X012/701

CHEMISTRY
ADVANCED HIGHER

Reference may be made to the Chemistry Higher and Advanced Higher Data Booklet (2007 edition).

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).
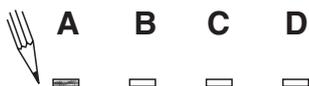
Changing an answer

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**.
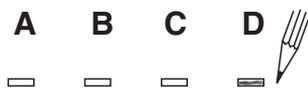
1. What type of bonding exists in an element which forms a gaseous oxide?

   A Ionic

   B Covalent (polar)

   C Covalent (non-polar)

   D Metallic

2. Which of the following compounds is likely to have the **most** covalent character?

   A Tin(IV) iodide

   B Iron(II) chloride

   C Lithium fluoride

   D Potassium bromide

3. Which of the following is **not** a form of electromagnetic radiation?

   A Beta radiation

   B Gamma radiation

   C Ultra-violet radiation

   D Infra-red radiation

4. **All** noble gases are characterised in terms of electrons by the completion of the outermost orbital. This orbital is

   A an s-orbital

   B a p-orbital

   C a d-orbital

   D an s or p-orbital.

5. Infra-red radiation can be used in the analysis and identification of organic compounds. Compared to visible radiation, infra-red 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.

6. When an ammonia molecule accepts a proton to form an ammonium ion, there is a change of shape from

   A pyramidal to tetrahedral

   B pyramidal to trigonal planar

   C trigonal planar to pyramidal

   D trigonal planar to tetrahedral.

7. Isoelectronic species are molecules or polyatomic ions with the same total number of electrons.

   Which of the following contains two isoelectronic species?

   A NH_4^+ and CH_4

   B NH_4^+ and BF_3

   C BF_3 and NH_3

   D PF_5 and BF_4^-

8. A superconductor is a material

   A whose electrical conductivity decreases with decreasing temperature

   B that does not conduct electricity unless doped with another material

   C that can conduct electricity with zero resistance

   D whose electrical conductivity increases with increasing temperature.

9. The statement that "an orbital can accommodate, at most, two electrons, and if so, they must be of opposite spin" is based on

   A Hund's rule

   B the aufbau principle

   C the Pauli exclusion principle

   D Heisenberg's uncertainty principle.

[Turn over

10.
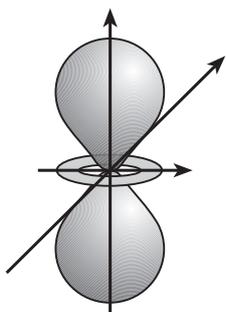
The above is a diagrammatic representation of the shape of

A   any p-orbital

B   a specific p-orbital

C   any d-orbital

D   a specific d-orbital.

11. An ionic compound is thought to contain hydride ions. One way to show this could be to

A   electrolyse the molten compound and test for hydrogen gas at the negative electrode

B   electrolyse the molten compound and test for hydrogen gas at the positive electrode

C   dissolve the compound in water and test for an acidic pH

D   dissolve the compound in water and test for an alkaline pH.

12.
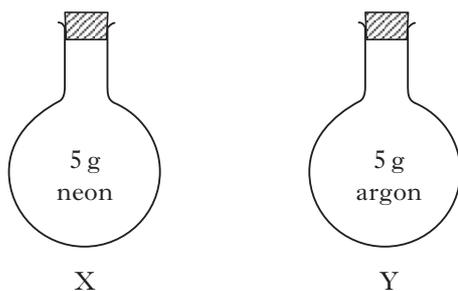
The number of atoms of gas in flask Y is approximately

A   equal to the number of atoms of gas in flask X

B   twice the number of atoms of gas in flask X

C   one half the number of atoms of gas in flask X

D   one quarter the number of atoms of gas in flask X.

13. In a gravimetric analysis of silver, a precipitate of silver(I) chromate was produced by adding excess potassium chromate to a solution containing silver(I) ions.

If $5 \cdot 795$ g of Ag_2CrO_4 was produced, the mass of silver in the solution was

A $1 \cdot 884$ g

B $3 \cdot 318$ g

C $3 \cdot 769$ g

D $8 \cdot 910$ g.

14. $N_2O_4(g) \rightleftharpoons 2NO_2(g) \qquad \Delta H^\circ = +57 \, kJ \, mol^{-1}$

Which of the following will increase the equilibrium constant for the reaction?

A   Use of a catalyst

B   Increase of pressure

C   Increase of temperature

D   Decrease of temperature

15. An aqueous solution of an organic acid, **X**, was shaken with ethoxyethane until the following equilibrium was established.

$$\mathbf{X}(\text{water}) \rightleftharpoons \mathbf{X}(\text{ethoxyethane})$$
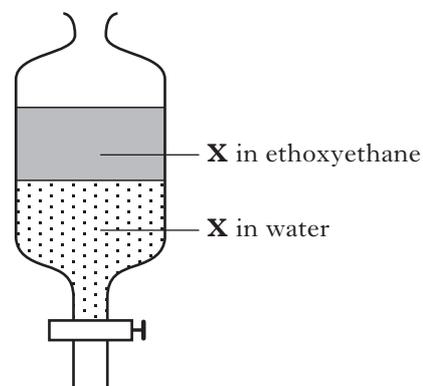
$20 \cdot 0 \, cm^3$ of the upper layer needed $15 \cdot 0 \, cm^3$ of $0 \cdot 010 \, mol \, l^{-1}$ NaOH(aq) for neutralisation.

$20 \cdot 0 \, cm^3$ of the lower layer needed $12 \cdot 0 \, cm^3$ of $0 \cdot 010 \, mol \, l^{-1}$ NaOH(aq) for neutralisation.

The value of the partition coefficient is

A $0 \cdot 80$

B $1 \cdot 25$

C $1 \cdot 33$

D $1 \cdot 67$.

16.

$$2Fe(s) + \tfrac{3}{2}O_2(g) \rightarrow Fe_2O_3(s) \quad \Delta H° = -822\,kJ\,mol^{-1}$$
$$C(s) + O_2(g) \rightarrow CO_2(g) \quad\quad \Delta H° = -394\,kJ\,mol^{-1}$$
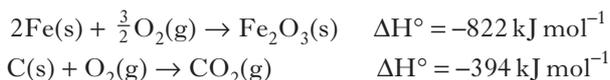
Which of the following is the standard enthalpy change, in $kJ\,mol^{-1}$, for the reaction shown below?

$$Fe_2O_3(s) + \tfrac{3}{2}C(s) \rightarrow 2Fe(s) + \tfrac{3}{2}CO_2(g)$$
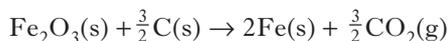
A   +231

B   +428

C   +1216

D   +1413

17. Which of the following can **not** be determined by a single experiment? The enthalpy of

A   formation of ethyne

B   combustion of methanol

C   solution of sodium hydroxide

D   neutralisation of hydrochloric acid by sodium hydroxide.

18. 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, in $kJ\,mol^{-1}$, for the following reaction?

```
     H   H
     |   |
H — C — C — H    +    Br — Br
     |   |
     H   H

            ↓

     H   H
     |   |
H — C — C — Br   +    H — Br
     |   |
     H   H
```
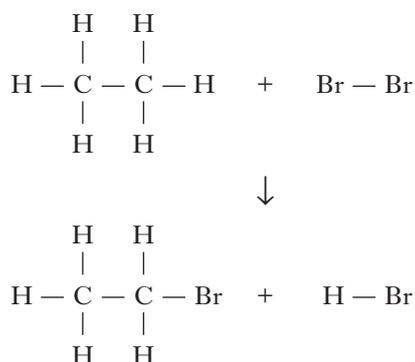
A   −1255

B   −39

C   +39

D   +1255

19. Which of the following is exothermic?

A $K(s) \rightarrow K(g)$

B $K(g) \rightarrow K^+(g) + e^-$

C $\tfrac{1}{2}Br_2(\ell) \rightarrow Br(g)$

D $Br(g) + e^- \rightarrow Br^-(g)$

20. Which of the following is likely to have the lowest standard entropy value at $100\,°C$?

A   Neon

B   Mercury

C   Sulphur

D   Phosphorus

21. An Ellingham diagram shows how $\Delta G°$ for a chemical reaction varies with

A $\Delta H°$

B $\Delta S°$

C   time

D   temperature.

22. Which of the following reactions must be exothermic? One in which

A $\Delta G°$ is negative

B $\Delta S°$ is positive

C   both $\Delta G°$ and $\Delta S°$ are negative

D   both $\Delta G°$ and $\Delta S°$ are positive.

23. In the electrochemical cell

$$Cr(s)\,|\,Cr^{3+}(aq)\,||\,Ag^+(aq)\,|\,Ag(s)$$

operating under standard conditions, which of the following is **not** true?

A   The emf is $1·54\,V$.

B   The silver electrode decreases in mass.

C   Oxidation takes place at the chromium electrode.

D   Electrons flow from chromium to silver in the external circuit.

[Turn over

24. The following reaction is first order with respect to each of the reactants.

$$A + B \rightarrow C + D$$
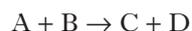
Which of the following is correct?

A The rate of the reaction is independent of the concentration of either A or B.

B The overall reaction is first order.

C If the initial concentrations of A and B are both doubled, the rate of the reaction will be doubled.

D As the reaction proceeds, its rate will decrease.

25. Which of the following does **not** apply to the reaction between methane and chlorine?

It involves

A homolytic fission

B a chain reaction

C a carbocation intermediate

D free radicals.

26. Which of the following amines has the lowest boiling point?

A $C_4H_9NH_2$

B $C_3H_7NHCH_3$

C $C_2H_5NHC_2H_5$

D $C_2H_5N(CH_3)_2$

27. Chlorobenzene, nitrobenzene and ethylbenzene can all be formed from benzene by

A electrophilic substitution

B electrophilic addition

C nucleophilic substitution

D nucleophilic addition.

28.

X   Y   Z
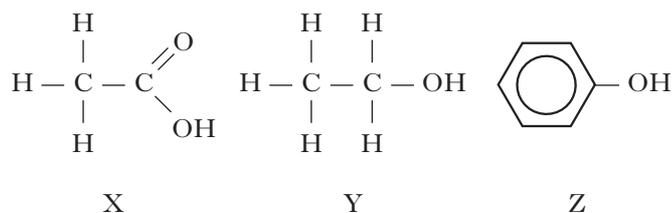
Which of the following shows the above compounds in order of **increasing** acid strength?

A X Y Z

B Y Z X

C Z X Y

D X Z Y

29. Which of the following has nucleophilic properties?

A Na

B Br^+

C CH_3^+

D NH_3

30. In the homologous series of amines, increase in chain length from CH_3NH_2 to $C_4H_9NH_2$ is accompanied by

	Volatility	Solubility in water
A	increased	increased
B	decreased	decreased
C	increased	decreased
D	decreased	increased

31. The end-on overlap of two atomic orbitals lying along the axis of a bond is known as

A hybridisation

B a sigma bond

C a pi bond

D a double bond.

32. Alkenes react with ozone (O_3) to form ozonides which can be hydrolysed to give carbonyl compounds.

$$\underset{/}{\overset{\backslash}{C}}=\underset{\backslash}{\overset{/}{C}} \xrightarrow{\;O_3\;} \text{OZONIDE} \xrightarrow{\;\text{hydrolysis}\;} \underset{/}{\overset{\backslash}{C}}=O + O=\underset{\backslash}{\overset{/}{C}}$$
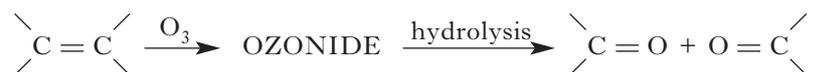
Which of the following alkenes will produce a mixture of propanone and ethanal when acted upon in this way?

A $CH_3CH=CHCH_2CH_3$

B $CH_3CH=CHCH_3$

C $(CH_3)_2C=CH_2$

D $CH_3CH=C(CH_3)_2$

---

33. Which of the following is the formula for a tertiary halogenoalkane?

A $CHBr_3$

B $(CH_3)_3CBr$

C $(CH_2Br)_3CH$

D $BrCH_2C(CH_3)_3$

34. A compound, X, has the formula C_6H_{12}. X **must** be

A   a hydrocarbon

B   an alkene

C   a cycloalkane

D   hexene.

35. A substance, X, is **readily** oxidised by acidified potassium dichromate solution to give a product which does **not** react with sodium carbonate, **nor** with Tollens' reagent.

Which of the following could represent the structure of X?

A $CH_3CH_2CH_2OH$

B $CH_3CH(OH)CH_3$

C $CH_3\underset{\underset{O}{\|}}{C}CH_3$

D $CH_3CH_2C\overset{\overset{O}{\diagup\!\!/}}{\underset{OH}{\diagdown}}$

36. Which of the following compounds would liberate one mole of hydrogen gas if one mole of it reacts with two moles of sodium?

A C_2H_5OH

B $HOCH_2CH_2OH$

C CH_3COOH

D CH_3CHO

37. Which of the following will **not** form a derivative with 2,4-dinitrophenylhydrazine?

A $CH_3CH_2C\overset{\overset{O}{\diagup\!\!/}}{\underset{H}{\diagdown}}$

B $CH_3CH_2C\overset{\overset{O}{\diagup\!\!/}}{\underset{OH}{\diagdown}}$

C $CH_3CH_2\underset{\underset{O}{\|}}{C}CH_3$

D $\bigcirc\!\!\!\!\!\bigcirc \!-\! C\overset{\overset{O}{\diagup\!\!/}}{\underset{H}{\diagdown}}$
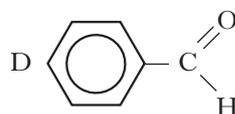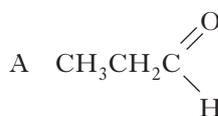
[Turn over

38. Spectral studies of an organic compound indicated the presence of a di-substituted benzene ring, two methyl groups and a molecular weight of 134.

Which of the following is a possible structure for the compound?

A

CH$_3$

COCH$_3$

B

CH$_3$

CHO

CH$_3$

C

CH$_3$CH$_2$

COCH$_3$

D

CH$_3$

CH$_2$CHO
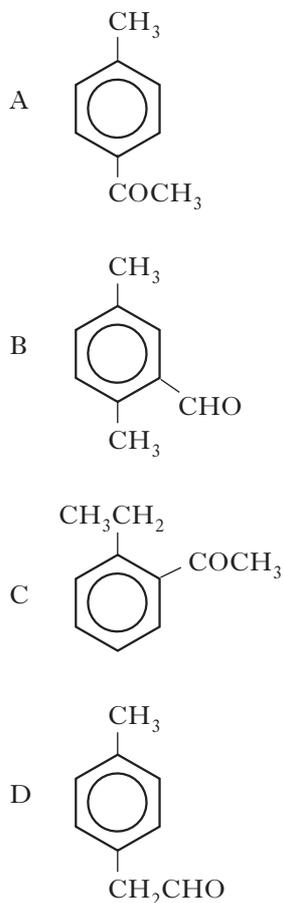
39. Which of the following compounds has a geometric isomer?

A

$$H-\underset{\underset{Cl}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{H}{|}}{\overset{\overset{Cl}{|}}{C}}-H$$

B

H   Cl

C = C

H   H

C

H   Cl

C = C

H   Cl

D

H   Cl

C = C

Cl   H
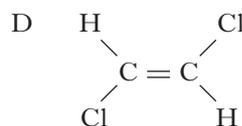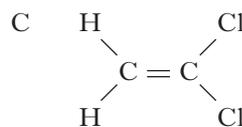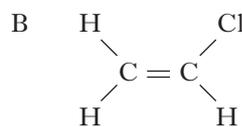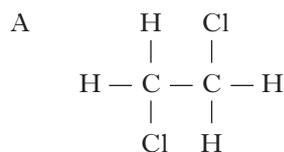
40. A simplified mass spectrum of an organic compound is shown.
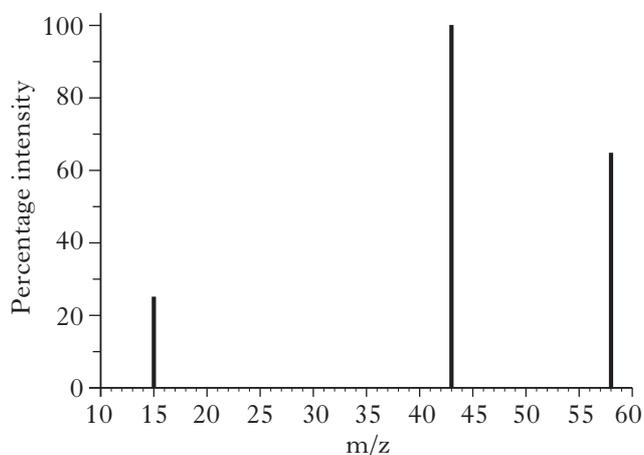
Which of the following compounds produces this spectrum?

A Propane

B Propan-1-ol

C Propan-2-ol

D Propanone

[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

60 marks are available in this section of the paper.

All answers must be written clearly and legibly in ink.

Marks

1. Barium carbonate decomposes on heating.

$$BaCO_3(s) \longrightarrow BaO(s) + CO_2(g) \qquad \Delta H° = +266\,kJ\,mol^{-1}$$

(a) Using the data from the table below, calculate the standard entropy change, $\Delta S°$, in $J\,K^{-1}mol^{-1}$, for the reaction.

Substance	Standard entropy, $S°/J\,K^{-1}mol^{-1}$
$BaCO_3(s)$	112·0
$BaO(s)$	72·1
$CO_2(g)$	213·8

1

(b) Calculate the temperature at which the decomposition of barium carbonate just becomes feasible.

3

(4)

2. Consider the following reaction.

$$CS_2(g) + 4H_2(g) \rightleftharpoons CH_4(g) + 2H_2S(g)$$
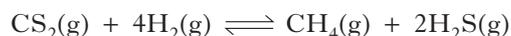
At 900 °C the equilibrium concentrations are:

$$[CS_2] = 0·012\,mol\,l^{-1} \qquad [H_2] = 0·0020\,mol\,l^{-1}$$
$$[H_2S] = 0·00010\,mol\,l^{-1} \qquad [CH_4] = 0·0054\,mol\,l^{-1}$$

(a) Write down the expression for the equilibrium constant, K, for this reaction.

1

(b) Calculate the value of the equilibrium constant, K, at 900 °C.

1

(2)

3. Fizzy drinks contain carbon dioxide dissolved in water which dissociates, as shown, to produce carbonic acid.

$$H_2O(\ell) + CO_2(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq) \qquad pK_a = 6·4$$
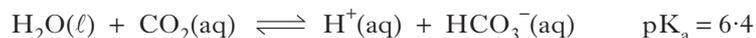
(a) What is the Bronsted-Lowry definition of an acid?

1

(b) Write the formula for the conjugate base in this reaction.

1

(c) Calculate the pH of a $0·1\,mol\,l^{-1}$ solution of carbonic acid.

2

(4)

[Turn over

4. The following table of results was obtained for the reaction below.

$$H_2O_2(aq) \quad + \quad 2HI(aq) \quad \longrightarrow \quad 2H_2O(\ell) \quad + \quad I_2(aq)$$

Experiment	$[H_2O_2]/mol\,l^{-1}$	$[HI]/mol\,l^{-1}$	Initial rate/$mol\,l^{-1}\,s^{-1}$
1	$3\cdot2 \times 10^{-4}$	$4\cdot1 \times 10^{-4}$	$4\cdot3 \times 10^{-9}$
2	$6\cdot4 \times 10^{-4}$	$4\cdot1 \times 10^{-4}$	$8\cdot6 \times 10^{-9}$
3	$3\cdot2 \times 10^{-4}$	$8\cdot2 \times 10^{-4}$	$8\cdot6 \times 10^{-9}$
4	$6\cdot4 \times 10^{-4}$	$8\cdot2 \times 10^{-4}$	$1\cdot72 \times 10^{-8}$

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

    (i) H_2O_2

    (ii)   HI.   **1**

(*b*) Write the rate equation for the reaction.   **1**

(*c*) Calculate a value for the rate constant, k, including the appropriate units.   **2**

    (4)

5. A student set up the following electrochemical cell at 25 °C.
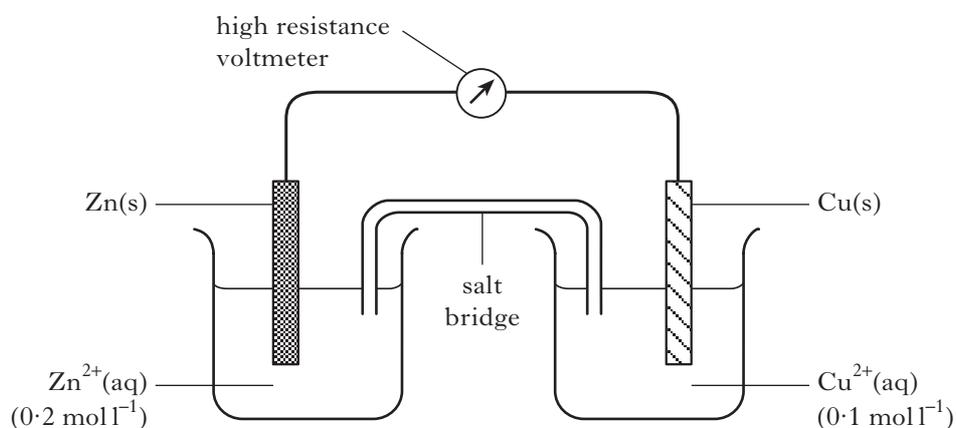
(*a*) Calculate ΔG, the actual free energy change, in $kJ\,mol^{-1}$, for this cell when the operating emf is $0\cdot94\,V$.   **3**

(*b*) What changes should the student make to this cell for it to be operating under standard conditions?   **1**

(*c*) Calculate the emf of a $Zn(s)\,|\,Zn^{2+}(aq)\,||\,Cu^{2+}(aq)\,|\,Cu(s)$ cell operating under standard conditions.   **1**

    (5)

6. In a PPA, 3·43 g of hydrated nickel(II) sulphate, $NiSO_4.6H_2O$, was dissolved in water and made up to $100 \, cm^3$ in a standard flask.

$20·0 \, cm^3$ of this solution was titrated against a $0·101 \, mol \, l^{-1}$ solution of EDTA using murexide as an indicator. The results are shown below.

	Rough titre	1st titre	2nd titre	3rd titre
Initial burette reading/cm^3	0·0	0·0	24·6	0·0
Final burette reading/cm^3	24·8	24·6	48·8	24·3
Volume of EDTA added/cm^3	24·8	24·6	24·2	24·3

(*a*) Give a reason why murexide is a suitable indicator in this titration reaction. **1**

(*b*) Calculate the percentage of nickel present in the hydrated salt from these experimental results. **3**

(*c*) The theoretical yield for the percentage of nickel in the hydrated salt is 22·3%. Suggest a reason for the difference between the theoretical percentage of nickel and the answer calculated in part (*b*). **1**

(5)

7. The electronic configuration for cobalt, Co, in its ground state, is

$$1s^2 \, 2s^2 \, 2p^6 \, 3s^2 \, 3p^6 \, 3d^7 \, 4s^2.$$
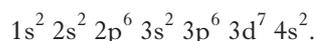
(*a*) In terms of s, p and d orbitals, write down the electronic configurations of

 (i) Cu **1**

(ii) Co^{2+} **1**

in their ground states.

(*b*) (i) Write an equation which represents the second ionisation energy for copper. **1**

  (ii) Explain why copper has a higher second ionisation energy than cobalt. **1**

(4)

[Turn over

8. The following table gives information about aluminium chloride and magnesium chloride.

	Aluminium chloride	Magnesium chloride
Action of heat	sublimes at 178 °C	melts at 714 °C
Relative formula mass in gaseous state	267	95
Action of water	reacts to give white fumes	dissolves

   (*a*) Using the above information determine

      (i) the main type of bonding in aluminium chloride and the main type of bonding in magnesium chloride   **1**

      (ii) the chemical formula for aluminium chloride in the gaseous state.   **1**

   (*b*) What are the white fumes given off when water is added to aluminium chloride?   **1**

   (*c*) Aluminium chloride can be used as a catalyst in the reaction between benzene and 2-chloropropane. Draw a structure for an organic product formed.   **1**

   (*d*) Many ionic compounds adopt the same lattice structure as either sodium chloride or caesium chloride.

      Sodium chloride has coordination 6:6 whereas caesium chloride has coordination 8:8.

      (i) Why do these chlorides have different lattice structures?   **1**

      (ii) Which of the above structures is iron(II) oxide most likely to adopt?

         Explain your answer.   **1**

         (6)

9. A common dietary supplement taken by athletes and slimmers is called chromium picolinate $[Cr(pic)_3]$. The structure of the picolinate ion, pic, is
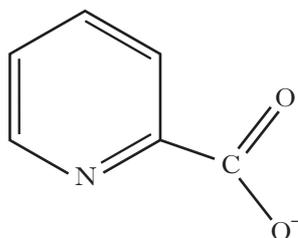
   (*a*) What feature of the picolinate ion makes it suitable for use as a ligand?   **1**

   (*b*) In the body, it is thought that the chromium in $[Cr(pic)_3]$ is changed into chromium(VI) by the action of hydrogen peroxide.

      (i) What is the oxidation state of chromium in $[Cr(pic)_3]$?   **1**

      (ii) What is the role of hydrogen peroxide in this reaction?   **1**

   (*c*) A simpler complex of chromium is $[Cr(CN)_6]^{4-}$. What is its systematic name?   **1**

         (4)

10. Isoamyl acetate is found naturally as the flavour and scent of bananas.

Its shortened structural formula is

$$CH_3COOCH_2CH_2CH(CH_3)_2$$

(*a*) (i) To which class of organic compounds does isoamyl acetate belong? **1**

(ii) Apart from flavouring agents, suggest another common use for this class of organic compound. **1**

Isoamyl acetate can be made in the laboratory by reacting ethanoic acid with another substance, **X**.

(*b*) (i) Write the systematic name of substance **X**. **1**

(ii) Name the type of reaction which takes place. **1**

(4)

11. Propoxyphene is a pain-killing drug. Its structure is shown below.
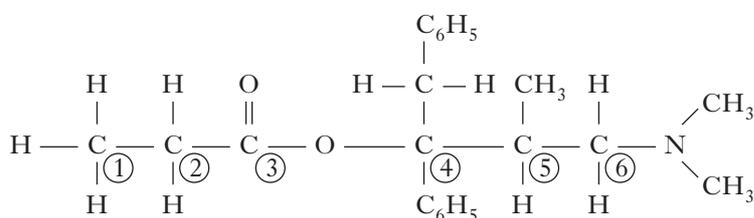
(*a*) There are two chiral carbons in propoxyphene.

Referring to the structure above, identify both chiral carbons. **1**

(*b*) Propoxyphene has a pharmacophore which binds to specific receptors.

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

(*c*) Propoxyphene stimulates the body's own natural response to pain.

What term is used to describe medicines which act in this way? **1**

(3)

[Turn over

12. A student designed the following reaction scheme starting from ethyl benzoate.
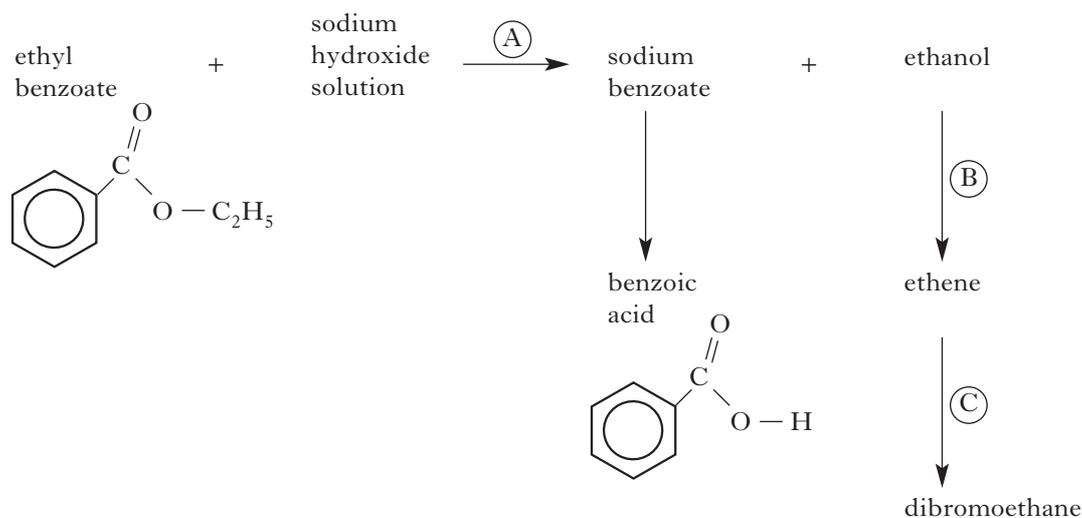
(*a*) In a PPA, benzoic acid was prepared from ethyl benzoate.

  (i) Name the type of reaction occurring in step Ⓐ. **1**

  (ii) What is added to sodium benzoate solution to precipitate out benzoic acid? **1**

  (iii) Name the procedure used to purify the benzoic acid. **1**

  (iv) Assuming the percentage yield is 70%, what is the minimum mass of ethyl benzoate required to produce at least 4·0 g of benzoic acid? **2**

(*b*) (i) Name the type of reaction occurring in step Ⓑ. **1**

  (ii) Using structural formulae, outline the mechanism for the reaction occurring in step Ⓒ. **2**

(8)

13. A compound **X** containing only carbon, hydrogen and oxygen, was subjected to elemental analysis. Complete combustion of 1·76 g of **X** gave 3·52 g of carbon dioxide and 1·44 g of water. No other product was formed.

(*a*) (i) Calculate the masses of carbon and hydrogen in the original sample and hence deduce the mass of oxygen present. **2**

(ii) Show, by calculation, that the empirical formula of compound **X** is C_2H_4O. **1**

(*b*) Given that the relative molecular mass of compound **X** is 88, deduce its molecular formula. **1**

(*c*) A low-resolution proton nmr spectrum of compound **X** is shown.
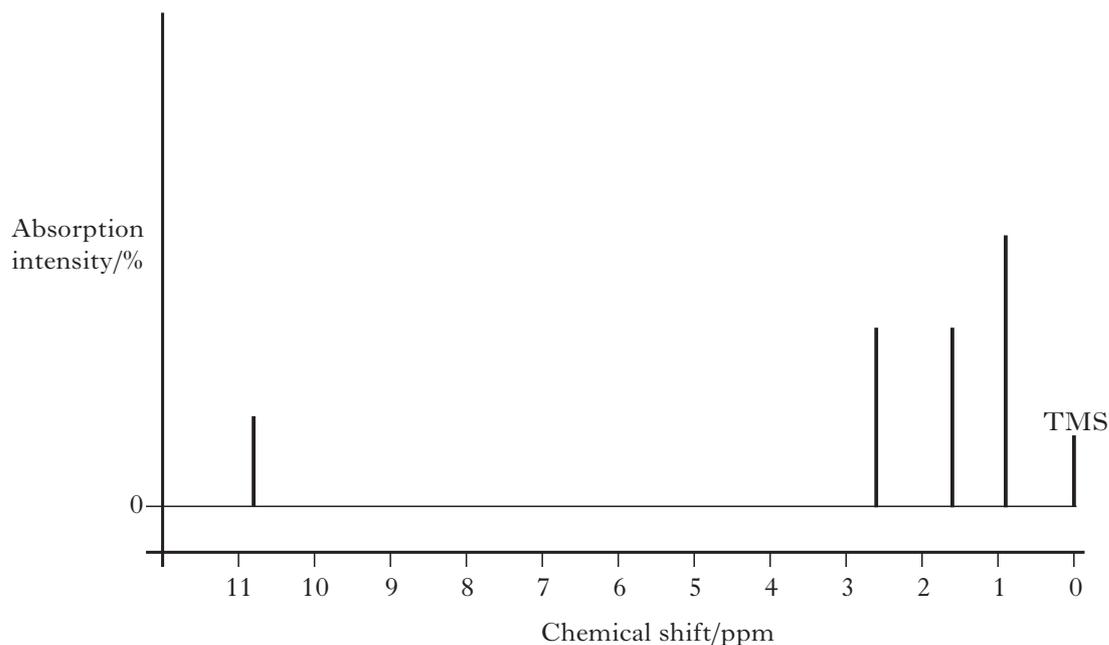
Analysis of this spectrum produced the data shown in the table below.

Chemical shift	Relative area under the peak
0·9	3
1·6	2
2·6	2
10·8	1

(i) Using information from the table and your answer to (*b*), draw a structural formula for compound **X** and give its systematic name. **2**

(ii) What is the function of "TMS" (tetramethylsilane) in the proton nmr spectrum? **1**

(7)

[*END OF QUESTION PAPER*]

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