X012/701

NATIONAL QUALIFICATIONS 2002

TUESDAY, 4 JUNE
9.00 AM – 11.30 AM

CHEMISTRY
ADVANCED HIGHER

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

SECTION A—Part 1 Questions 1–30 and Part 2 Questions 31–33

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 **Part 1** and **Part 2** are given on pages two and eight respectively.

SECTION B

All questions should be attempted.

SCOTTISH QUALIFICATIONS AUTHORITY

SECTION A

PART 1

In questions 1 to 30 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 Part 1 of the answer sheet—see the sample question below.

For each question there is only ONE correct answer.

This part of the paper is worth 30 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

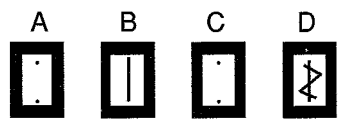
B chromatography

C fractional crystallisation

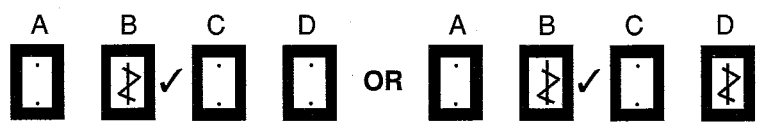
D filtration.

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. $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$

$\Delta H^\circ_{forward} = +92{\cdot}4\,kJ\ mol^{-1}$

The conditions favouring the decomposition of ammonia are

A low pressure and low temperature

B high pressure and low temperature

C low pressure and high temperature

D high pressure and high temperature.

2. The lattice of caesium chloride has 8 chloride ions round each caesium ion, while that of sodium chloride has 6 chloride ions round each sodium ion. This difference in structure is due to the fact that caesium and sodium have different

A electronegativities

B ionic radii

C electrode potentials

D ionisation energies.

3. The bond enthalpy of the C — H bond is 414 kJ mol^{-1}. From this information it can be calculated that

A when 1 mole of methane is burned in excess oxygen 1656 kJ are evolved

B 1656 kJ must be supplied to dissociate 1 mole of methane into free carbon and hydrogen atoms

C 1656 kJ must be supplied for the complete combustion of 1 mole of methane

D when 1 mole of graphite combines with 2 moles of hydrogen gas (H_2) 1656 kJ are evolved.

4. 18 g of an oxide of copper was strongly heated and hydrogen gas was passed over it. When the oxide was completely reduced, 16 g of copper remained. The empirical formula for the oxide is

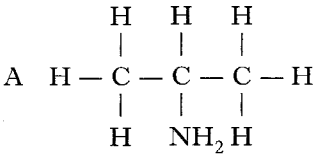
A Cu_2O_3

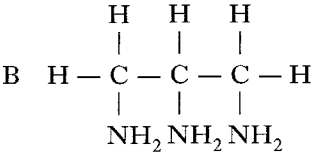
B CuO_2

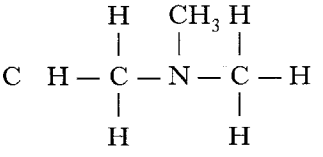
C Cu_2O

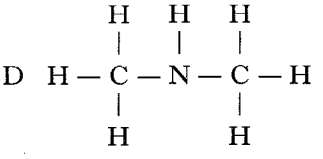
D CuO.

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

A


B


C


D


6. Given the equations:

$Mg(s) + 2H^+(aq) \rightarrow Mg^{2+}(aq) + H_2(g)$
$\Delta H^\circ = a\ kJ\ mol^{-1}$

$Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$
$\Delta H^\circ = b\ kJ\ mol^{-1}$

$Mg(s) + Zn^{2+}(aq) \rightarrow Mg^{2+}(aq) + Zn(s)$
$\Delta H^\circ = c\ kJ\ mol^{-1}$

Then, according to Hess's Law

A $a - b = c$

B $a + b = c$

C $a - b = -c$

D $a + b = -c$.

7. Which of the following hydrides, when added to water, would give the most acidic solution?

A Sodium hydride

B Magnesium hydride

C Silicon hydride

D Sulphur hydride

[Turn over

8. Which statement best describes a semiconductor?

A Its conductivity increases with increasing temperature.

B It has zero electrical resistance at temperatures near absolute zero.

C It is a substance which does not conduct when solid but conducts when molten.

D Its electrical resistance increases on exposure to light.

9. The equilibrium constant for the dissociation of a base is given by K_b.

$20\,cm^3$ of $0{\cdot}1\ mol\,l^{-1}$ solutions of each of the bases in the table below were neutralised by $20\,cm^3$ of $0{\cdot}1\ mol\,l^{-1}$ hydrochloric acid and the pH of the resulting salt solutions measured.

Which base would have given the salt solution with the highest pH?

	Base	K_b
A	Ammonia	$1{\cdot}8 \times 10^{-5}$
B	Methylamine	$4{\cdot}5 \times 10^{-4}$
C	Phenylamine	$4{\cdot}3 \times 10^{-10}$
D	Phenylmethylamine	$2{\cdot}4 \times 10^{-5}$

10. $$P + Q \rightleftharpoons R + S$$

At 298 K the equilibrium constant for this reaction is $1{\cdot}2 \times 10^{10}$.

Which of the following must be true?

A Increasing the concentration of P will not change the equilibrium constant.

B The value of ΔG° is positive.

C Adding a catalyst will change the equilibrium constant.

D The value of ΔS° is positive.

11. The pH ranges over which some common indicators change colour are given below. Which indicator would be most suitable for the titration of ethanoic acid with sodium hydroxide?

	Indicator	pH range
A	Methyl orange	3·1 – 4·5
B	Methyl red	4·2 – 6·3
C	Bromothymol blue	6·0 – 7·6
D	Phenolphthalein	8·3 – 10·0

12. The lattice enthalpy of a salt is $-2913\ kJ\ mol^{-1}$ and its enthalpy of hydration is $-2871\ kJ\ mol^{-1}$.

From this information only it can be stated that this salt

A will not dissolve in water

B will dissolve in water because of an increase in entropy

C if soluble, will dissolve in water giving out heat

D if soluble, will dissolve in water taking in heat.

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

A $C(s) + H_2O(g) \rightarrow CO(g) + H_2(g)$

B $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$

C $Cu^{2+}(aq) + Mg(s) \rightarrow Mg^{2+}(aq) + Cu(s)$

D $Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$

14. In a series of experiments P and Q reacted to form R. The time taken to produce a fixed concentration of R was recorded.

Experiment	Initial conc^n of P/mol l^{-1}	Initial conc^n of Q/mol l^{-1}	Time/s
1	0·05	0·05	46
2	0·05	0·10	23
3	0·10	0·05	46

The rate equation for this reaction is

A Rate = k[P]

B Rate = k[Q]

C Rate = $k[Q]^2$

D Rate = k[P][Q].

15. The standard enthalpy of formation of magnesium bromide is the enthalpy change for the reaction

A $Mg^{2+}(g) + 2Br^-(g) \rightarrow Mg^{2+}(Br^-)_2(s)$

B $Mg^{2+}(g) + 2Br^-(g) \rightarrow Mg^{2+}(Br^-)_2(g)$

C $Mg(s) + Br_2(g) \rightarrow Mg^{2+}(Br^-)_2(s)$

D $Mg(s) + Br_2(\ell) \rightarrow Mg^{2+}(Br^-)_2(s)$.

16. Which is likely to have the lowest standard entropy value at 100 °C?

A Mercury

B Neon

C Phosphorus

D Sulphur

17. Which is likely to show most covalent character?

A Tin(IV) iodide

B Iron(II) chloride

C Lithium fluoride

D Potassium bromide

18. A complex ion with the name hexaammine nickel(II) will have the formula

A $[Ni(NH_2)_6]^{2+}$

B $[Ni(NH_3)_6]^{2+}$

C $[Ni(NH_3)_6]^{4-}$

D $[Ni(NH_4)_6]^{2+}$.

19. The highest oxidation state of chlorine is present in

A $HClO$

B $HClO_2$

C $HClO_3$

D $HClO_4$.

20. Which of the following will react with 0·01 mol of hydrochloric acid so that both reactants would be used up?

A 0·50 g of calcium carbonate

B 100 cm^3 of 0·10 mol l^{-1} barium hydroxide solution

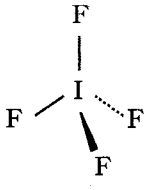
C 0·243 g of magnesium

D 25 cm^3 of 0·20 mol l^{-1} silver(I) nitrate solution

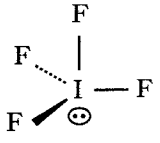
21. Which diagram best represents the arrangement of atoms in the IF_4^- ion?

Note: ⊙ represents a lone pair of electrons.

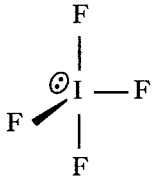
A



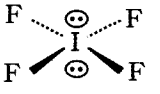
B



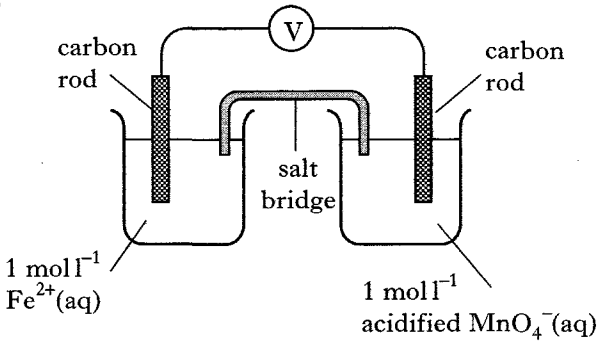
C



D



22.



The emf of the electrochemical cell shown above, operating under standard conditions, would be

A 0·74 V

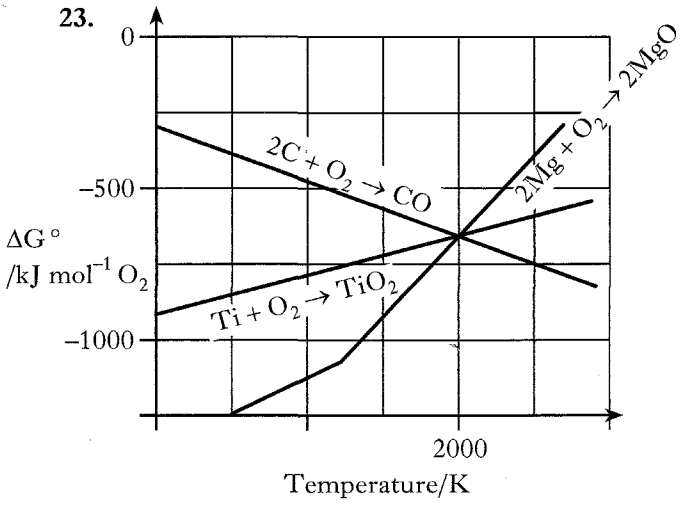
B 1·07 V

C 1·95 V

D 2·28 V.

[Turn over

23.



From the graph above it can be deduced that

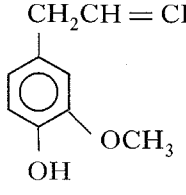
A magnesium can be used to reduce titanium oxide **below** 2000 K, and carbon can be used to reduce titanium oxide **below** 2000 K

B magnesium can be used to reduce titanium oxide **above** 2000 K, and carbon can be used to reduce titanium oxide **below** 2000 K

C magnesium can be used to reduce titanium oxide **below** 2000 K, and carbon can be used to reduce titanium oxide **above** 2000 K

D magnesium can be used to reduce titanium oxide **above** 2000 K, and carbon can be used to reduce titanium oxide **above** 2000 K.

24. Eugenol is the main constituent of oil of cloves and has the structural formula given below.



To isolate eugenol, oil of cloves is first treated with KOH(aq).

Which part of the structure of eugenol is most likely to react with KOH(aq)?

A The $-OCH_3$ group

B The aromatic ring

C The $-OH$ group

D The unsaturated side-chain

25. An organic compound X forms an addition product with hydrogen cyanide and can be reduced by lithium aluminium hydride.

It can be concluded that X

A can be oxidised to an acid

B contains a carbonyl group

C is an alkene

D is a ketone.

26. Which of the following compounds would be expected to have the highest boiling point?

A Methoxyethane

B Propanal

C Propan-2-ol

D Propanone

27. 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_2ONa and $CH_3CH_2CH_2I$

C $CH_3CH_2CH_2OH$ and CH_3COONa

D CH_3CH_2ONa and CH_3CHICH_3

28. 0·5 mol of an organic compound, X, required 24 litres of hydrogen for complete hydrogenation.

Assuming the molar volume of hydrogen to be 24 litres mol^{-1} under the reaction conditions, X could be

A $CH_3C \equiv CH$

B CH_3CH_2CHO

C $HC \equiv CCH_2CH = CH_2$

D $CH_3CH = CHCH_2OH$.

29. 1·204 g of a metal sulphate was dissolved in water. Addition of excess barium chloride solution resulted in the precipitation of 2·334 g of barium sulphate.

The original metal sulphate used was

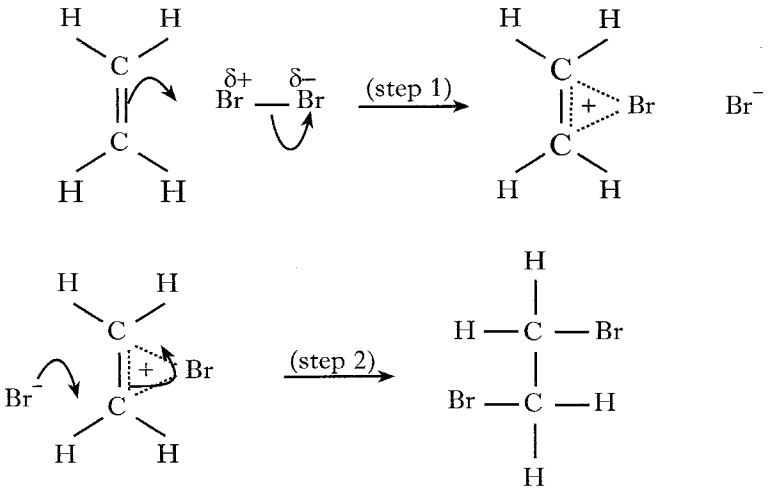
A calcium sulphate

B copper(II) sulphate

C magnesium sulphate

D sodium sulphate.

30.



The two steps in the reaction mechanism shown can be described as

A ethene acting as a nucleophile and Br^- acting as an electrophile

B ethene acting as an electrophile and Br^- acting as a nucleophile

C ethene acting as a nucleophile and Br^- acting as a nucleophile

D ethene acting as an electrophile and Br^- acting as an electrophile.

[Turn over

31. The boxes in the grid below contain the names of techniques used in chemistry.

A Infra-red spectroscopy	B Proton NMR spectroscopy	C Visible spectroscopy
D Ultra-violet spectroscopy	E Mass spectrometry	F X-ray crystallography

(*a*) Which technique(s) will involve the absorption of energy to promote electrons to higher energy levels?

(*b*) In which technique will the test sample be destroyed?

(*c*) Which technique(s) will produce a diffraction pattern which enables the precise three-dimensional structure of a compound to be determined?

32. The boxes in the grid below show electronic configurations of different species.

A $1s^2 2s^2 2p^6$	B $1s^2 2s^2 2p^6 3s^1$	C $1s^2 2s^2 2p^6 3p^1$
D $1s^2 2s^2 2p^6 3s^2\ 3p^6 3d^4 4s^2$	E $1s^2 2s^2 2p^6 3s^2\ 3p^6 3d^5 4s^1$	F $1s^2 2s^2 2p^6 3s^2\ 3p^6 3d^6$

(*a*) Which is the electronic configuration of a chromium atom in the ground state?

(*b*) Which is the electronic configuration of a sodium atom in an excited state?

(*c*) Which electronic configuration(s) will have a total of 4 unpaired electrons?

33. The boxes in the grid below contain the formulae for various oxides.

A H_2O	B SiO_2	C Al_2O_3
D CO_2	E CO	F Na_2O

Identify the amphoteric oxide(s).

[Turn over

SECTION B

Marks

1. At room temperature, titanium(III) chloride is a solid which dissolves in water to give a purple solution. However, titanium(IV) chloride is a liquid at room temperature which reacts vigorously with water giving off white fumes.

(*a*) What are the white fumes given off when titanium(IV) chloride reacts with water? **1**

(*b*) Which type of bonding is present in titanium(IV) chloride? **1**

(*c*) Write the electronic configuration of the titanium(III) ion in terms of s, p and d orbitals. **1**

(*d*) A solution of titanium(III) chloride absorbs light at 500 nm.
Calculate the energy, in kJ mol^{-1}, associated with this wavelength. **2**

(5)

2. The shapes of molecules depend on the number of bonding and non-bonding electron pairs present.

(*a*) Draw a diagram to show the molecular shape of

(i) methane

(ii) hydrogen sulphide. **1**

(*b*) Explain why the bond angle in hydrogen sulphide is less than that in methane. **2**

(3)

3. Information about the decomposition of silver(I) nitrate is given below.

$$AgNO_3(s) \rightarrow Ag(s) + \tfrac{1}{2}O_2(g) + NO_2(g)$$

Substance	ΔH_f° / kJ mol^{-1}	S°/JK^{-1} mol^{-1}
$AgNO_3$	−123·6	141·5
Ag	0	42·6
O_2	0	205·2
NO_2	34·0	241·4

For the decomposition of $AgNO_3$, calculate

(*a*) ΔH° **1**

(*b*) ΔS° **1**

(*c*) the theoretical temperature at which the reaction just becomes feasible. **2**

(4)

4. Difluoromethanimine, FN = CHF, can exist in two isomeric forms.

When a sample of the *trans*-isomer was dissolved in an organic solvent at 22 °C it was slowly converted into the *cis*-isomer. After 7 days, 95% of the *trans*-isomer had been converted and no further conversion occurred thereafter.

(*a*) Draw the full structural formula of *trans*-difluoromethanimine. **1**

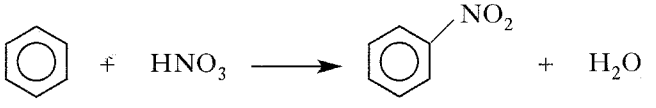
(*b*) Difluoromethanimine contains a pi bond.
Explain how a pi bond is formed. **1**

(*c*) Calculate the equilibrium constant for the conversion of *trans*-difluoromethanimine into its *cis*-isomer at 22 °C. **1**

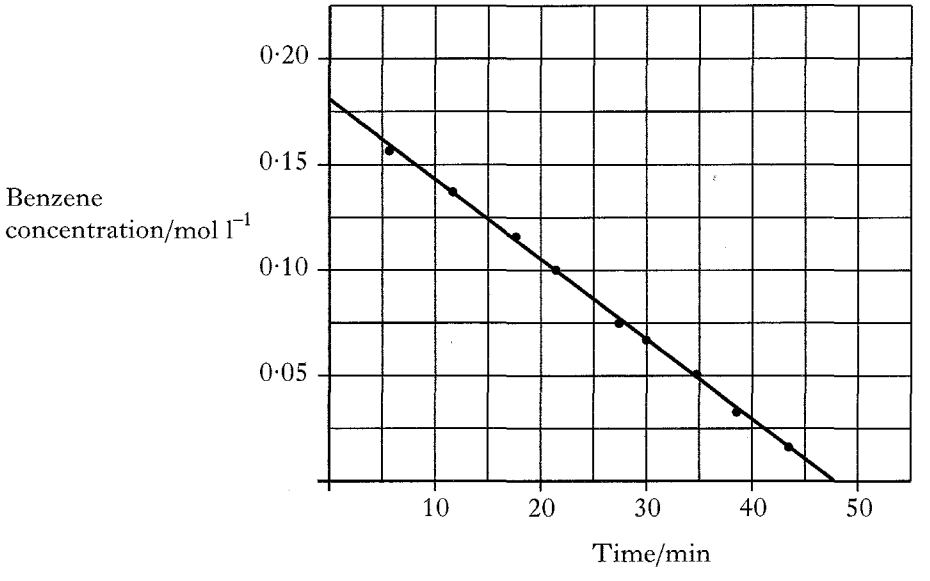
(*d*) Suppose a sample of *cis*-difluoromethanimine was dissolved in the same organic solvent at 22 °C. Predict the percentage amount of the *cis*-isomer present in the solution after 7 days. **1**

(4)

5. Benzene can be nitrated by reaction with concentrated nitric acid.



The graph below shows the results obtained on nitrating benzene in an excess of concentrated nitric acid.



Results from a separate experiment showed the reaction to be first order with respect to nitric acid.

(*a*) (i) From the graph, deduce the order of the reaction with respect to benzene. **1**

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

(iii) What must be the **minimum** number of steps in the reaction mechanism for it to be consistent with this rate equation? **1**

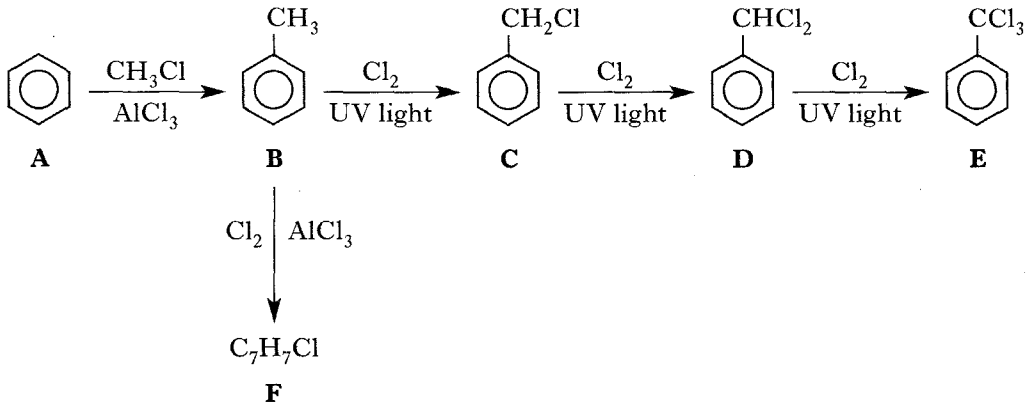
(*b*) The nitration of benzene is normally achieved using a mixture of concentrated nitric and sulphuric acids. The latter react in the following way:

$$HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + H_3O^+ + 2HSO_4^-$$

Give the formula of the acid and its conjugate base in this reaction. **1**

(4)

6. Consider the following reaction sequence.



(*a*) Name the type of substitution reaction taking place in the conversion of **A** into **B** and **B** into **F**. **1**

(*b*) **F** is a mixture of three isomers. Draw the structural formula of one of these isomers. **1**

(c) **B** is converted into **C** by a free radical mechanism.

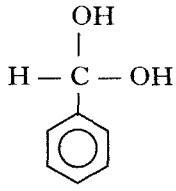
Write an equation for

(i) the initiation step

(ii) one of the propagation steps

in this mechanism. **2**

(*d*) **D** reacts with aqueous sodium hydroxide to form



which is unstable and immediately loses water to form a stable aldehyde.

Compound **E** reacts in a similar way with aqueous sodium hydroxide forming an intermediate which also loses water to give a stable product.

Draw the structure of this stable product. **1**

(5)

7. The determination of manganese in steel can be carried out by a colorimetric method.

The manganese is first oxidised to manganese(II) ions using nitric acid.

$$Mn(s) \rightarrow Mn^{2+}(aq) + 2e^{-}$$

The manganese(II) ions are then further oxidised to permanganate ions using a stronger oxidising agent.

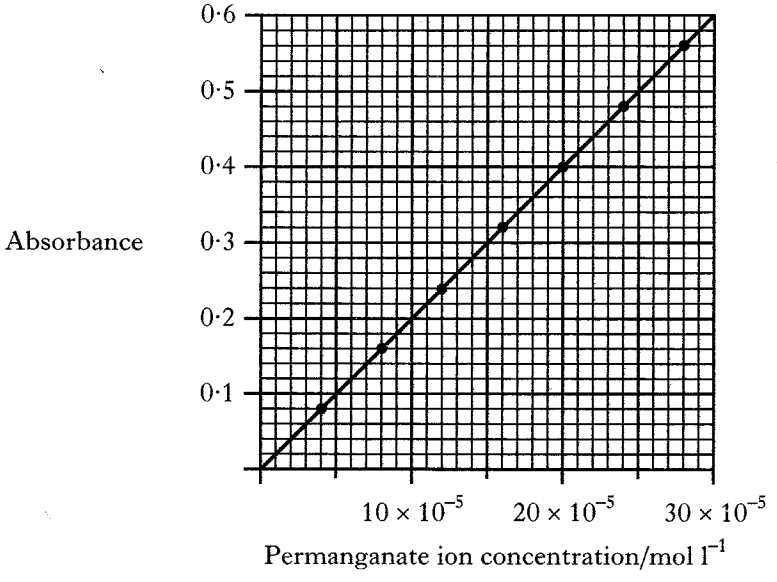
The absorbance of the permanganate solution formed is then measured in a colorimeter. The concentration of the solution corresponding to the absorbance can then be read from a previously constructed calibration graph.

(*a*) Write the ion-electron equation for the conversion of manganese(II) ions to permanganate ions. **1**

(*b*) Why is a colorimetric method particularly suitable for determining manganese in steel? **1**

(*c*) In a determination, the manganese in 0·214 g of steel was oxidised to permanganate ions and the solution made up to 100 cm^3 in a standard flask. The absorbance of the solution was measured as 0·22.

Use this information and the following calibration graph to calculate the percentage of manganese in this sample of steel. **3**



(5)

[Turn over

8. The nickel-cadmium battery is extensively used nowadays. It is a small battery with two electrodes made of steel grids. The negative electrode is packed with cadmium and the positive electrode is packed with hydrated nickel(IV) oxide. The electrolyte is a concentrated solution of potassium hydroxide.

The relevant ion-electron equations are

$$Cd(s) + 2OH^-(aq) \rightarrow Cd(OH)_2(s) + 2e^-$$
$$NiO_2.2H_2O(s) + 2e^- \rightarrow Ni(OH)_2(s) + 2OH^-(aq) \quad E^\circ = 0{\cdot}49\,V$$

The overall cell voltage is 1·30 V.

(*a*) Calculate the standard reduction potential at the negative electrode. **1**

(*b*) Calculate the standard free energy change, in kJ mol^{-1}, for the cell reaction. **2**

(3)

9. 11·70 g of sodium chloride was added to 150 cm^3 of water at 18·5 °C. The sodium chloride dissolved, with stirring, and the temperature of the water fell to 14·9 °C.

(*a*) Using the experimental results, calculate the enthalpy of solution of sodium chloride. **2**

(*b*) The enthalpy of solution of an ionic compound can be calculated from its lattice enthalpy and the enthalpy of hydration of its ions.

Using information from the Data Booklet, calculate the enthalpy of solution of sodium chloride. **2**

(*c*) Suggest a reason for the difference in the answers to (*a*) and (*b*). **1**

(5)

10. Butanoic acid can be synthesised from 1-bromopropane by a two stage process.

$$CH_3CH_2CH_2Br \xrightarrow[KCN(aq)]{\text{stage } \mathbf{1}} \mathbf{Y} \xrightarrow{\text{stage } \mathbf{2}} CH_3CH_2CH_2COOH$$

(*a*) Draw the structural formula of **Y**. **1**

(*b*) Name the type of reaction taking place in stage **2**. **1**

(*c*) Using information from the Data Booklet, calculate the pH of 0·010 mol l^{-1} aqueous butanoic acid. **2**

(*d*) A buffer solution can be prepared by mixing aqueous solutions of butanoic acid and sodium butanoate. Explain how this solution can maintain its pH when a small volume of acid is added to it. **2**

(6)

11. A monocarboxylic acid, **X**, has an empirical formula of CH_2O. When 10·0 cm^3 of an aqueous solution of **X**, containing 7·85 g l^{-1}, was titrated against 0·049 mol l^{-1} sodium hydroxide the titre volume was 17·8 cm^3.

(*a*) Show, by calculation, that the relative formula mass of **X** is 90. **2**

(*b*) What is the molecular formula of **X**? **1**

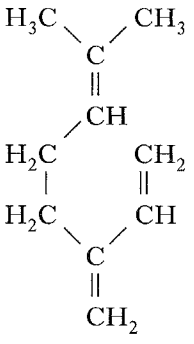
(*c*) **X** contains an asymmetric carbon atom.

(i) Deduce the structural formula of **X**. **1**

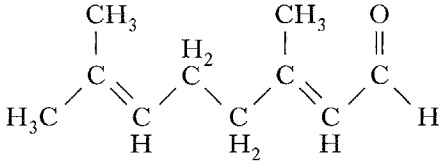
(ii) Plane-polarised light is **not** rotated when passed through an aqueous solution of **X**. Suggest a reason for this. **1**

(5)

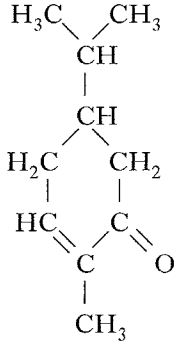
12. Myrcene, citral and carvone belong to a large group of compounds known as terpenes.



myrcene



citral



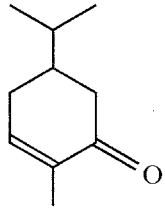
carvone

(*a*) The molecular unit from which terpenes are synthesised is 2-methylbuta-1,3-diene.
Draw the structural formula of 2-methylbuta-1,3-diene. **1**

(*b*) A 0·019 mol sample of one of the above terpenes required 47·5 cm^3 of 1·20 mol l^{-1} bromine solution for complete reaction.
Identify, by calculation, the terpene used in the reaction. **Show your working.** **2**

(*c*) Myrcene undergoes addition with excess hydrogen bromide. Assuming that the addition follows Markovnikov's rule, draw the structural formula of the product. **1**

(*d*) The skeletal structural formula of carvone is



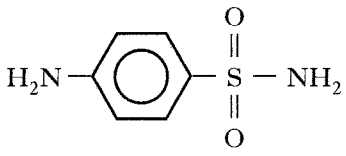
Draw the skeletal structural formula of citral. **1**

(*e*) Lithium aluminium hydride does **not** reduce myrcene but will reduce citral and carvone.
Draw the structural formula of the organic product formed on reducing **citral** with lithium aluminium hydride. **1**

(6)

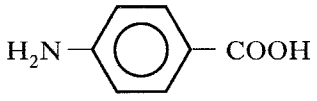
[Turn over

13. Sulphonamides are a group of organic compounds some of which are antibacterial agents. Sulphanilamide was the first to be synthesised.



sulphanilamide

It acts as an enzyme inhibitor and blocks the biosynthesis of folic acid which is essential for cell growth. It does this by mimicking 4-aminobenzoic acid which is one of the reactants required in folic acid synthesis.



4-aminobenzoic acid

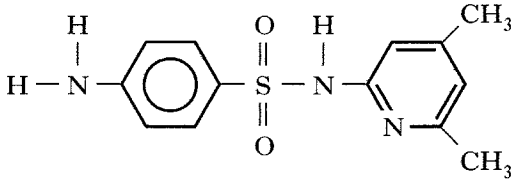
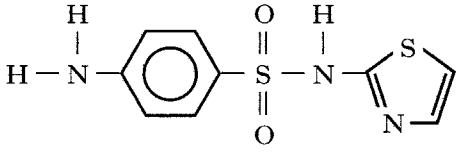
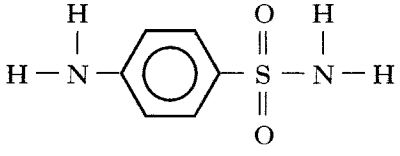
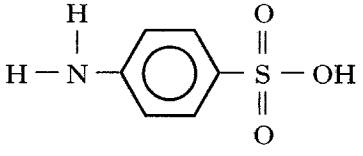
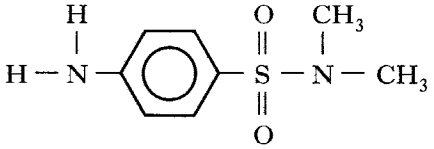
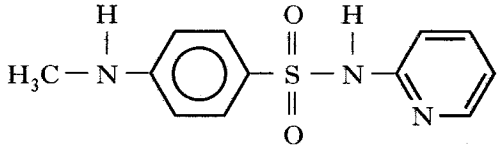
The sulphanilamide molecule prevents the 4-aminobenzoic acid molecule binding to the active site of the enzyme. As a result, folic acid can no longer be synthesised and the bacterial cell stops dividing.

(*a*) Suggest why the sulphanilamide molecule prevents the 4-aminobenzoic acid molecule binding to the active site of the enzyme. **1**

(*b*) State whether sulphanilamide plays the role of agonist or antagonist and explain your answer. **2**

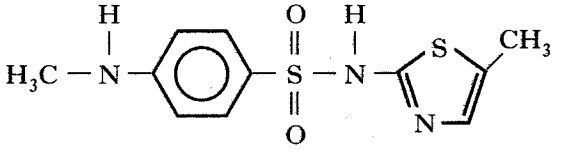
13. (continued)

(*c*) The structural formulae of some sulphonamides including sulphanilamide are listed in the following table together with their antibacterial activity.

Sulphonamide	Antibacterial activity
	active
	active
	active
	inactive
	inactive
	inactive

(i) Draw the structure of the sulphonamide pharmacaphore. **1**

(ii) Explain whether the sulphonamide with structure



would be effective as an antibacterial agent. **1**

(5)

[END OF QUESTION PAPER]