X012/701

NATIONAL QUALIFICATIONS 2003

FRIDAY, 23 MAY
1.00 PM – 3.30 PM

CHEMISTRY
ADVANCED HIGHER

Reference may be made to the Chemistry Higher and Advanced Higher Data Booklet (1999 edition).

SECTION A

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

Fill in the details required on the answer sheet.

Rough working, if required, should be done only on this question paper, or on the rough working sheet provided—**not** on the answer sheet.

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

SECTION B

All questions should be attempted.

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In questions 1 to 40 of this part of the paper, an answer is given by indicating the choice A, B, C or D by a stroke made in INK in the appropriate place in the answer sheet—see the sample question below.

For each question there is only ONE correct answer.

This part of the paper is worth 40 marks.

SAMPLE QUESTION

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

A fractional distillation

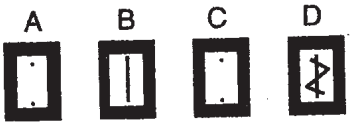
B chromatography

C fractional crystallisation

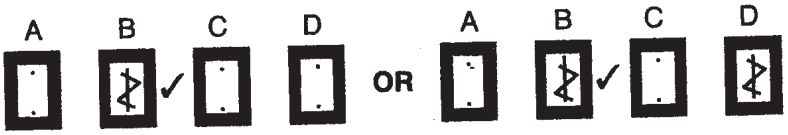
D filtration.

The correct answer is B—chromatography. A **heavy** vertical line should be drawn joining the two dots in the appropriate box in the column headed **B** as shown **in the example on the answer sheet.**

If, after you have recorded your answer, you decide that you have made an error and wish to make a change, you should cancel the original answer and put a vertical stroke in the box you now consider to be correct. Thus, if you want to change an answer **D** to an answer **B**, your answer sheet would look like this:



If you want to change back to an answer which has already been scored out, you should **enter a tick (✓)** to the RIGHT of the box of your choice, thus:



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

   A β-radiation

   B γ-radiation

   C UV-radiation

   D IR-radiation

2. An aqueous solution of potassium permanganate is coloured purple. In which region of the visible spectrum is it absorbing?

   A Red

   B Orange

   C Green

   D Violet

3. Which of the following is a correct statement about the series of alkali metals from lithium to caesium?

   A The melting point of the elements increases.

   B The ionic nature of their chlorides increases.

   C The first ionisation energy of the elements increases.

   D The crystal lattice structure of their chlorides is the same.

4. In which species does vanadium have the highest oxidation state?

   A VOF_3

   B $V(OH)_2$

   C VCl_4

   D $VSO_4.7H_2O$

5. A $0{\cdot}1\ mol\ l^{-1}$ solution of metal ions (M^+) was mixed in varying proportions with a $0{\cdot}1\ mol\ l^{-1}$ solution of a neutral ligand (L) giving coloured solutions. Each mixture was placed in a colorimeter and the absorbance measured.

   Maximum absorbance was obtained when $3{\cdot}5\ cm^3$ of the metal ion solution was mixed with $7{\cdot}0\ cm^3$ of the ligand solution. The formula of the complex ion formed is most likely to be

   A $[ML_2]^+$

   B $[ML_2]^{2+}$

   C $[M_2L]^+$

   D $[M_2L]^{2+}$.

6. When electrons occupy degenerate orbitals, they do so in such a way as to maximise the number of parallel spins. This statement is known as

   A the Pauli exclusion principle

   B Heisenberg's uncertainty principle

   C the aufbau principle

   D Hund's rule.

7. The electronic configuration of $Co^{2+}(g)$ is

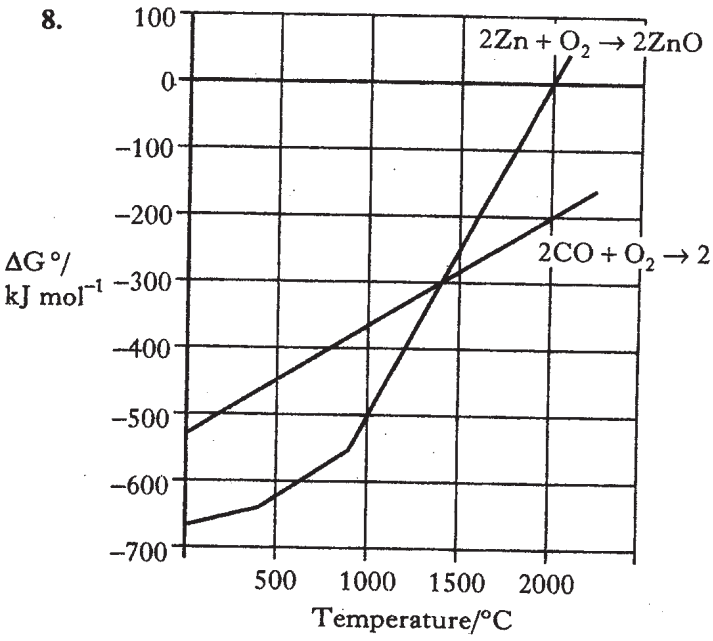
   A [Ar] $4s^2\ 3d^7$

   B [Ar] $4s^2\ 3d^5$

   C [Ar] $3d^9$

   D [Ar] $3d^7$.

   Note: [Ar] denotes the electronic configuration of argon.

8. 

   At approximately which temperature does zinc oxide decompose?

   A 400 °C

   B 900 °C

   C 1400 °C

   D 2000 °C

[Turn over

9. What volume of 0·25 mol l^{-1} calcium nitrate is required to make, by dilution with water, 500 cm^3 of a solution with a **nitrate** ion concentration of 0·1 mol l^{-1}?

A 50 cm^3

B 100 cm^3

C 200 cm^3

D 400 cm^3

10. Solid ammonium dichromate decomposes to produce chromium(III) oxide, nitrogen and water. The complete decomposition of one mole of ammonium dichromate would give

A a total of one mole of all the products

B 3 moles of water

C 2 moles of chromium(III) oxide

D 1 mole of nitrogen.

11. Which of the following is present in one mole of $BaCl_2(s)$?

A 3 moles of atoms

B 1 mole of molecules

C 1 mole of positive ions

D 2 moles of positive ions

12. $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(\ell)$

$Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-$

25 cm^3 of 0·1 mol l^{-1} $K_2Cr_2O_7$ was required to react completely with an acidified solution of Fe^{2+}. How many moles of Fe^{2+} did the original solution contain?

A 0·00042

B 0·0025

C 0·0075

D 0·015

13. Phosphoric acid undergoes partial dissociation according to the equation

$$H_3PO_4 \rightleftharpoons H_2PO_4^- + H^+$$

The extent of dissociation at equilibrium could be increased by the addition of

A sodium hydroxide

B sulphuric acid

C a catalyst

D sodium dihydrogenphosphate.

14. When one mole of phosphorus(V) chloride was heated in a closed vessel, 50% dissociated as shown.

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

How many moles of gas were present in the equilibrium mixture?

A 0·5

B 1·0

C 1·5

D 2·0

15. Which of the following indicators should be used in the titration of aqueous potassium hydroxide solution with aqueous ethanoic acid solution?

A Phenolphthalein, pH range 8·3 – 10·0

B Bromothymol blue, pH range 6·0 – 7·6

C Methyl red, pH range 4·2 – 6·3

D Methyl orange, pH range 3·1 – 4·4

16. Which of the following decreases when an aqueous solution of ethanoic acid is diluted?

A pH

B $[H^+]$

C pK_a

D Degree of dissociation

17. What is the concentration of hydroxide ions, in mol l^{-1}, in an aqueous solution of pH 14?

A 10^{-14}

B 10^0

C 10^1

D 10^{14}

18. In which of the following examples does X represent the bond enthalpy for the O—H bond in water?

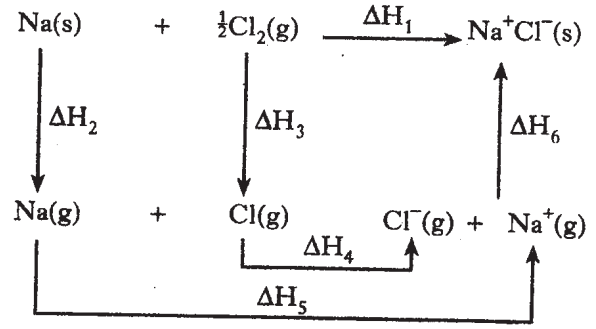
A $H_2O(g) \rightarrow O(g) + H_2(g)$ $\Delta H = 2X$

B $H_2O(g) \rightarrow O(g) + 2H(g)$ $\Delta H = X$

C $H_2O(g) \rightarrow O(g) + H_2(g)$ $\Delta H = X$

D $H_2O(g) \rightarrow O(g) + 2H(g)$ $\Delta H = 2X$

Questions 19 and **20** refer to the Born-Haber cycle below.



19. The enthalpy change which requires the input of most energy is

A ΔH_2

B ΔH_3

C ΔH_4

D ΔH_5.

20. The main enthalpy term which ensures that ΔH_1 is exothermic is

A ΔH_3

B ΔH_4

C ΔH_5

D ΔH_6.

21. The following reaction is first order with respect to P and second order with respect to Q.

$$P + Q \rightarrow R + S$$

Which of the following statements is correct?

A The reaction occurs by a simple one step mechanism.

B The reaction is second order overall.

C If the initial concentration of Q is doubled, the rate of the reaction will be doubled.

D As the reaction proceeds its rate will decrease.

22. A reaction **must** be exothermic if

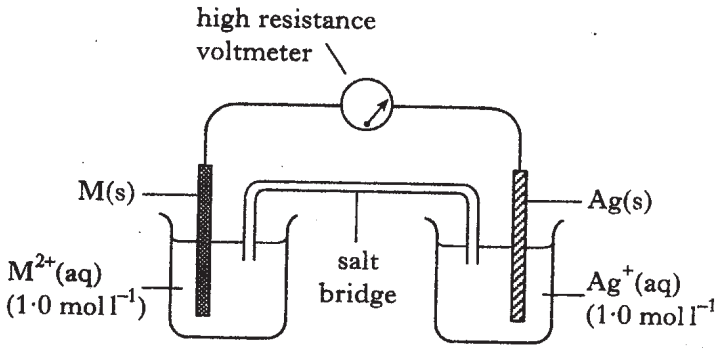
A $\Delta G°$ is negative

B $\Delta S°$ is positive

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

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

Questions 23, 24 and **25** refer to the electrochemical cell below which contains silver and an unknown metal, M.



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

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

A Fe(s) and $Fe^{2+}(aq)$

B Ni(s) and $Ni^{2+}(aq)$

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

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

24. 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.

25. Sodium chloride is an unsuitable substance for 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(s) does not conduct electricity.

[Turn over

26. Which of the following reactions exhibits a positive entropy change?

A The formation of ice from water

B The combination of ammonia and hydrogen chloride gases to give solid ammonium chloride

C The polymerisation of propene

D The decomposition of solid ammonium nitrate into nitrogen, oxygen and steam

27. A white crystalline compound, soluble in water, was found to react with both dilute hydrochloric acid and sodium hydroxide solution. Which of the following might it have been?

A Aminobenzene

B Aminoethanoic acid

C Ethylamine

D Ethylammonium chloride

28. 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 $C_2H_5N(CH_3)_2$

29. Which of the following does **not** occur in the reaction between methane and chlorine?

A Homolytic fission

B An addition reaction

C A chain reaction

D Free radical formation

30. Which of the following is **not** caused by hydrogen bonding?

A The higher melting points of fats compared to those of oils

B The formation of dimers in pure ethanoic acid

C The higher boiling point of methanol compared with that of ethane

D The miscibility of propanone with water

31. Which statement about ethanol and its isomer, methoxymethane, is true?

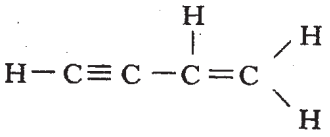
A They have similar volatility.

B They have similar reactivity.

C They produce similar infra-red spectra.

D They produce similar products when burned in excess oxygen.

32. Which line in the table has the correct number and type of bonds in



	Number of σ–bonds	Number of π–bonds
A	7	3
B	5	3
C	5	2
D	5	5

33. Which halide will be most resistant to attack by nucleophilic reagents?

A CH_3CH_2Br

B C_6H_5Br

C $(CH_3)_3CCl$

D $(CH_3)_2CHCl$

34. A compound, X, reduces hot copper(II) oxide and the organic product dissolves in water forming a neutral solution.

X could be

A an aldehyde

B a ketone

C a secondary alcohol

D a tertiary alcohol.

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

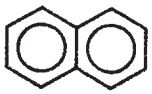
A $(CH_3)_3CBr$

B $CHBr_3$

C $CH(CH_2Br)_3$

D $(CH_3)_3CCH_2Br$

36. Naphthalene and anthracene are examples of polycyclic aromatic hydrocarbons.

Naphthalene:
Structural formula 

Molecular formula $C_{10}H_8$

Anthracene:
Structural formula 

The molecular formula of anthracene is

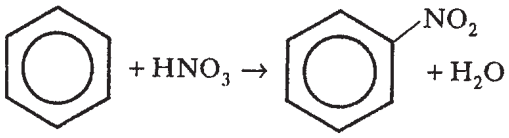
A $C_{14}H_{10}$

B $C_{12}H_{10}$

C $C_{14}H_{12}$

D $C_{12}H_{12}$.

37. In the reaction between benzene and nitric acid in the presence of concentrated sulphuric acid



A the benzene molecule acts as an electrophile

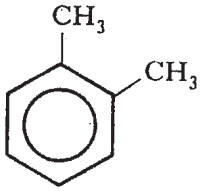
B the ion, NO_3^-, acts as a nucleophile

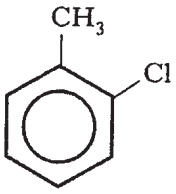
C the ion, NO_2^+, acts as an electrophile

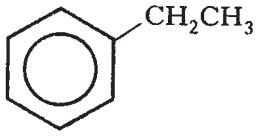
D the HNO_3 is oxidised.

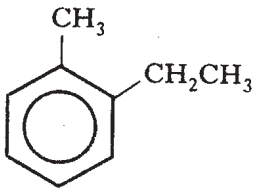
Q38 is at the top of the next column.

38. Which of the following will be produced when methylbenzene is reacted with chloromethane in the presence of aluminium chloride?

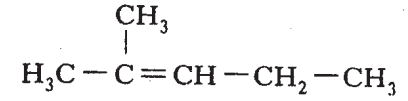
A 

B 

C 

D 

39. The major product in the reaction of HCl with 2-methylpent-2-ene,



is

A 2-chloro-2-methylpentane

B 3-chloro-2-methylpentane

C 2,3-dichloro-2-methylpentane

D 4-chloro-4-methylpentane.

40. Which line in the table below identifies the set of information that could be used to calculate the bond enthalpy of a carbon to carbon double bond?

	Enthalpy of formation	Enthalpy of combustion	Enthalpy of sublimation	Bond enthalpies
A	ethene	ethene	–	C—H, H—H
B	benzene	benzene	–	C—H, H—H
C	ethene	–	carbon	C—H, H—H
D	benzene	–	carbon	C—H, H—H

Marks

1. In the reaction

$$NH_3(aq) + H^+(aq) \rightarrow NH_4^+(aq)$$

a **dative** covalent bond is formed.

(*a*) What is meant by a **dative** covalent bond? 1

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

(*c*) Draw a diagram which shows the three dimensional shape of an ammonium ion. 1

(3)

2. In an experiment 0·25 g of an impure sample of magnesium carbonate was added to 40 cm^3 of 0·16 mol l^{-1} hydrochloric acid.
8·1 cm^3 of 0·11 mol l^{-1} sodium hydroxide solution was required to neutralise the excess hydrochloric acid.

(*a*) Show by calculation that 0·0055 mol of hydrochloric acid reacted with the magnesium carbonate. 2

(*b*) (i) Write the balanced equation for the reaction of magnesium carbonate with hydrochloric acid. 1

(ii) Calculate the percentage purity of the magnesium carbonate. 2

(5)

3. The melting points of selected oxides of the elements of the third period are shown in the table below.

Oxide	Melting Point/°C
Na_2O	sublimes at 1275
MgO	2852
Al_2O_3	2072
SiO_2	1610
P_4O_{10}	sublimes at 300
SO_2	–73
Cl_2O	–20

(*a*) In which of these oxides are covalent bonds broken as the substance melts? 1

(*b*) (i) What is meant by the term "amphoteric"? 1

(ii) Which oxide in the table is amphoteric? 1

(*c*) Considering the number of electron pairs present, draw the molecular shape of Cl_2O. 1

(4)

Marks

4. The bright green compound, potassium trioxalatoferrate(III), has the formula $K_3[Fe(C_2O_4)_3]$. It can be prepared from ammonium iron(II) sulphate, $(NH_4)_2Fe(SO_4)_2$, in three steps as shown by the equations below.

Step 1 $(NH_4)_2Fe(SO_4)_2 + H_2C_2O_4 \rightarrow FeC_2O_4 + H_2SO_4 + (NH_4)_2SO_4$

Step 2 $6FeC_2O_4 + 3H_2O_2 + 6K_2C_2O_4 \rightarrow 4K_3[Fe(C_2O_4)_3] + 2Fe(OH)_3$

Step 3 $2Fe(OH)_3 + 3H_2C_2O_4 + 3K_2C_2O_4 \rightarrow 2K_3[Fe(C_2O_4)_3] + 6H_2O$

A student, starting with 5·0 g of hydrated ammonium iron(II) sulphate, $(NH_4)_2Fe(SO_4)_2.6H_2O$, obtained 1·2 g of the hydrated product $K_3[Fe(C_2O_4)_3].3H_2O$.

(*a*) What is the value of the co-ordination number of the iron ion in the final product? **1**

(*b*) What is the function of the hydrogen peroxide in step two? **1**

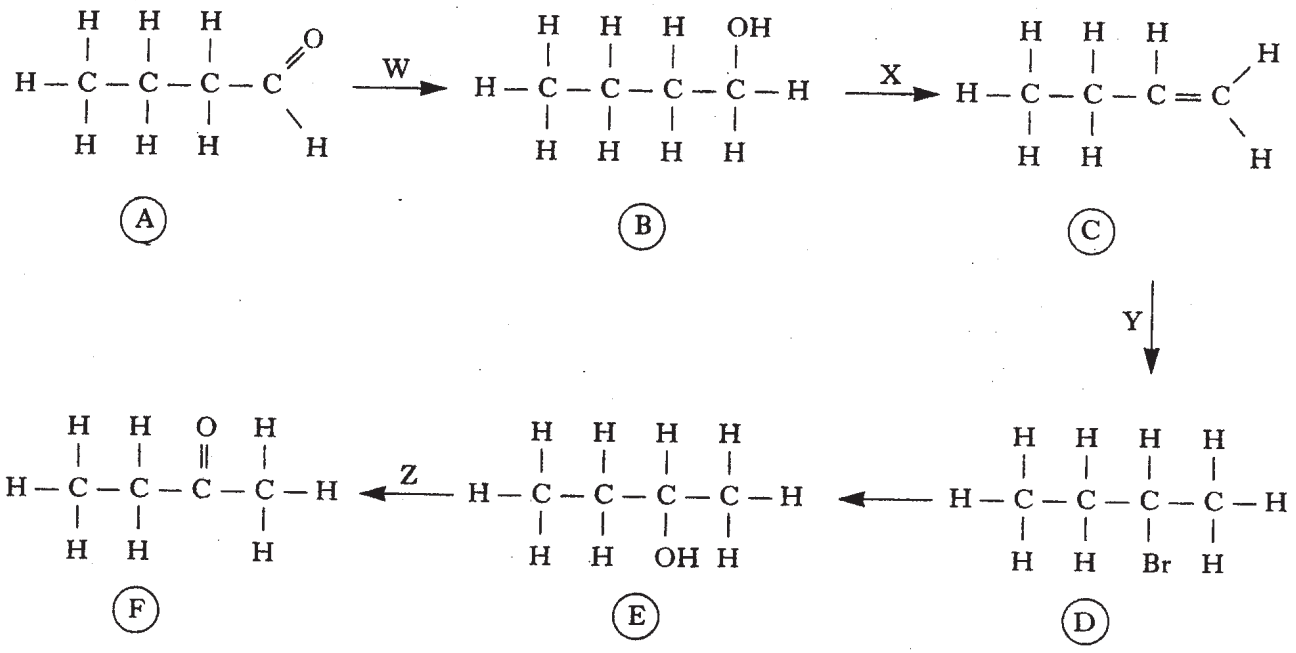
(*c*) From the equations given, how many moles of $K_3[Fe(C_2O_4)_3]$ will be formed from 1 mole of $(NH_4)_2Fe(SO_4)_2$? **1**

(*d*) Calculate the percentage yield of $K_3[Fe(C_2O_4)_3].3H_2O$ from the student's results. **3**

(6)

[Turn over

5. A student designed the following reaction sequence.



(*a*) Suggest a suitable reagent to carry out

(i) step W

(ii) step Y. **2**

(*b*) What type of reaction occurs at

(i) step X

(ii) step Z? **2**

(*c*) Name the other product which is likely to be formed in step Y. **1**

(*d*) Name a reagent which could be used to distinguish between (A) and (F). **1**

(*e*) (i) Why does (C) not have geometric isomers despite the presence of a carbon to carbon double bond? **1**

(ii) Which of the compounds (A) – (F) have optical isomers? **2**

(9)

Marks

6. 1-Bromobutane and 2-bromo-2-methylpropane are isomers which can be converted to their corresponding alcohols using hydroxide ions.

(*a*) The conversion of 2-bromo-2-methylpropane to 2-methylpropan-2-ol involves an S_N1 mechanism.

(i) Explain the meaning of the abbreviation S_N1. **2**

(ii) Outline the two steps in this mechanism using structural formulae. **2**

(*b*) Explain why the conversion of 1-bromobutane to butan-1-ol is unlikely to proceed by an S_N1 mechanism. **1**

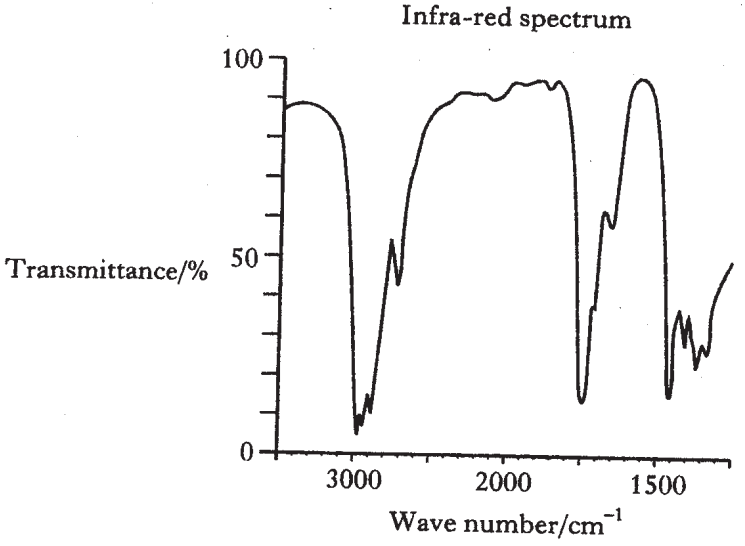
(c) 2-Bromo-2-methylpropane reacts with ethoxide ions to form an ether. Draw a structural formula for this ether. **1**

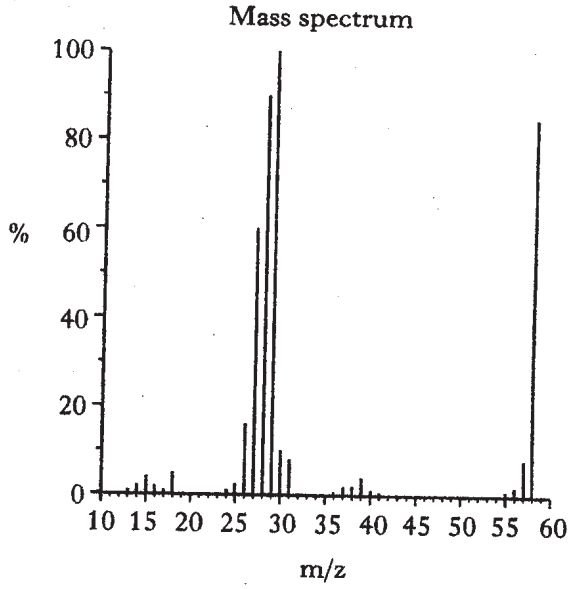
(6)

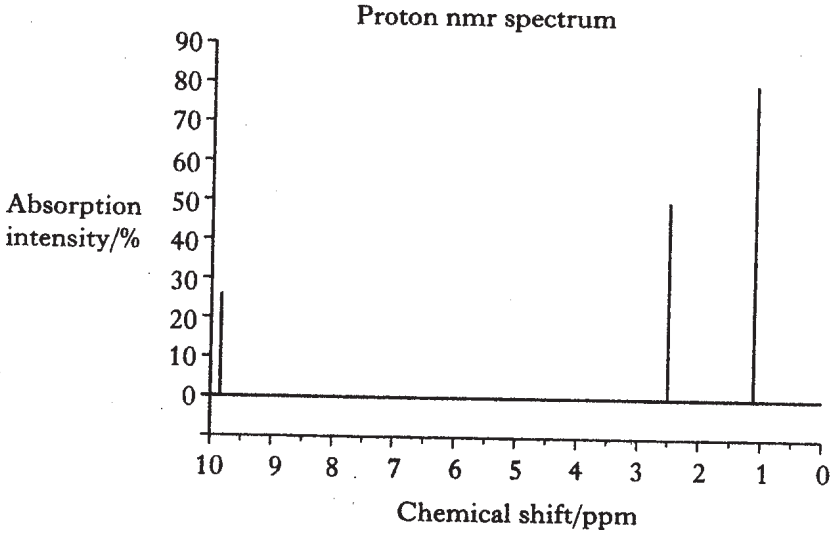
[Turn over

Marks

7. The following simplified spectra were obtained for a pure organic compound containing carbon, hydrogen and oxygen only.







The proton nmr spectrum was analysed and the data are presented in the table below.

Chemical shift	Area under the peak	H atom ratio
1·1	6·9	X
2·5	4·5	Y
9·8	2·3	Z

(*a*) Identify the functional group causing the absorption at 1730 cm^{-1} in the infra-red spectrum. **1**

(*b*) Identify a possible ion fragment responsible for the peak at m/z 29 in the mass spectrum. **1**

(*c*) From the proton nmr spectrum what is the whole number ratio of hydrogen atoms, X:Y:Z? **1**

(*d*) From the information above draw a structural formula for this compound. **2**

(*e*) How would Brady's reagent (2,4-dinitrophenylhydrazine solution) be used to confirm your answer to (*d*)? **2**

(7)

Marks

8. Sulphanilamide and penicillin are antibiotics which are antagonists whereas salbutamol is a bronchodilator which acts as an agonist.

All of these medicines have **pharmacophores** which bind to specific **receptors**.

(*a*) Explain the difference in behaviour between an agonist and an antagonist. **1**

(*b*) Explain the meanings of the **two** words in bold. **2**

(3)

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

$$H_2O_2(aq) + 3I^-(aq) + 2H^+(aq) \longrightarrow I_3^-(aq) + 2H_2O(\ell)$$

Experiment	$[H_2O_2]$/ mol l^{-1}	$[I^-]$/ mol l^{-1}	$[H^+]$/ mol l^{-1}	Initial rate/ mol $l^{-1}s^{-1}$
1	0·3	0·3	0·002	$2{\cdot}07 \times 10^{-3}$
2	0·6	0·3	0·002	$4{\cdot}14 \times 10^{-3}$
3	0·3	0·6	0·002	$4{\cdot}14 \times 10^{-3}$
4	0·3	0·3	0·004	$2{\cdot}07 \times 10^{-3}$

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

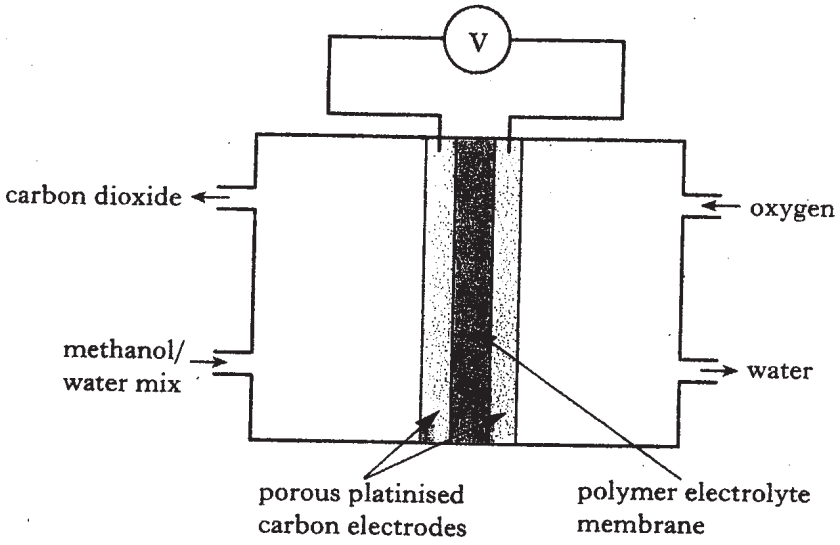
(*b*) Calculate the rate constant for this reaction giving the appropriate units. **3**

(4)

[Turn over

Marks

10. The methanol fuel cell below was designed to power military radios.



The cell can be represented as:

$$CH_3OH(\ell) \,|\, CO_2(g) \,\|\, O_2(g) \,|\, H_2O(\ell).$$

The overall reaction occurring in the cell is:

$$CH_3OH(\ell) + \tfrac{3}{2}O_2(g) \rightarrow CO_2(g) + 2H_2O(\ell) \quad \Delta H^\circ = -727 \text{ kJ mol}^{-1}.$$

Substance	S°/J K^{-1} mol^{-1}
$CH_3OH(\ell)$	127·0
$O_2(g)$	205·2
$CO_2(g)$	213·8
$H_2O(\ell)$	69·9

(*a*) Calculate the entropy change, ΔS°, in J K^{-1} mol^{-1}, for the overall cell reaction. **1**

(*b*) Calculate ΔG°, the standard free energy change, in kJ mol^{-1}, for the overall reaction at 298 K. **2**

(*c*) The ion-electron equation for the reaction occurring in the left hand side of the cell is

$$CH_3OH(\ell) + H_2O(\ell) \rightarrow CO_2(g) + 6H^+(aq) + 6e^-.$$

Write the ion-electron equation for the reaction occurring in the right hand side of the cell. **1**

(*d*) Which ion migrates through the polymer electrolyte membrane? **1**

(5)

Marks

11. Octanoic acid is a weak acid with a dissociation constant, $K_a = 1{\cdot}27 \times 10^{-5}$ and $pK_a = 4{\cdot}9$.

One litre of $0{\cdot}20\,mol\,l^{-1}$ octanoic acid solution was prepared.

(*a*) Calculate the pH of the solution. **2**

(*b*) $0{\cdot}20\,mol\,l^{-1}$ sodium hydroxide solution was then added to the solution of the acid until the pH became 4·5. It was observed that when a few drops of dilute hydrochloric acid were added to this new solution, the pH remained at 4·5.

Explain briefly why the pH of this solution does not change. **2**

(4)

12. A very dilute solution of a pH indicator in a pH 7 buffer solution was prepared. This was placed in a spectrophotometer and the absorption spectrum was recorded. The indicator is a weak acid and dissociates as shown below.

$$HIn(aq) \rightleftharpoons H^+(aq) + In^-(aq)$$

Two peaks were observed in the absorption spectrum, one corresponding to the undissociated form of the indicator, (HIn (aq)) and one to the indicator ion (In^- (aq)). The intensity of each absorption was used to determine the concentration of each species.

Species	Colour	Concentration/mol l^{-1}
HIn(aq)	blue	$1{\cdot}3 \times 10^{-5}$
In^-(aq)	yellow	$3{\cdot}9 \times 10^{-4}$

(*a*) Calculate the value of K_{In} for this indicator. **3**

(*b*) What colour will the indicator appear when added to a solution with a pH value of 10? **1**

(4)

[END OF QUESTION PAPER]