[92/301]

1982

CERTIFICATE OF SIXTH YEAR STUDIES

CHEMISTRY

PAPER I

Tuesday, 11th May—9.30 a.m. to 12 noon

Dalziel High School
Chemistry Department

1982 CSYS

TE&S 92/301 6/6/5726
1982 Scottish Certificate of Education

1. Which of the following reactions is exothermic?

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

   B $\frac{1}{2}Cl_2(g) \rightarrow Cl(g)$

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

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

2. Which of the following contains the greatest number of molecules of hydrogen?

   A 6 litres of hydrogen at s.t.p.

   B 6×10^{23} molecules of hydrogen

   C 6 grams of hydrogen

   D 6 moles of hydrogen molecules

3. The position of equilibrium in a chemical reaction is dependent on

   A the state of subdivision of the reactants

   B the temperature at which the reaction takes place

   C the presence or absence of a catalyst

   D the time to reach a state of equilibrium.

4. How many moles of $Sn^{4+}(aq)$ ions would be produced by the oxidation of excess $Sn^{2+}(aq)$ ions by 1 mole of acidified potassium permanganate solution?

   A 0·5

   B 2·0

   C 2·5

   D 5·0

5. Dilute sulphuric acid is electrolysed using platinum electrodes. How many litres of gas, corrected to s.t.p., are produced at the positive electrode after the passage of one faraday of electricity?

   A 5·6

   B 11·2

   C 22·4

   D 44·8

6. A mixture of 1 volume of propane and 8 volumes of oxygen is sparked in a closed tube. The equation for the reaction occurring is

$$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$$

What is the molar ratio of the remaining gases at 100 °C after the reaction has taken place?

	Propane	Oxygen	Carbon Dioxide	Steam
A	0	0	3	4
B	0	0	3	0
C	0	3	3	4
D	1	5	3	4

7. Which of the following are emitted during the radioactive decay of $^{238}_{92}U$ to $^{206}_{82}Pb$?

   A 6 alpha and 8 beta particles

   B 8 alpha and 2 beta particles

   C 8 alpha and 6 beta particles

   D 10 alpha and 8 beta particles

8. The reaction $P + Q \rightarrow R + S$ is endothermic. Which one of the following situations would most favour the production of R and S?

   A $P(g) + Q(g) \rightarrow R(l) + S(l)$

   B $P(g) + Q(s) \rightarrow R(s) + S(g)$

   C $P(s) + Q(s) \rightarrow R(s) + S(l)$

   D $P(s) + Q(l) \rightarrow R(g) + S(g)$

9. For a reaction

$$\triangle H = +17{\cdot}6 \text{ kJ mol}^{-1}$$
$$\text{and } \triangle S = +77{\cdot}0 \text{ J K}^{-1} \text{ mol}^{-1}$$

This reaction will

   A never be thermodynamically feasible

   B be thermodynamically feasible at all temperatures

   C be thermodynamically feasible below some definite temperature

   D be thermodynamically feasible above some definite temperature.

10. Which of the following reactions has the **lowest** activation energy?

A $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$

B $2CO(g) + O_2(g) \rightarrow 2CO_2(g)$

C $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$

D $2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$

11. Which of the following reactions is most likely to exhibit a decrease in entropy?

A Combustion of an alkane

B Dissolution of an electrovalent solid

C Dilution of an acid

D Polymerisation of an alkene

12. The energy of a quantum of electromagnetic radiation is directly proportional to

A the frequency of the radiation

B the wavelength of the radiation

C the velocity of the radiation

D the reciprocal of the wave number.

13. In a mass spectrum which of the following would give a line at the same place as $[^{29}Si^1H_3]^{2+}$?

A $[^{16}O_2]^+$

B $[^{14}N^1H_2]^+$

C $[^{14}C^1H_2]^{2+}$

D $[^7Li^1H]^{2+}$

14. If in a 0·1 M solution of a monoprotic acid 1 % of the acid molecules dissociate, the pH of the solution is

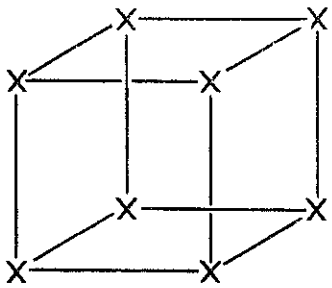
A 1

B 2

C 3

D 4.

15. The element X exists as X≡X or as X_8 with the following cubic structure



The X—X bond dissociation energy is 163 kJ mol^{-1}.

The X≡X bond dissociation energy is 944 kJ mol^{-1}.

Which of the following is the value of $\triangle H$ for the reaction $X_8 \rightarrow 4X_2$?

A -1820 kJ mol^{-1}

B $+1820$ kJ mol^{-1}

C -2472 kJ mol^{-1}

D $+2472$ kJ mol^{-1}

16. What is the likely structure of an antimony(V) chloride molecule?

A Linear

B Tetrahedral

C Trigonal bipyramidal

D Octahedral

17. In liquid argon the atoms are held together mainly by

A covalent bonding

B ionic bonding

C metallic bonding

D van der Waals forces.

[Turn over

18. Two half-cells are connected by a salt bridge. In the first half-cell metal X is in a 1·0 M solution of X^{3+} ions. In the second half-cell Cu is in a 1·0 M solution of Cu^{2+} ions.

The E° values are as follows:

$X^{3+}(aq) + 3e \rightarrow X(s)$ $\quad E° = -1{\cdot}70$ V
$Cu^{2+}(aq) + 2e \rightarrow Cu(s)$ $\quad E° = +0{\cdot}34$ V

In the reaction taking place when X and Cu are joined by a wire, which of the following is oxidised?

A X(s)

B $X^{3+}(aq)$

C Cu(s)

D $Cu^{2+}(aq)$

19. In the equilibrium $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ the forward reaction is endothermic. Which one of the following causes an increase in the value of the equilibrium constant?

A An increase of pressure

B The removal of NO_2

C An increase of temperature

D A decrease of temperature

20. Which of the following changes will be associated with the largest positive $\triangle G°$ value?

Appropriate E° values are given as follows

$Sn^{4+} + 2e \rightarrow Sn^{2+}$ $\quad E° = +0{\cdot}15$ V
$PbO_2 + 4H^+ + 2e \rightarrow Pb^{2+} + 2H_2O$ $\quad E° = +1{\cdot}7$ V

A $Sn(II) \rightarrow Sn(IV)$

B $Sn(IV) \rightarrow Sn(II)$

C $Pb(II) \rightarrow Pb(IV)$

D $Pb(IV) \rightarrow Pb(II)$

21. The electron distributions for two uncharged atoms X and Y are as follows:

X $1s^2 2s^2 2p^6 3s^1$

Y $1s^2 2s^2 2p^6 4s^1$

Which of the following statements is true?

A Energy is absorbed in changing Y to X.

B Atom Y will ionise more readily than X.

C Atom X is in an excited state.

D Both atoms have vacant 2d orbitals.

22. From the equation and statement about $\triangle H$ for the equilibrium reaction

$$H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$$

(for the forward reaction $\triangle H = -180$ kJ mol^{-1}) it can be deduced that the forward reaction

A is endothermic

B is a chain reaction

C is unaffected by pressure change

D has a high activation energy.

23. Consider the reaction

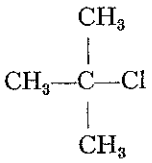
$$C_2H_5OH + CH_3COOH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

When 1 mole ethanol and 1 mole ethanoic acid are mixed, it is found that, at equilibrium, the mixture contains 0·67 mole ethyl ethanoate and 0·67 mole water.

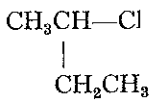
Which of the following, when mixed, would result in the same concentrations at equilibrium as those obtained above?

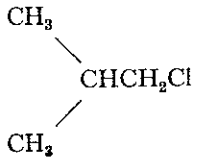
	Moles of ethanol	Moles of ethanoic acid	Moles of ethyl ethanoate	Moles of water
A	0	0	0·67	0·67
B	0	0	1·00	1·00
C	0·33	0·33	1·00	1·00
D	0·67	0·67	0	0

24. Which one of the following compounds most readily undergoes substitutions by an S_N1 mechanism?

A 

B $CH_3CH_2CH_2CH_2Cl$

C 

D 

25. A compound C_3H_8O is almost insoluble in water. It is also unaffected by sodium metal and does not react with hot copper(II) oxide. It is likely to be an

A alcohol

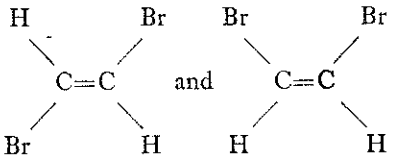
B ether

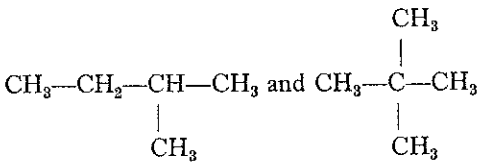
C aldehyde

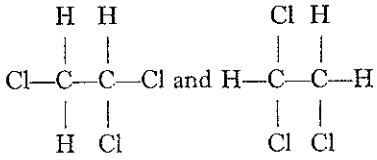
D acid.

26. Which of the following have the same physical and chemical properties?

A $CH_2{=}CH{-}CH_2{-}CH_3$ and $CH_3{-}CH{=}CH{-}CH_3$

B  and

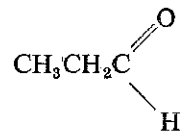
C 

D 

27. When 0·5 mole of organic compound X was dissolved in a suitable solvent and reacted with hydrogen in the presence of a nickel catalyst, 22·4 litres of hydrogen at s.t.p. were required for complete reaction.

Which of the following is X?

A $CH_3CH{=}CHCH_2OH$

B 

C $CH{\equiv}CCH_2CH{=}CH_2$

D $CH_3C{\equiv}CH$

28. A solid compound, C_2H_8NCl, reacted with sodium hydroxide solution. The gas evolved was bubbled into water.

The resulting solution

(i) had a pH value greater than 7,

(ii) gave a blue precipitate with copper(II) sulphate solution.

Which of the following gases is most likely to have been liberated from C_2H_8NCl?

A Ammonia

B Methylamine

C Ethylamine

D Nitrogen

29. Propanal and ethyl magnesium iodide, when allowed to react together, give a product which, on hydrolysis, yields

A pentan-1-ol

B pentan-2-ol

C pentan-3-ol

D 2-methylbutan-2-ol.

30. Which one of the following substances would give an acid solution in water?

A $CH_3COO^-Na^+$

B $CH_3NH_3^+NO_3^-$

C $(CH_3)_2NH$

D $(CH_3)_2CO$

31. If equal volumes of equimolar solutions of the following pairs of substances were mixed, which pair would constitute a buffer solution?

A Ammonia and methylamine

B Hydrochloric acid and sodium chloride

C Hydrochloric acid and sodium hydroxide

D Ammonia and ammonium chloride

[Turn over

32. Approximate values for the dissociation constants, K_a, of three acids are given below.

3-chloropropanoic acid	$= 1{\cdot}0 \times 10^{-4}$
ethanoic acid	$= 1{\cdot}8 \times 10^{-5}$
hydrocyanic acid	$= 4{\cdot}9 \times 10^{-10}$

From this information it can be said that

A in 0·01 M solutions hydrocyanic acid is ionised to a greater extent than is ethanoic acid

B in 0·01 M solutions 3-chloropropanoic acid is likely to be the poorest conductor of electricity of the three

C hydrocyanic acid is the weakest acid of the three

D in 0·01 M solutions the pH value of all three acids is less than 3.

33. Why is it not practicable to find the concentration of a solution of propanoic acid by titration with standard methylamine solution?

A The salt of the above acid and alkali is subject to hydrolysis by water.

B The pH change at the end-point is small.

C An insoluble salt is formed.

D An organic base neutralises an organic acid very slowly.

34. Each of the following compounds contains a complex ion.

Which one of the compounds will have the highest electrical conductivity when equimolar solutions of them are compared?

(Assume that in each complex ion the central transition metal ion has six ligands attached to it.)

A K_2PtCl_6

B $Co(NH_3)_6Cl_3$

C $Cr(NH_3)_4Cl_3$

D $Pt(NH_3)_6Cl_4$

35. Which one of the following would **not** act as a ligand in the formation of a complex with a transition metal ion?

A CN^-

B NH_4^+

C NH_3

D $NH_2CH_2CH_2NH_2$

36. In which of the following is the metal in the +1 oxidation state?

A MnO_4^-

B $[Ni(CN)_3]^{2-}$

C $[V(NH_3)_6]^{5+}$

D $[Cr(H_2O)_5Cl]^{2+}$

37. Which of the following ions is most paramagnetic in a weak ligand field?

A Ti^{3+}

B Co^{2+}

C Mn^{2+}

D Ni^{2+}

To answer questions 38 to 40 use the following code.

If all the responses 1, 2 and 3 are correct, select A.

If only 1 and 2 are correct, select B.

If only 3 is correct, select C.

If none of the responses, or if some other response, or if some other combination of responses, is correct, select D.

38. The following are statements about the properties of the Group IV elements.

1 The elements form stable alkyl derivatives whose molecules have tetrahedrally arranged bonds.

2 The tendency of the elements to form chain compounds decreases rapidly as we go down the group.

3 The metallic character of the elements decreases as we go down the group.

39. The atomic emission spectrum of hydrogen can be used to determine

1 the ionisation energy of hydrogen

2 the quanta of radiation emitted by excited electrons as they fall to lower levels

3 the bond vibrational energy of a hydrogen molecule.

40. A change in the nature of a ligand round a transition metal ion may result in a change in

1 colour

2 degree of paramagnetism

3 the charge on the complex ion.

[END OF QUESTION PAPER]

Marks

1. Copy the table into your answer book and complete it, showing the signs (positive or negative) of ΔH and ΔS for the processes given.

Process	*Sign of* ΔH	*Sign of* ΔS
Combustion of carbon		
Evaporation of ether		
Formation of snow flakes		

(3)

2. The table shows the values of ΔG° (for the forward reaction) for the two equilibria Ⓐ and Ⓑ at temperatures 200 K and 500 K.

	ΔG° (kJ mol^{-1})	
	At 200 K	At 500 K
Ⓐ $\frac{1}{2} I_2 + \frac{1}{2} Cl_2 \rightleftharpoons ICl$	+ 2	−21
Ⓑ $\frac{1}{2} I_2 + \frac{3}{2} Cl_2 \rightleftharpoons ICl_3$	−44	+22

(*a*) (i) Use the graph paper provided.

(ii) Draw a vertical axis, and choosing a suitable scale (after reading (iv) and (v) below), label it 'Standard free energy change, ΔG°, (kJ mol^{-1})'.

(iii) Draw a horizontal axis, and choosing a suitable scale (again after reading (iv) and (v) below), label it 'Temperature (K)'.

(iv) Using the data in the table, draw a straight line to show the change in ΔG° with temperature for equilibrium Ⓐ. Label it Ⓐ.

(v) Now repeat procedure (iv) for equilibrium Ⓑ using the same vertical and horizontal axes. Label this line Ⓑ. **2**

(*b*) Using your answer to (*a*)

(i) state which compound's formation is the more favoured thermodynamically at 250 K. Explain your answer. **2**

(ii) state at what temperature the formation of the other compound becomes more favoured. Explain your answer. **2**

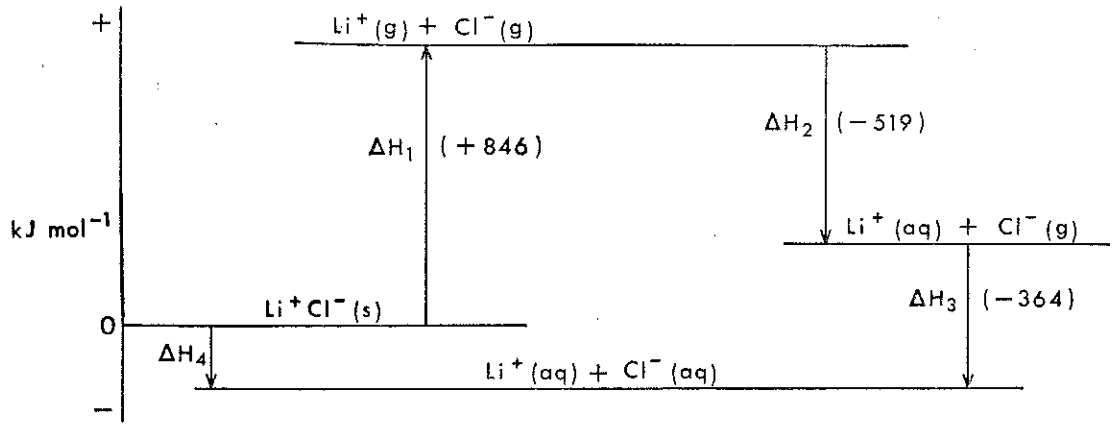
(*c*) Explain the effect upon the quantities of $I_2(s)$ and $ICl_3(s)$ present in the equilibrium Ⓑ at 300 K if the pressure of chlorine gas is increased. **2**

(8)

Marks

3. The diagram shows the enthalpy changes (in kJ mol^{-1}) at 298 K and 1 atmosphere pressure for the dissolution of lithium chloride in water.

The diagram is **not** drawn to exact scale.



(*a*) Name the enthalpy changes ΔH_1, ΔH_2, ΔH_3 and ΔH_4. **2**

(*b*) Calculate the value of ΔH_4 in the diagram. **1**

(*c*) For the dissolution of silver chloride in water under the same conditions, $\Delta H_1 = +905$ kJ mol^{-1}, and $\Delta H_2 = -464$ kJ mol^{-1}. Calculate the value of ΔH_4 for silver chloride. **1**

(4)

4. Answer **EITHER A OR B.**

A. A sample of potassium bromide contains potassium chloride as an impurity. 1·00 g of the salt is dissolved in water and the solution is made up to 100 cm^3 with water.

20 cm^3 of this solution is titrated with 0·10 M silver nitrate solution. 17·3 cm^3 of this silver nitrate solution is required to completely precipitate the mixed salt as follows:

$$Ag^+(aq) + Br^-(aq) \rightarrow Ag^+Br^-(s)$$
$$Ag^+(aq) + Cl^-(aq) \rightarrow Ag^+Cl^-(s)$$

The remaining 80 cm^3 of the original solution is warmed with dilute nitric acid. The bromide ions present are in this way oxidised to bromine, which is liberated as a vapour. The volume remains at 80 cm^3.

20 cm^3 of the solution, now containing no bromide ions, is titrated with 0·010 M silver nitrate solution. 25·8 cm^3 of this silver nitrate solution is required to completely precipitate the remaining chloride as follows:—

$$Ag^+(aq) + Cl^-(aq) \rightarrow Ag^+Cl^-(s)$$

(*a*) Calculate

(i) the number of moles of halide ions in 20 cm^3 of solution;

(ii) the number of moles of chloride ions in 20 cm^3 of solution. **2**

(*b*) Hence calculate the number of moles of bromide ions in 100 cm^3 of the original solution. **2**

(*c*) Calculate from your answer in (*b*)

(i) the mass of potassium bromide in the original 1·00 g sample,

hence (ii) the percentage purity of the sample. **3**

(7)

[Turn over

Marks

OR

B. Copper pyrites ore has a composition represented by the formula $CuFeS_2$. Insoluble silicate material may be present in the ore as impurity. 2·00 g of a sample of ore is treated with nitric and sulphuric acids to dissolve the copper and iron compounds; and the insoluble silicate material is filtered off. The dissolved copper is then separated from the dissolved iron by precipitation as copper(II) sulphide, and redissolved in acid to give 100 cm^3 of a solution containing copper ions. This solution is then analysed volumetrically as follows.

Excess potassium iodide solution is added to 20 cm^3 of the solution. This precipitates the copper as copper(I) iodide, and liberates iodine as follows.

$$2\ Cu^{2+}(aq) + 4\ I^-(aq) \rightarrow 2\ CuI(s) + I_2(aq)$$

The liberated iodine is titrated with 0·10 M sodium thiosulphate solution. The equation for this is:

$$2\ S_2O_3^{2-}(aq) + I_2(aq) \rightarrow S_4O_6^{2-}(aq) + 2\ I^-(aq)$$

18·3 cm^3 of the thiosulphate solution are required for complete reaction.

(*a*) Calculate, from the result of this titration, the number of moles of iodine molecules (I_2) liberated. **2**

(*b*) Hence calculate the number of moles of copper(II) ions present in 100 cm^3 of the solution formed on redissolving the copper(II) sulphide. **2**

(*c*) Calculate, from your answer to (*b*),

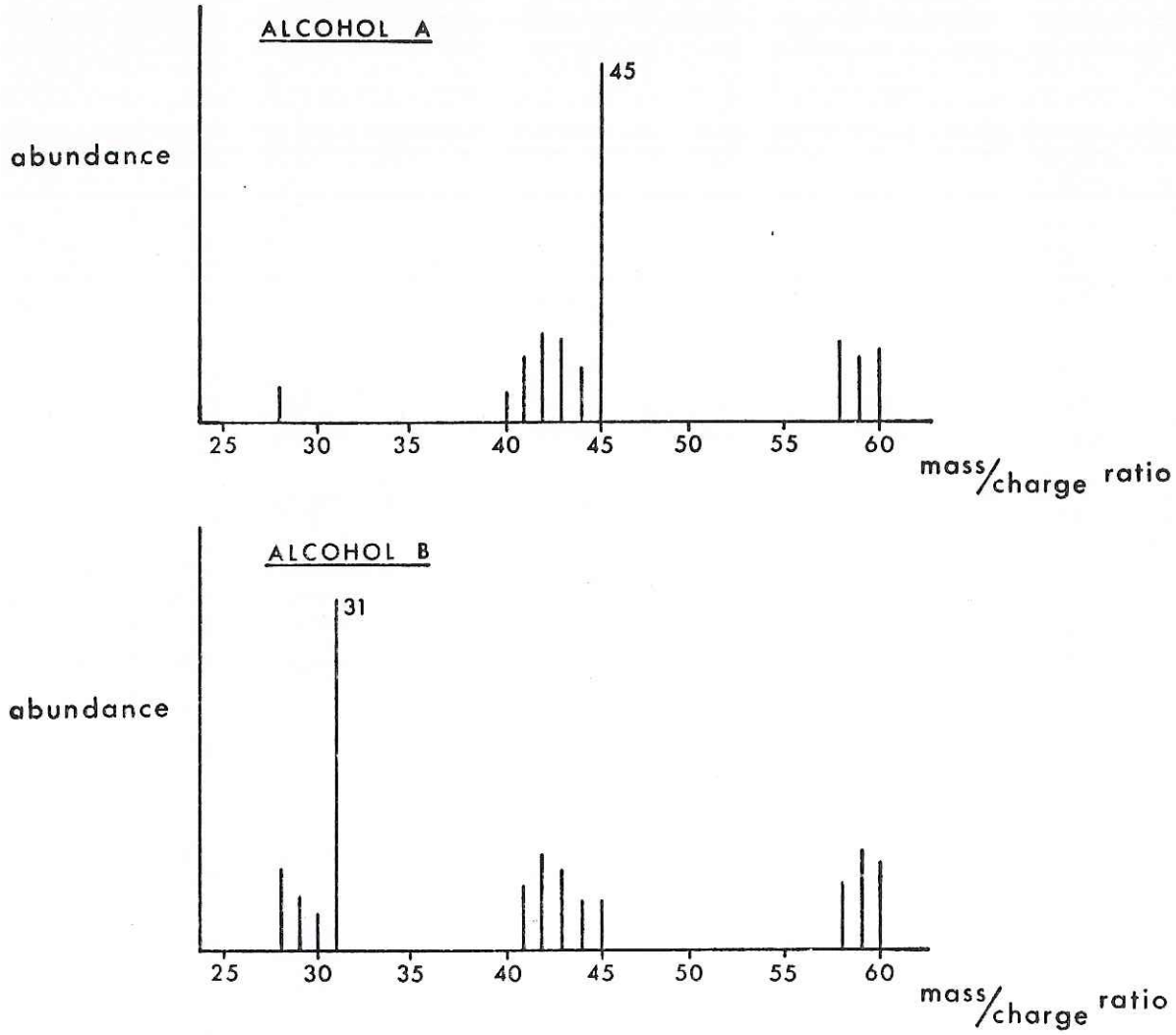
(i) the mass of copper pyrites ($CuFeS_2$) in the 2·00 g sample of ore, and hence

(ii) the percentage purity of the sample. **3**

(7)

Marks

5. The mass spectra of two isomeric alcohols, A and B, are given below.



(*a*) Draw the extended structural formulae of the two alcohols which have molecular ion peaks at 60. **2**

(*b*) Which formula corresponds to alcohol A, and which to alcohol B?
Explain your answers. **3**

(5)

[Turn over

Marks

Answer **EITHER A OR B.**

A. Electronegativity values are given on page 29 of the Data Book.

(*a*) What is meant by electronegativity? **1**

(*b*) Draw molecules of ammonia (NH_3), phosphine (PH_3) and phosphorus(V) chloride (PCl_5), clearly showing their molecular shapes and bond polarities. **3**

(*c*) Why is phosphine a much weaker base than ammonia? **1**

(5)

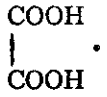
OR

B. (*a*) Solutions of Fe^{3+} and Fe^{2+} ions in water are acidic.

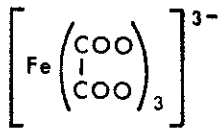
(i) Taking Fe^{3+} as an example, explain how this acidity arises. **2**

(ii) Why are solutions of Fe^{2+} less acidic than those of Fe^{3+}? **1**

(*b*) Rust stains can be removed from clothing by treatment with ethanedioic acid (oxalic acid) whose formula is



The ethanedioate ions react with the Fe^{3+} ions forming the complex ion



Using  to represent an ethanedioate ion, draw a diagram of the complex ion to show its three-dimensional arrangement. **2**

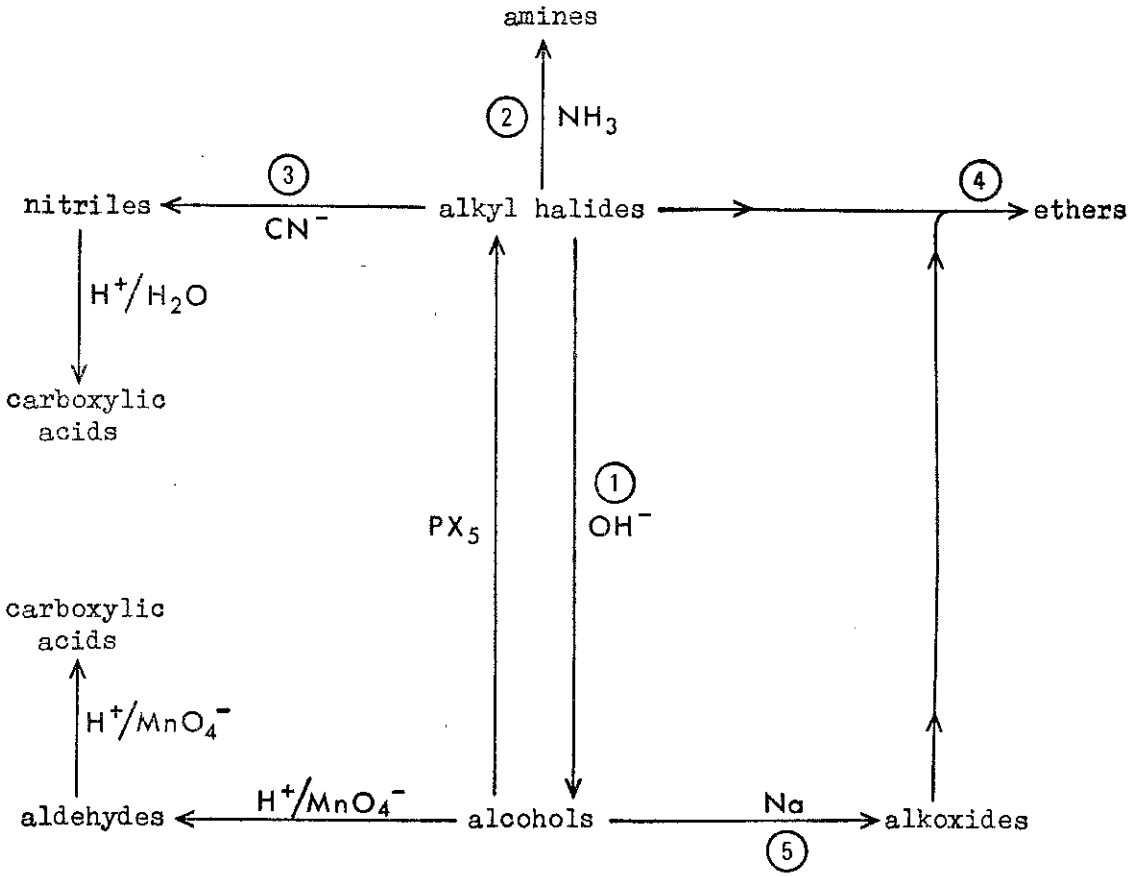
(5)

7. Cadmium forms the compound CdO. It is also possible to prepare a second substance whose formula, by analysis, is Cd_2O. Outline how X-ray powder diffraction could be used to determine whether this second substance is a compound or a physical mixture of Cd and CdO. **(2)**

Marks

8. Answer **EITHER A OR B.**

A.



(*a*) **Explain** why alkyl halides can take part **in** reactions of the types shown in ①, ②, ③ and ④. **1**

(*b*) Write the equation for the formation of methoxyethane (ethyl methyl ether) from chloroethane and a suitable alkoxide (see reactions ④ and ⑤). **2**

(*c*) Which route would you choose to make a carboxylic acid from butan-2-ol? Give reasons for your choice. **2**

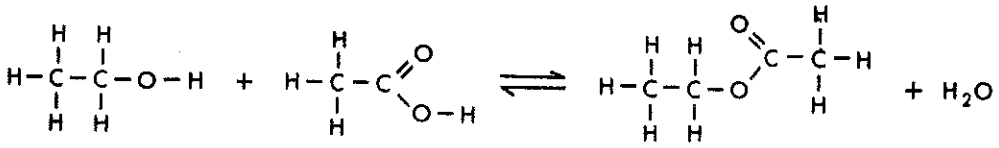
(*d*) Attempts to prepare 2-methylpropan-2-ol from a suitable alkyl halide by reaction ① give poor yields. Suggest another way by which this alcohol can be prepared from an alkyl halide, but **not** involving any of the routes in the above diagram. **2**

(7)

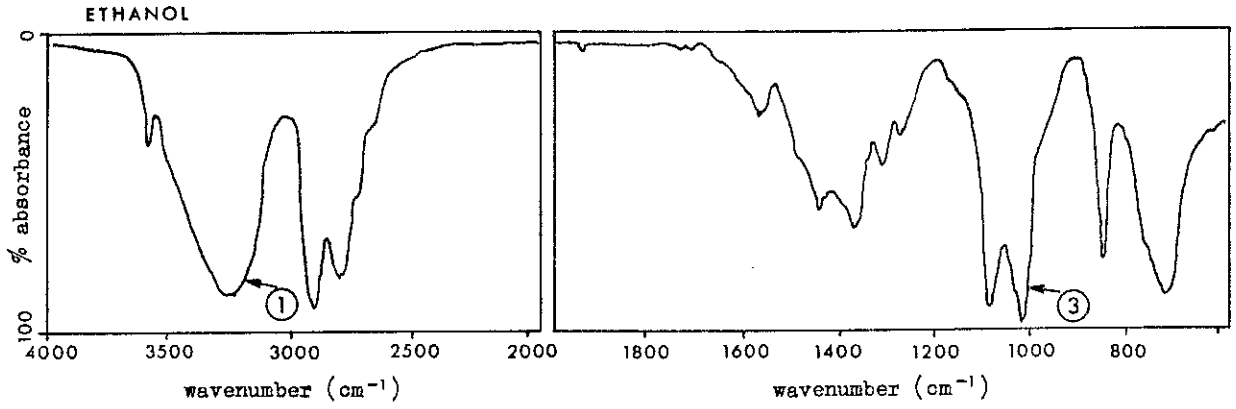
[Turn over

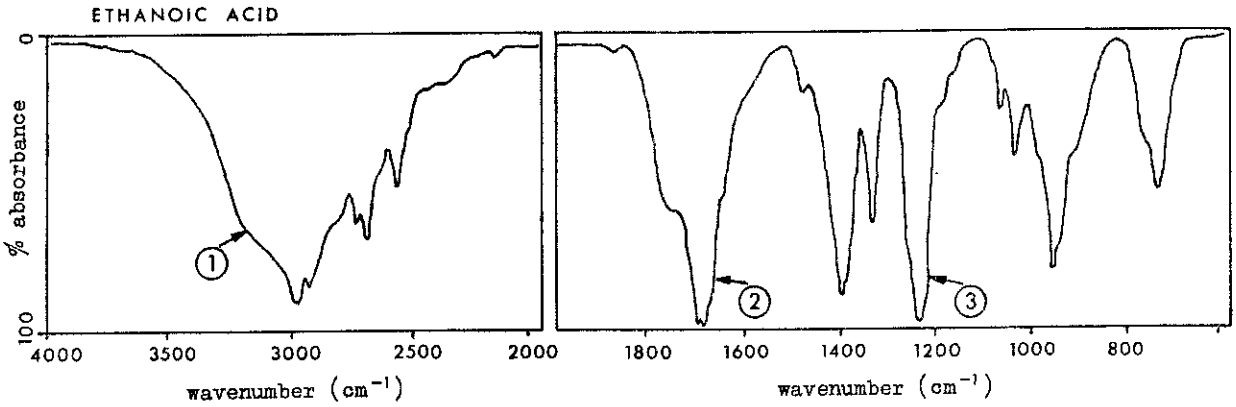
OR

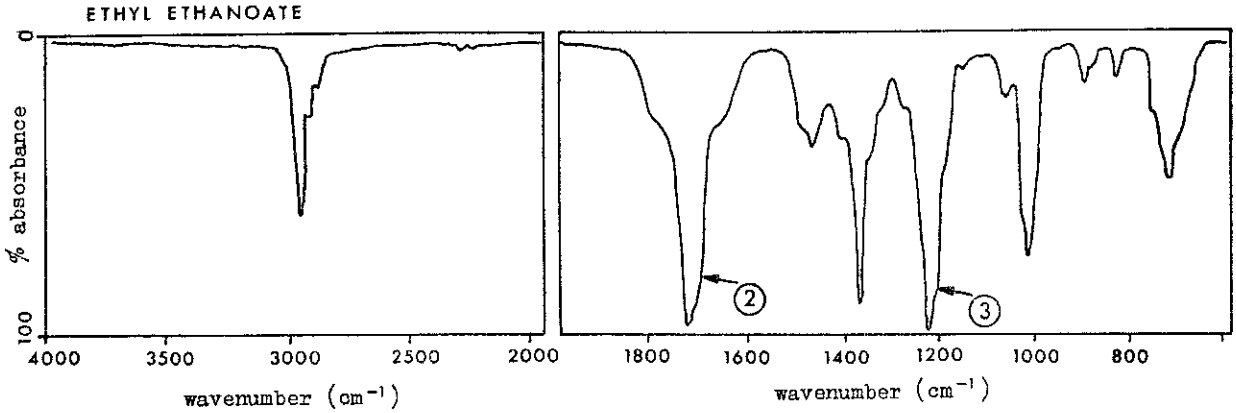
B. The formation of ethyl ethanoate is examined using infra-red spectroscopy.



The infra-red spectra of ethanol, ethanoic acid and ethyl ethanoate are given below.







Marks

(*a*) A broad absorption ① occurs in the spectra of ethanol and ethanoic acid, but not in that of ethyl ethanoate. Which bond gives rise to this absorption? **1**

(*b*) (i) Which bond gives rise to the strong absorption ②, occurring in the spectra of ethanoic acid and ethyl ethanoate? **1**

(ii) Which bond gives rise to the strong absorption ③, occurring in the spectra of all three compounds? This absorption is not present in the spectra of hydrocarbons. **1**

(*c*) To encourage the formation of the ester, water is removed continuously from the reaction mixture. Samples of the reaction mixture taken periodically are examined in an infra-red spectrometer. How is it possible to follow the progress of the reaction from the spectra so obtained? **2**

(*d*) How might infra-red spectroscopy be used to

(i) follow the oxidation of ethanol to ethanoic acid?

(ii) analyse propanone for the presence of water? **2**

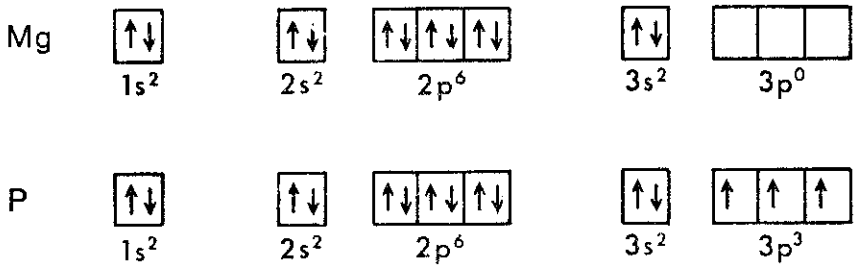
(7)

9. (*a*) What is meant by

(i) the Principal Quantum Number of an electron;

(ii) degenerate orbitals? **2**

(*b*) The electron configurations of magnesium and phosphorus are respectively



In a magnesium atom the two electrons in the third level occupy the same orbital, whereas in a phosphorus atom the three electrons in the 3p orbitals occupy separate orbitals. Account for this difference. **2**

(4)

[Turn over

Marks

10. Titration of 15 cm^3 of 0·40 M phosphoric acid with potassium hydroxide solution.

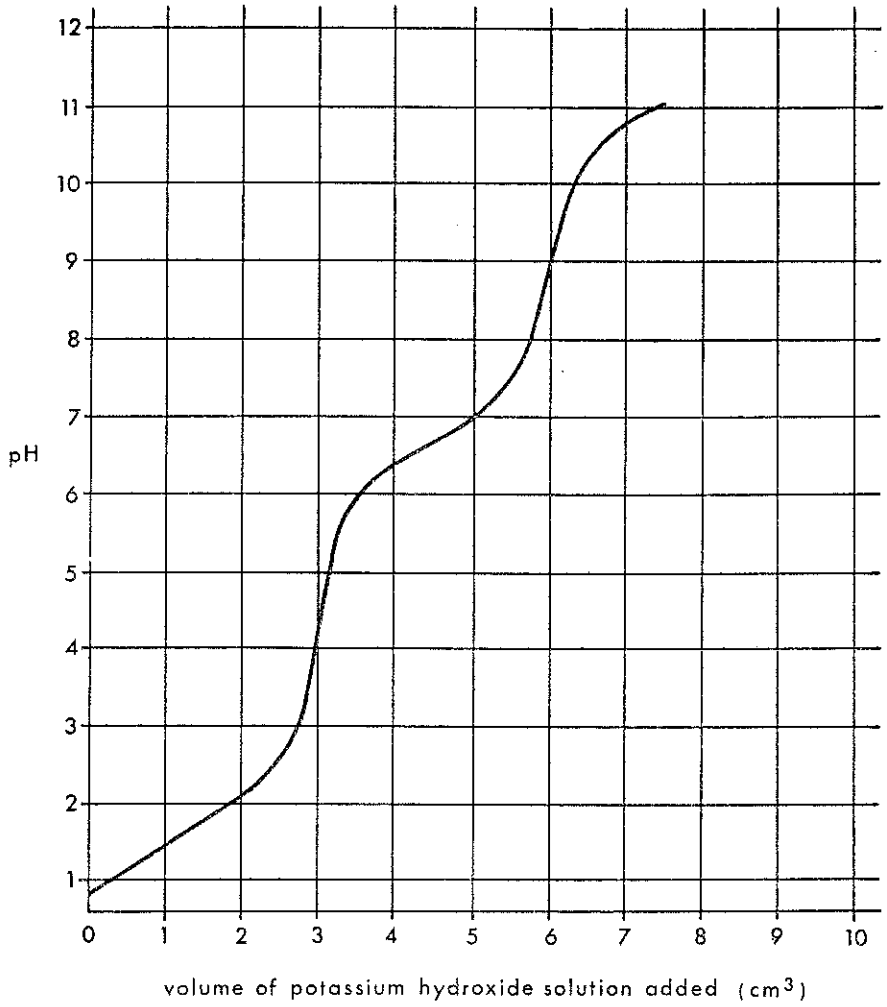


Table of data for pH indicators.

Indicator	*Range for indicator (pH)*	*Colour change*
Thymol blue	1·2 to 2·8	Red to Yellow
Bromophenol blue	3·4 to 4·6	Yellow to Blue
Bromocresol purple	5·2 to 6·8	Yellow to Purple
Bromothymol blue	6·0 to 7·6	Yellow to Blue
Phenolphthalein	8·4 to 9·4	Colourless to Red
Alizarin yellow	10·2 to 12·0	Yellow to Orange

The graph shows the changes in pH when a 15 cm^3 sample of 0·40 M phosphoric acid (H_3PO_4, a triprotic acid) is **partially** titrated using potassium hydroxide solution.
The table gives a list of common indicators, the pH range over which each changes colour, and the colour involved.

(*a*) With the help of the data in the table, select two indicators which could be added together to the sample of phosphoric acid to indicate when

(i) the first, and

(ii) the second stage of titration is complete.

Justify your selection of indicators, and list the expected colours of the solution at different pH values during the titration. **4**

(*b*) Predict the volume of potassium hydroxide solution required to complete all three stages of titration of the sample of phosphoric acid solution. **1**

(*c*) Calculate the molarity of the potassium hydroxide solution. **2**

(7)

Marks

11. Answer **EITHER A OR B.**

A.

	Mean bond energy (kJ mol^{-1})
Cl-Cl	243
Br-Br	194

Use the data to explain why the photobromination of butane will proceed in artificial light, whereas the photochlorination of butane needs daylight or ultraviolet light. **(3)**

OR

B. Silicon carbide (SiC) has a melting point of approximately 3000 K and is very hard. Suggest in words, or by a diagram, a likely structure for silicon carbide, and account for its hardness and high melting point. **(3)**

12. Chromium(II) sulphate is isomorphous with vanadium(II) and iron(II) sulphates.

(*a*) What is meant by isomorphous? **1**

(*b*) What property of these transition metals gives rise to isomorphism in their sulphates? Explain how this property arises. **3**

(4)

13. Chromium(VI) oxide (CrO_3) has a melting point of 469 K. It dissolves in water readily and it reacts with alkalis according to the equation

$$CrO_3(s) + 2\ OH^-(aq) \rightarrow CrO_4^{2-}(aq) + H_2O$$

The yellow CrO_4^{2-} ion and the orange $Cr_2O_7^{2-}$ ion are both powerful oxidising agents. In solution these ions exist together in equilibrium.

$$2\ CrO_4^{2-}(aq) + 2\ H^+(aq) \rightleftharpoons Cr_2O_7^{2-}(aq) + H_2O$$

(*a*) What can be inferred about the type of bonding in CrO_3? **1**

(*b*) What is the oxidation state of chromium in CrO_4^{2-} and $Cr_2O_7^{2-}$? **1**

(*c*) Why are these ions powerful oxidising agents? **1**

(*d*) Why should solutions of CrO_4^{2-} ions turn orange at low pH? **1**

(4)

[Turn over

Marks

14. (*a*)

Complex ion	*Wavelength of maximum absorption (nm)*
A $[Cu(H_2O)_6]^{2+}$	790
B $[Cu(NH_3)(H_2O)_5]^{2+}$	730
C $[Cu(NH_3)_2(H_2O)_4]^{2+}$	670
D $[Cu(NH_3)_3(H_2O)_3]^{2+}$	610
E $[Cu(NH_3)_4(H_2O)_2]^{2+}$	570

The table gives the position of maximum absorption in the visible region of the spectrum for a series of complex ions as the water molecules are replaced progressively as ligands by ammonia molecules. During this replacement the colour changes progressively from blue in A to a deep blue/violet in E.

(i) What happens to these ions when they absorb light? **1**

(ii) Why are these ions coloured? **1**

(iii) Why does the absorption maximum move to shorter wavelengths as the water ligands are replaced by ammonia ligands? **2**

(iv) Name a ligand which could be substituted for the ligands in A to shift the absorption maximum to longer wavelengths? **1**

(*b*) Why is the complex ion $[Cu(CN)_4]^{2-}$ colourless? **1**

(*c*) $VO_2^+(aq) \rightarrow VO^{2+}(aq) \rightarrow [V(H_2O)_6]^{3+}(aq) \rightarrow [V(H_2O)_6]^{2+}(aq)$
colourless blue green violet

The basis of the colour changes above is not merely ligand replacement. What other difference between the above ions could account for their differences in colour? **1**

(7)

15. Write an essay on **ONE** of the following topics. Each topic has a number of sub-headings which may help you to answer the question. These sub-headings are suggestions only and there is no need to adopt them unless you so wish. The Data Book may be a useful additional source of information.

The examiners will assess the essay for scientific content, organisation, presentation and English usage.

A. Analytical Methods in Chemistry.
Possible sub-headings:
Chemical methods;
Physical methods;
Advantages and limitations of each method;
Applications of these methods.

OR

B. Theories of Bonding.
Possible sub-headings:
The electronic theory of bonding;
Bond energies;
Intermolecular bonding;
Stereochemistry (molecular shapes and ionic lattices);
Experimental evidence in support of these theories.

OR

C. Factors Controlling Chemical Reactions.
Possible sub-headings:
Thermodynamic factors;
Kinetic factors. **(10)**

[END OF QUESTION PAPER]