1{\cdot}99 \times 10^{-7}$

B 60·0

C 239

D $2{\cdot}39 \times 10^{5}$.

3. The electronic configuration of a vanadium atom in its ground state is

A $ls^2 2s^2 2p^6 3s^2 3p^6 3d^5$

B $ls^2 2s^2 2p^6 3s^2 3p^6 4s^2 4p^3$

C $ls^2 2s^2 2p^6 3s^2 3p^6 3d^3 4s^2$

D $ls^2 2s^2 2p^6 3s^2 3p^6 3d^4 4s^1$.

4. In absorption spectroscopy, as the concentration of an ion in solution increases, there is an increase in the

A wavelength of radiation absorbed

B frequency of radiation absorbed

C intensity of radiation absorbed

D intensity of radiation transmitted.

5. Which of the following compounds is likely to show the least ionic character?

A KCl

B CaO

C BF_3

D PH_3

6. Which of the following has bond angles equal to 90°?

A SF_6

B NH_4^+

C $SiCl_4$

D BeF_4^{2-}

7. Which of the following does **not** have a pyramidal structure?

A BF_3

B NH_3

C OH_3^+

D PH_3

8. The highest oxidation state of chlorine is present in

A HClO

B $HClO_2$

C $HClO_3$

D $HClO_4$.

9. Silicon carbide has a similar structure to diamond with silicon and carbon atoms alternating throughout the lattice.

In solid silicon carbide

A each CSi_4 molecule contains one carbon atom surrounded by four silicon atoms

B each SiC_4 molecule contains one silicon atom surrounded by four carbon atoms

C each carbon atom is surrounded tetrahedrally by four silicon atoms

D each carbon atom is surrounded octahedrally by four silicon atoms.

[Turn over

10. A solution of a weak base is to be standardised.

Which of the following properties must be possessed by an acid to be suitable as a primary standard for this purpose?

A It must have exactly the same concentration as the base.

B It must have a high purity and stability.

C It must have about the same strength as the base.

D One mole of the acid must neutralise one mole of the base.

11. A reaction in dynamic equilibrium is one in which

A the concentration of the product is always independent of reaction conditions

B the enthalpy changes for the forward and the reverse reactions are equal

C the activation energies for the forward and the reverse reactions are equal

D the rates of the forward and the reverse reactions are equal.

12. The reaction

$CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$

has an equilibrium constant of 3·9 at 950 °C.

The equilibrium concentrations of CO(g), $H_2(g)$ and $H_2O(g)$ are given in the table.

Substance	Equilibrium concentration/mol l^{-1}
CO(g)	$5{\cdot}0 \times 10^{-2}$
$H_2(g)$	$1{\cdot}0 \times 10^{-2}$
$H_2O(g)$	$4{\cdot}0 \times 10^{-3}$

What is the equilibrium concentration of $CH_4(g)$, in mol l^{-1}, at 950 °C?

A $2{\cdot}0 \times 10^{-7}$

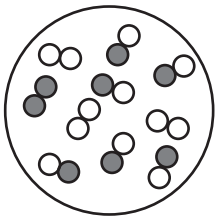
B $4{\cdot}9 \times 10^{-5}$

C $3{\cdot}1 \times 10^{-5}$

D $4{\cdot}9 \times 10^{-1}$

13. The diagram below represents an equilibrium mixture for the reaction

$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$



What is the value of equilibrium constant?

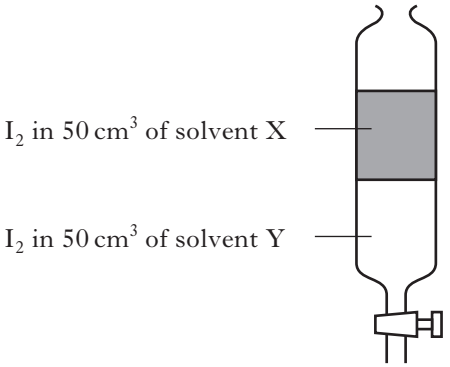
A 0·083

B 0·50

C 2·0

D 12

14.



Iodine was added to 50 cm^3 of two immiscible solvents X and Y in a separating funnel. After shaking, the following equilibrium was established.

$I_2(Y) \rightleftharpoons I_2(X)$

An extra 10 cm^3 of solvent X was added, the mixture shaken and equilibrium re-established.

Which of the following statements is correct?

A The concentration of I_2 in Y increases.

B The concentration of I_2 in Y decreases.

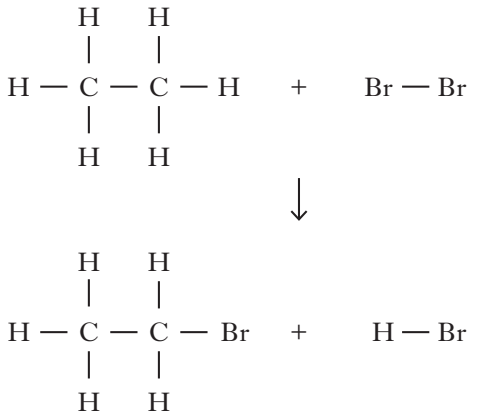
C The equilibrium constant increases.

D The equilibrium constant decreases.

15. Consider the following bond enthalpies.

Bond	Enthalpy/kJ mol^{-1}
Br—Br	194
H—Br	362
C—H	414
C—Br	285

What is the enthalpy change for the following reaction?



A –1255 kJ mol^{-1}

B –39 kJ mol^{-1}

C +39 kJ mol^{-1}

D +1255 kJ mol^{-1}

16. $C_2H_5Cl(g) \rightarrow 2C(g) + 5H(g) + Cl(g)$

The enthalpy change, in kJ mol^{-1}, for the above reaction is

A 3088

B 2844

C 2742

D 2396.

17. Which of the following changes would have a negative ΔH value?

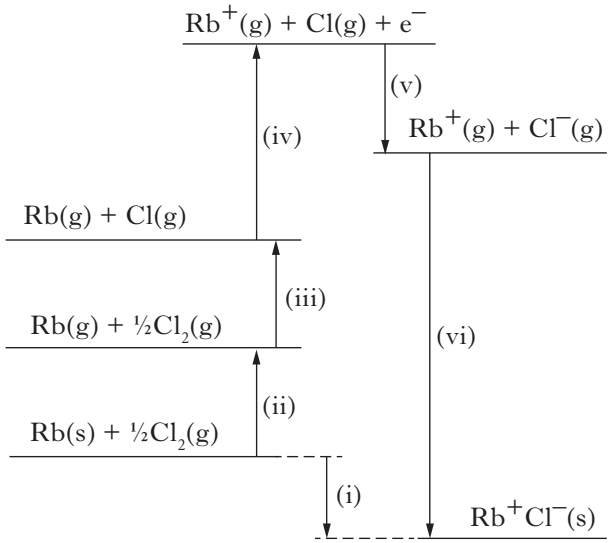
A $Cl_2(g) \rightarrow 2Cl(g)$

B $Cl^-(g) + aq \rightarrow Cl^-(aq)$

C $Na(g) \rightarrow Na^+(g) + e^-$

D $Na^+Cl^-(s) \rightarrow Na^+(g) + Cl^-(g)$

Questions 18 and 19 refer to the Born-Haber cycle (not drawn to scale) for rubidium chloride.



18. Which type of enthalpy change corresponds to step (ii)?

A Lattice enthalpy

B Electron affinity

C Enthalpy of formation

D Enthalpy of atomisation

19. Which type of enthalpy change corresponds to step (vi)?

A Lattice enthalpy

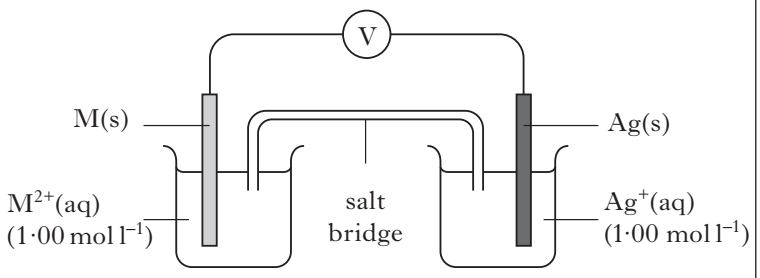
B Electron affinity

C Enthalpy of formation

D Enthalpy of atomisation

[Turn over

Questions 20, 21 and 22 refer to the electrochemical cell below which contains silver and an unknown metal, M.



Emf of cell = 1·03 V Temperature = 25 °C

20. To produce this emf, M(s) and M^{2+}(aq) should be

A Ni(s) and Ni^{2+}(aq)

B Fe(s) and Fe^{2+}(aq)

C Pb(s) and Pb^{2+}(aq)

D Cu(s) and Cu^{2+}(aq).

21. The standard free energy change, $\Delta G°$, for this cell per mole of M^{2+} ions is

A –44·4 kJ

B –49·7 kJ

C –99·4 kJ

D –198·8 kJ.

22. Sodium chloride is unsuitable for use in the salt bridge because

A Na^{+}(aq) will reduce Ag^{+}(aq)

B Ag^{+}(aq) will oxidise Cl^{-}(aq)

C Cl^{-}(aq) will precipitate Ag^{+}(aq)

D NaCl(aq) does not conduct electricity.

23. A suggested mechanism for the reaction

$2X + Y \rightarrow X_2Y$

is a two-step process

$X + Y \rightarrow XY$ (slow)

$XY + X \rightarrow X_2Y$ (fast)

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].

24. 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.

25. 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.

26. 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.

27. Which of the following substances could **not** be a product in the chain reaction between ethane and chlorine?

A HCl

B C_2H_3Cl

C C_2H_5Cl

D C_4H_{10}

28. The formula $C_4H_{10}O$ could represent an alcohol (C_4H_9OH) or an ether ($C_2H_5OC_2H_5$).

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

A They are flammable.

B They are used as solvents.

C They have hydrogen bonds between their molecules.

D They can be made by nucleophilic substitution from a halogenoalkane.

29. Which of the following will react to form $CH_3CH_2OCH_2CH_2CH_3$?

A CH_3CH_2OH and CH_3CH_2COONa

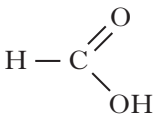
B $CH_3CH_2CH_2OH$ and CH_3COONa

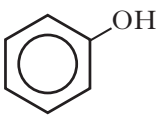
C CH_3CH_2ONa and $CH_3CH_2CH_2I$

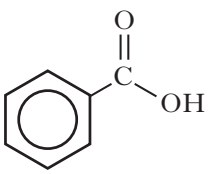
D CH_3CH_2ONa and CH_3CHICH_3

30. Which of the following is least acidic?

A CH_3OH

B 

C 

D 

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

A C=O and —OH each retain their own properties, unaffected by the other.

B The properties of the C=O are changed but the —OH is unaffected.

C The properties of the —OH are changed but the C=O is unaffected.

D The properties of the C=O and the —OH are each affected by the other.

32. Which of the following reagents can be used directly to distinguish between an aldehyde and a ketone?

A Fehling's solution

B Bromine solution

C 2,4-Dinitrophenylhydrazine

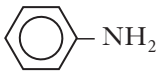
D Lithium aluminium hydride

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

A $(CH_3)_3N$

B CH_3NHCH_3

C $H_2NCH_2NH_2$

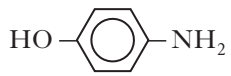
D 

34. 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

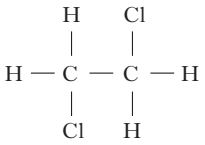
B $H_2NCH_2NH_2$

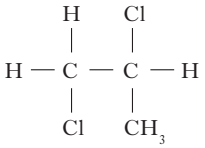
C $HOOCCH_2NH_2$

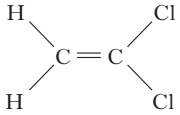
D 

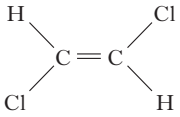
[Turn over

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

A 

B 

C 

D 

36. 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 cm^3 0·1 mol l^{-1} **X** and 75 cm^3 of 0·1 mol l^{-1} **Y**?

A –79°

B –39·5°

C +39·5°

D +79°

37. The two isotopes of bromine have mass numbers 79 and 81.

In the mass spectrum of

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

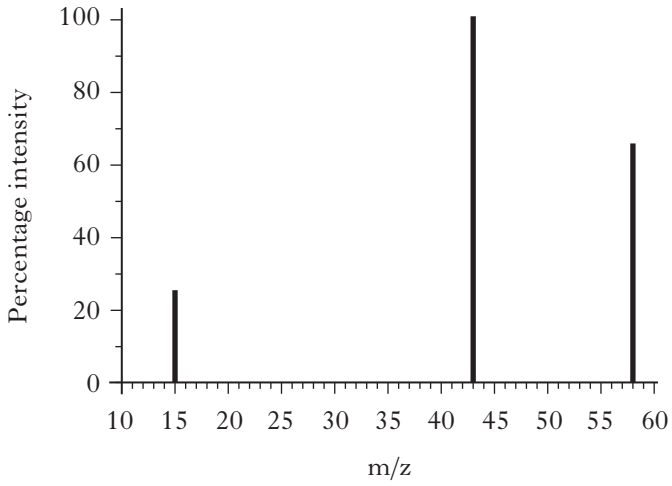
A $[CHBr]^-$

B $[CH_2Br]^+$

C $[C_6H_4NH_2]^-$

D $[C_6H_4NH_2]^+$.

38. 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

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

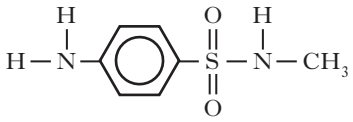
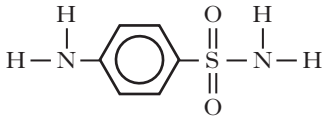
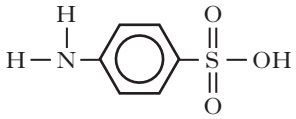
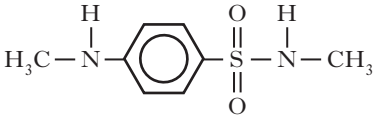
A Nuclear magnetic resonance spectroscopy

B Atomic emission spectroscopy

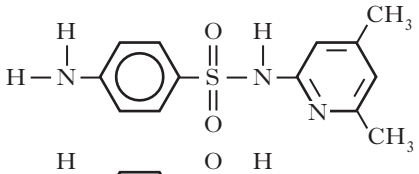
C Infra-red spectroscopy

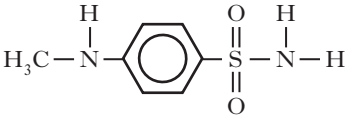
D Mass spectrometry

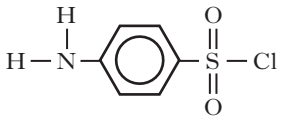
40. The table shows the structural formulae of some sulphonamides and their antibacterial activity.

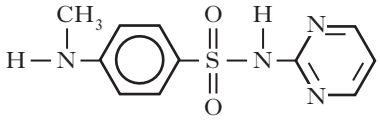
Sulphonamide	Antibacterial activity
	active
	active
	inactive
	inactive

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 ten*

SECTION B

Marks

60 marks are available in this section of the paper.

All answers must be written clearly and legibly in ink.

1. Consider the following compounds

$NaCl$ Na_2O MgO Al_2O_3 $SiCl_4$ PCl_3

(*a*) Which two compounds, when added to water, will **not** change the pH? **1**

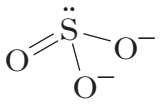
(*b*) Which two compounds will react with water to form white fumes of hydrogen chloride? **1**

(*c*) Aluminium oxide is said to be amphoteric.
What does amphoteric mean? **1**

(*d*) What is the shape of a PCl_3 molecule? **1**

(4)

2. A resonance structure for the sulphite ion is



(*a*) Draw another resonance structure for the sulphite ion. **1**

(*b*) Draw a Lewis electron dot diagram for the sulphite ion. **1**

(*c*) What is the oxidation number of sulphur in the sulphite ion? **1**

(3)

Marks

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

The overall equation for the reaction is

$$CH_4(g) + \tfrac{1}{2}O_2(g) \longrightarrow CH_3OH(\ell)$$

Substance	ΔH_f^o/kJ mol^{-1}	S^o/J K^{-1} mol^{-1}
$CH_4(g)$	–75	187
$O_2(g)$	–	205
$CH_3OH(\ell)$	–239	127

(*a*) For the conversion of methane into methanol, calculate

(i) the standard enthalpy change, ΔH^o **1**

(ii) the standard entropy change, ΔS^o. **1**

(*b*) Calculate the maximum temperature above which the reaction becomes no longer feasible. **2**

(4)

4. A chromium compound is known to exist in the following three isomeric forms. The co-ordination number of chromium is the same in each isomer.

A $[Cr(H_2O)_6]^{3+}(Cl^-)_3$

B $[Cr(H_2O)_5Cl]^{2+}(Cl^-)_2.H_2O$

C $[Cr(H_2O)_4Cl_2]^{+}(Cl^-).2H_2O$

(*a*) State the co-ordination number. **1**

(*b*) Name the complex ion in isomer **A**. **1**

(*c*) All three forms have different colours in solution.

(i) Explain how colour arises in transition metal compounds such as those above. **2**

(ii) Suggest why the three solutions have different colours. **1**

(*d*) What is the shape of the complex ion in isomer **B**? **1**

(e) State the electronic configuration of **chromium(I)** in terms of s, p and d orbitals. **1**

(*f*) 2·565 g of one of the above forms of the compound was dissolved in water to give 100 cm^3 of solution.

Silver(I) nitrate solution was added until no more precipitate was formed.

The mass of silver(I) chloride produced was 2·748 g.

(i) Calculate the number of moles of chromium compound dissolved. **1**

(ii) How many moles of silver(I) chloride were produced? **1**

(iii) Which one of the three isomers had been dissolved? **1**

(10)

Marks

5. The dicarboxylic acid, oxalic acid, has molecular formula $H_2C_2O_4$.

It can be prepared by reacting calcium oxalate with sulphuric acid.

$$H_2SO_4(aq) + CaC_2O_4(s) + xH_2O \rightarrow CaSO_4.xH_2O(s) + H_2C_2O_4(aq)$$

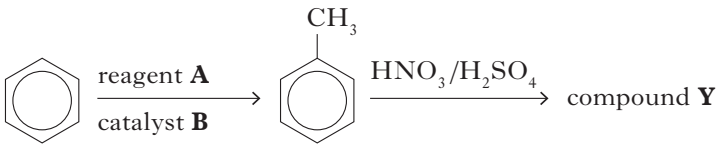
(*a*) Draw a structural formula for oxalic acid. **1**

(*b*) 4·94 g of $CaSO_4.xH_2O$ was dehydrated to produce 3·89 g of $CaSO_4$.

Determine the value of x. **2**

(3)

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**

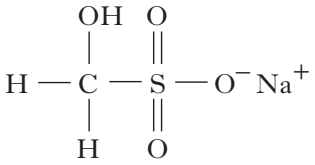
(*c*) What name is given to the type of reaction taking place in both steps? **1**

(3)

Marks

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

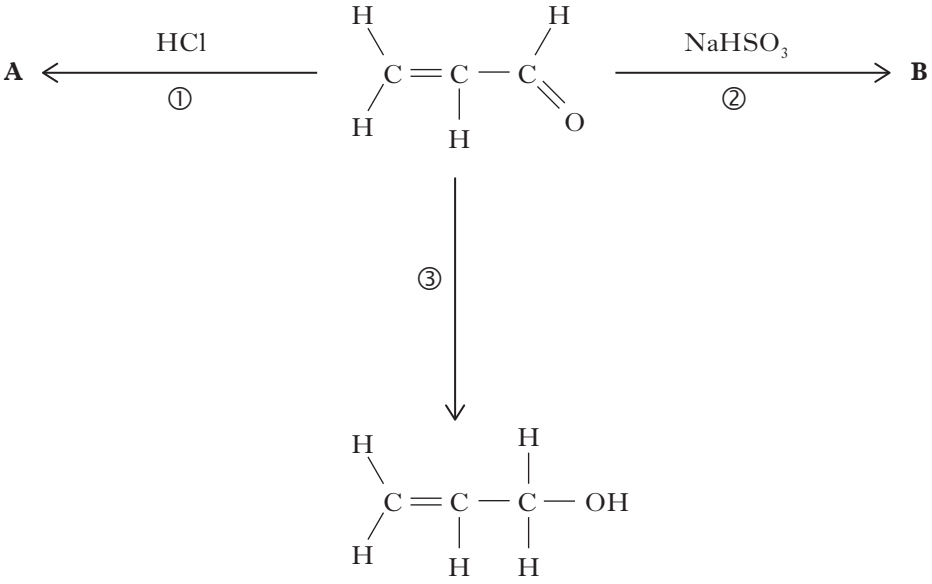
(*a*) When methanal is reacted with a saturated solution of sodium hydrogensulphite the following product is formed.



(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 hydrogensulphite in the same way as methanal. **1**

(iii) Which reagent could be used to carry out reaction③? **1**

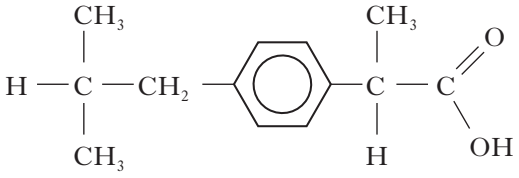
(5)

[Turn over

Marks

8. Ibuprofen is one of the most commonly used non-steroidal anti-inflammatory drugs (NSAIDs).

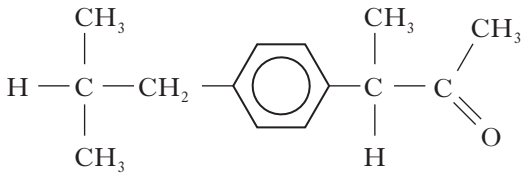
The structure of ibuprofen is shown.



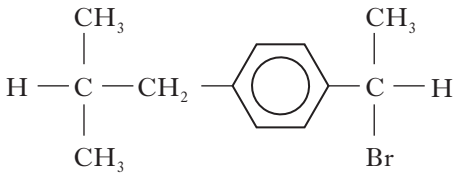
ibuprofen

(*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.



A



B

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) Describe a chemical test that could be used to distinguish between compounds **A** and **B**. **1**

(iii) Suggest how compound **B** could be converted into ibuprofen. **2**

(5)

9. In a PPA, aspirin, $C_9H_8O_4$, was prepared by reacting 2-hydroxybenzoic acid with ethanoic anhydride. A catalyst was added and when the crude aspirin had formed, impurities were removed by dissolving them in a suitable solvent. The crystals of aspirin were dried in an oven before determining the purity and the percentage yield.

(*a*) What catalyst was used in this reaction? **1**

(*b*) Name the solvent added to remove the impurities. **1**

(*c*) The percentage yield for the reaction was 67%. Calculate the minimum mass of 2-hydroxybenzoic acid required to produce 5·00 g of aspirin. **3**

(5)

Marks

10. The results of experiments on the alkaline hydrolysis of 2-iodobutane, $CH_3CHIC_2H_5$, are shown in the table below.

The equation for the hydrolysis is

$$CH_3CHIC_2H_5(\ell) + OH^-(aq) \rightarrow CH_3CH(OH)C_2H_5(\ell) + I^-(aq)$$

Experiment	**$[CH_3CHIC_2H_5]$/mol l^{-1}**	**$[OH^-]$/mol l^{-1}**	**Initial Rate/mol $l^{-1}s^{-1}$**
1	0·10	0·10	$1{\cdot}4 \times 10^{-4}$
2	0·20	0·20	$2{\cdot}9 \times 10^{-4}$
3	0·30	0·10	$4{\cdot}1 \times 10^{-4}$

(*a*) Determine the order of reaction with respect to

(i) $CH_3CHIC_2H_5$ **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 structural formulae and your answers to part (*a*), outline the mechanism for the above reaction. **2**

(*d*) If the sample of 2-iodobutane contained molecules of only one optical isomer, the product would have no effect on plane-polarised light.

Explain this in terms of the mechanism. **1**

(8)

[Turn over

Marks

11.

$$CH_3COCH_3(aq) + I_2(aq) \xrightarrow{H^+(aq)} CH_3COCH_2I\,(aq) + HI(aq)$$

The reaction between propanone and iodine is first order with respect to both propanone and hydrogen ions.

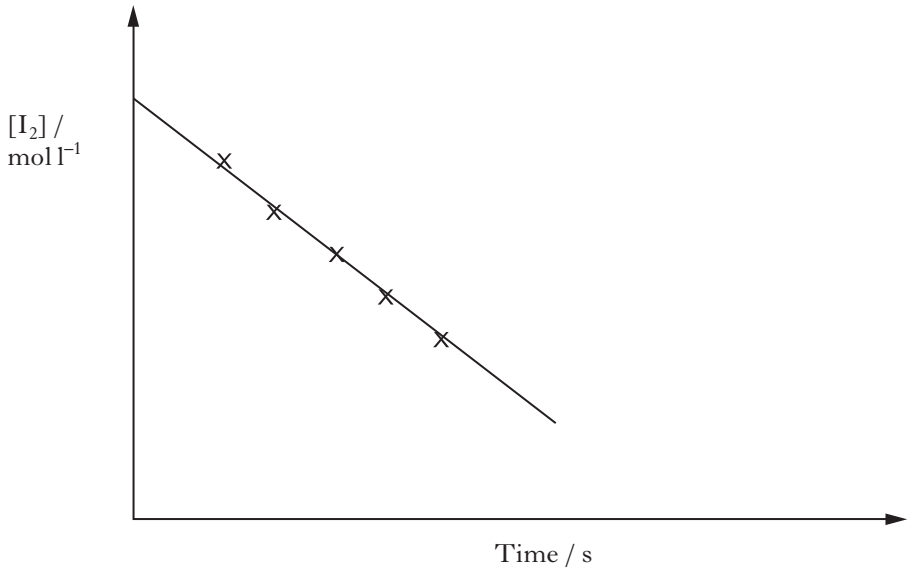
In a PPA the order with respect to iodine was determined by using very high initial concentrations of propanone and hydrogen ions compared with that of iodine. Samples of the reaction mixture were removed at regular intervals and added to a solution that essentially stopped the reaction. The iodine concentration was then determined by titration using starch solution as an indicator.

(*a*) Why were very high concentrations of propanone and hydrogen ions used in the experiment? **1**

(*b*) Name the solution used to stop the reaction between iodine and propanone. **1**

(*c*) Name the titrating solution used to determine the iodine concentration. **1**

(*d*) The graph shows how the iodine concentration varies as the reaction proceeds.



From the graph above determine the order of the reaction with respect to iodine. **1**

(4)

Marks

12. 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.

$20{\cdot}0\,cm^3$ of $1{\cdot}00\,mol\,l^{-1}$ potassium hydroxide solution was added to $40{\cdot}0\,cm^3$ of $1{\cdot}00\,mol\,l^{-1}$ 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)

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