X012/701

CHEMISTRY
ADVANCED HIGHER

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

SECTION A – 40 marks

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

SECTION B – 60 marks

All questions should be attempted.

Read carefully

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

2 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.

3 If any of this information is wrong, tell the Invigilator immediately.

4 If this information is correct, **print** your name and seat number in the boxes provided.

5 Use **black** or **blue ink** for your answers. **Do not use red ink**.

6 The answer to each question is **either** A, B, C or D. Decide what your answer is, then 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   fractional distillation

B   chromatography

C   fractional crystallisation

D   filtration.

The correct answer is **B**—chromatography. The answer **B** has been clearly marked with a horizontal line (see below).
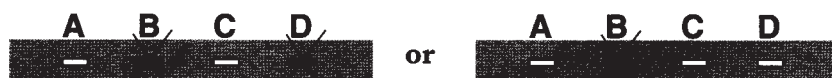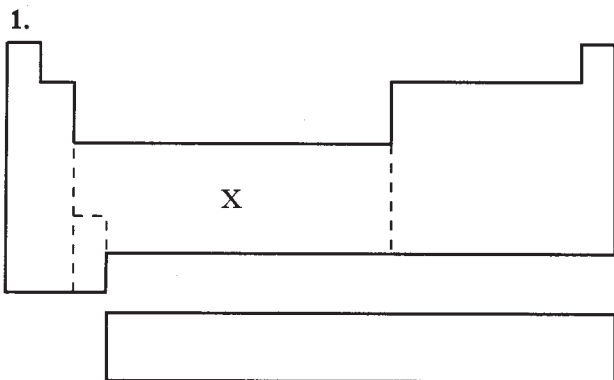

Changing an answer

If you decide to change your answer, cancel your first answer by putting a cross through it (see below) and fill in the answer you want. The answer below has been changed to **B**.

If you then decide to change back to an answer you have already scored out, put a tick (✓) to the **right** of the answer you want, as shown below:
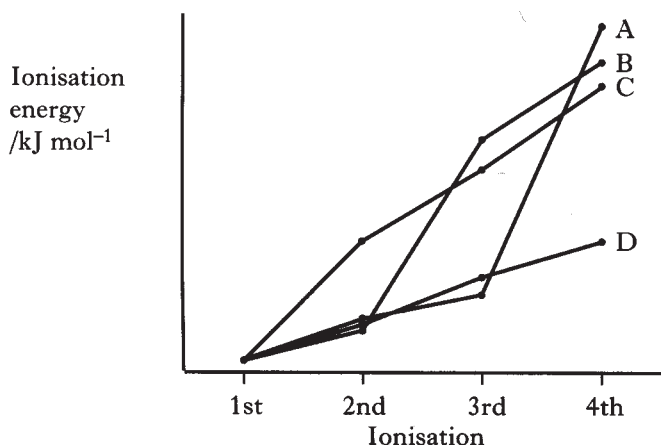
1.

In the Periodic Table outlined above, one area is marked "X". Moving across area "X", from one element to the next, the extra electron usually occupies an orbital of type

A   s

B   p

C   d

D   f.

2. Which of the following graphs represents the trend in successive ionisation energies of a Group 3 element?

3. Which of the diagrams below correctly represents the distribution of electrons in the outer orbitals of an atom in its ground state?

4. Neon gas discharge lamps produce a red glow because electrons in neon atoms are

A   absorbing radiation from the blue end of the visible spectrum

B   emitting radiation from the red end of the visible spectrum

C   emitting radiation from the blue end of the visible spectrum

D   absorbing radiation from the red end of the visible spectrum.

5. In the emission line spectrum of hydrogen, there are many lines. How many of these lines are caused by all the possible electron transitions between the four lowest energy levels of the hydrogen atom?

A   3

B   4

C   6

D   10

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

A   wavelength of radiation absorbed

B   frequency of radiation absorbed

C   intensity of radiation absorbed

D   intensity of radiation emitted.

7. Which of the following representations is the least likely resonance structure for a carbonate ion?
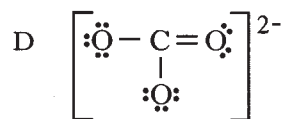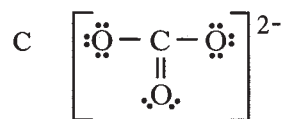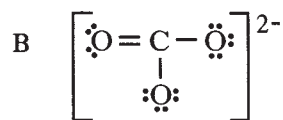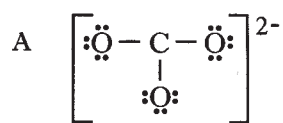
8. Which of the following compounds is likely to show the least ionic character?

A KCl

B CaO

C BH_3

D PH_3

9. What is the change in the three-dimensional arrangement of the bonds round the P atom in the following reaction?

$$PF_5 \rightarrow PF_3 + F_2$$

A Trigonal bipyramidal to trigonal planar

B Tetrahedral to pyramidal

C Octahedral to trigonal planar

D Trigonal bipyramidal to pyramidal

10. 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 because caesium and sodium have different

A electronegativities

B ionic radii

C electrode potentials

D ionisation energies.

11. Which of the following would be most useful as a reagent in the gravimetric analysis of silver?

A Sodium nitrate

B Barium carbonate

C Potassium sulphate

D Ammonium chloride

12. What volume of **water** needs to be added to $25\,cm^3$ of $0 \cdot 2\,mol\,l^{-1}$ calcium chloride solution to produce a solution with a **chloride** ion concentration of $0 \cdot 1\,mol\,l^{-1}$?

A $25\,cm^3$

B $50\,cm^3$

C $75\,cm^3$

D $100\,cm^3$

13. In which of the following will an increase in pressure lead to an increase in concentration of the product(s)?

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

B $2N_2O_5(g) \rightleftharpoons 2N_2O_4(g) + O_2(g)$

C $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

D $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

14. When sulphur dioxide and oxygen react the following equilibrium is established.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$
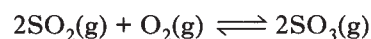
The equilibrium constant for the reaction is 3300 at 630 °C and 21 at 850 °C.

Which line in the table is correct for the reaction?

	Sign of ΔH	Product yield as the temperature increases
A	–	increases
B	–	decreases
C	+	increases
D	+	decreases

15. Which of the following statements is **not** always true for aqueous solutions at 298 K?

A $[H^+] = [OH^-] = 10^{-7}\,mol\,l^{-1}$

B $K_w = 10^{-14}$

C $[H^+]\,[OH^-] = 10^{-14}$

D $pH = -\log_{10}[H^+]$

16. Which of the following, when dissolved in distilled water, gives rise to a solution with a pH value greater than 7?

A Lithium chloride

B Potassium ethanoate

C Sodium sulphate

D Ammonium nitrate

17. Which of the following when added to aqueous NH_4Cl can produce a buffer solution?

A Ammonia

B Ethanoic acid

C Potassium chloride

D Ammonium sulphate

18. For any acid-base indicator, the colour change occurs around pH = pK_{In}. The equilibrium constant, K_{In}, of an indicator used in an acid-base titration where the pH at the end point was 5·2, is

A $6\cdot3 \times 10^{-6}$

B 0·72

C 5·2

D $1\cdot6 \times 10^{-5}$.

19. $C(s) + O_2(g) \rightarrow CO_2(g) \quad \Delta H^\circ = -394\,kJ\,mol^{-1}$

$CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g) \quad \Delta H^\circ = -284\,kJ\,mol^{-1}$

From the above data, it can be deduced that ΔH°, in $kJ\,mol^{-1}$, for the reaction

$C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g)$ is
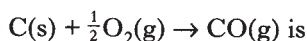
A −678

B −110

C +110

D +678.

20. Which of the following reactions will have a positive ΔS° value?

A $2H_2(g) + C_2H_2(g) \rightarrow C_2H_6(g)$

B $LiH(s) + H_2O(\ell) \rightarrow LiOH(aq) + H_2(g)$

C $Ca(OH)_2(aq) + CO_2(g) \rightarrow CaCO_3(s) + H_2O(\ell)$

D $C_2H_4(g) + Br_2(\ell) \rightarrow C_2H_4Br_2(\ell)$

21. For a reaction in dynamic equilibrium, which of the following must be correct?

A $\Delta G = 0$.

B $K = 1$.

C Activation energy of forward reaction = activation energy of reverse reaction.

D ΔH for forward reaction = ΔH for reverse reaction.

22. Tin can exist in two different forms, "white tin" and "grey tin". For the change

"white tin" $\rightarrow$ "grey tin"

$\Delta H^\circ = 2\cdot5\,kJ\,mol^{-1}$

$\Delta S^\circ = -6\cdot7\,J\,K^{-1}\,mol^{-1}$

and hence, ΔG° at 298 K, in $kJ\,mol^{-1}$, will be

A −0·5

B −4·2

C +4·5

D +9·2.

23. For a certain reaction at 298 K,
$\Delta H^\circ = +240\,kJ\,mol^{-1}$ and $\Delta G^\circ = -92\,kJ\,mol^{-1}$.

The reaction is

A endothermic and feasible

B exothermic and feasible

C endothermic and not feasible

D exothermic and not feasible.

24.
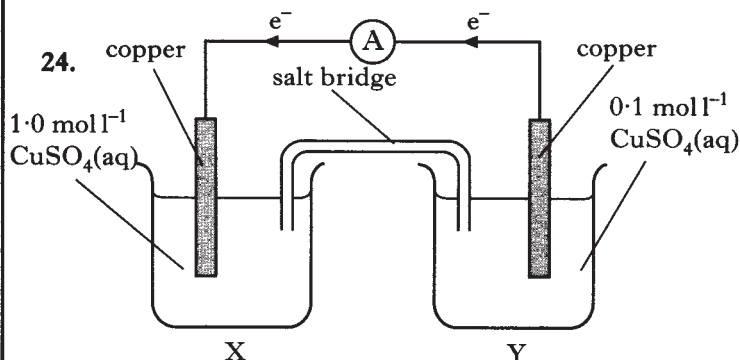
Which of the following will occur in the above cell?

A The blue colour in Y will become less intense.

B The mass of the electrode in Y will decrease.

C The concentration of the solution in X will increase.

D Electrons will flow from X to Y through the salt bridge.

[Turn over

25. Which of the following is a correct statement about a catalyst?

For a chemical reaction it

A does not alter the value of the rate constant

B alters the value of the equilibrium constant

C alters the reaction mechanism

D has no effect on the value of the activation energy.

26. The type of reaction involved in the conversion of propanoic acid into propan-1-ol is

A elimination

B substitution
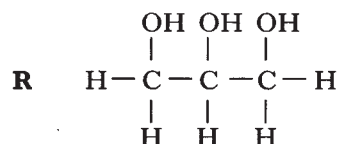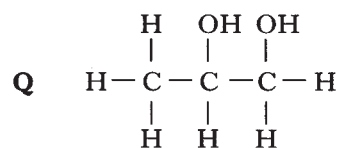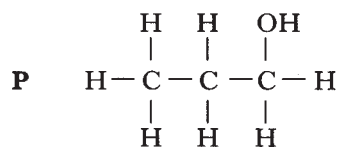
C oxidation

D reduction.

27. Which of the following represents a propagation step in a chain reaction?

A $Cl\bullet + Cl\bullet \rightarrow Cl_2$

B $Cl\bullet + CH_4 \rightarrow CH_3\bullet + HCl$

C $CH_3\bullet + Cl\bullet \rightarrow CH_3Cl$

D $Cl_2 \rightarrow Cl\bullet + Cl\bullet$

28. Which of the following molecules is likely to produce the most stable carbocation intermediate in a hydrolysis reaction?

A $(CH_3)_3CCl$

B CH_3CH_2Cl

C $CH_3CHICH_2CH_3$

D CH_3CH_2I

29. The structures of three alcohols, **P**, **Q** and **R** are shown.

P   H—C—C—C—H
      with H H OH on top, H H H on bottom

Q   H—C—C—C—H
      with H OH OH on top, H H H on bottom

R   H—C—C—C—H
      with OH OH OH on top, H H H on bottom

Which line in the table describes correctly the trends in boiling points and viscosities on moving from **P** to **Q** to **R**?

	Boiling point	Viscosity
A	increases	increases
B	increases	decreases
C	decreases	increases
D	decreases	decreases

30. Which of the following is an essential property of a solvent to be used for recrystallisation purposes?

A Insoluble in water

B A low boiling point

C Ability to dissolve more solute when hot than when cold

D Ability to dissolve more solute when cold than when hot

31. Consider

 OH in relation to C_2H_5OH

and

 NH_2 in relation to $C_2H_5NH_2$
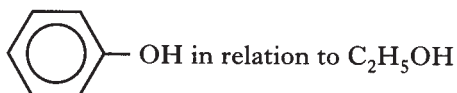
The benzene ring makes

A OH less acidic and NH_2 less basic

B OH less acidic and NH_2 more basic

C OH more acidic and NH_2 less basic

D OH more acidic and NH_2 more basic.

32. Alkenes may **not** be prepared by

A thermal cracking of alkanes

B partial hydrogenation of alkynes

C dehydration of primary alcohols
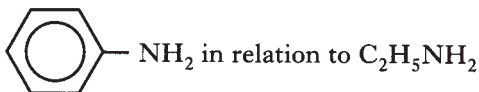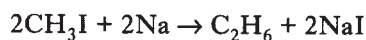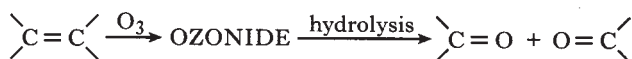
D direct synthesis from carbon and hydrogen.

33. Some alkanes may be prepared by adding an iodoalkane dropwise to sodium in a suitable solvent, eg

$$2CH_3I + 2Na \rightarrow C_2H_6 + 2NaI$$

When a mixture of iodomethane and iodoethane is used as a starting material, the product will contain

A propane only

B methane and ethane

C ethane, propane and butane

D methane, ethane, propane and butane.

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

$$\begin{array}{c} \diagdown \\ \diagup \end{array} C = C \begin{array}{c} \diagup \\ \diagdown \end{array} \xrightarrow{O_3} \text{OZONIDE} \xrightarrow{\text{hydrolysis}} \begin{array}{c} \diagdown \\ \diagup \end{array} C = O + O = C \begin{array}{c} \diagup \\ \diagdown \end{array}$$

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 $CH_3C = CH_2$
      $\quad\ \ |$
      $\quad CH_3$

D $CH_3CH = CCH_3$
      $\qquad\qquad |$
      $\qquad\quad CH_3$

35. When but-1-ene reacts with hydrogen chloride, 1-chlorobutane and 2-chlorobutane are formed. According to Markovnikov's rule

A there will be more of the 2-chlorobutane than the 1-chlorobutane

B there will be more of the 1-chlorobutane than the 2-chlorobutane

C there will be equal proportions of both products

D it is impossible to tell the relative proportion of each product.

36. Which of the following best describes the bonding in ethane?

A sp^2 hybridisation of the carbon atoms giving sigma bonds only

B sp^2 hybridisation of the carbon atoms giving sigma and pi bonds

C sp^3 hybridisation of the carbon atoms giving sigma bonds only

D sp^3 hybridisation of the carbon atoms giving sigma and pi bonds

37. A compound, **X**, reacts with the product of its own oxidation to form an ester.
X could be

A propanal

B propan–1–ol

C propan–2–ol

D propanoic acid.

38. Ethanal reacts with an alkaline solution of iodine to form a yellow solid called iodoform, CHI_3. This reaction can be repeated with any compound containing the CH_3C — group
$\qquad\qquad\qquad\qquad\qquad\quad \underset{O}{\overset{\|}{}}$

or one which can be readily oxidised to form this group. Iodoform will **not** be produced when an alkaline solution of iodine reacts with

A ethanol

B propanone

C butan-2-ol

D pentan-3-one.

[Turn over

39. An organic compound forms a cyanohydrin with HCN and can be reduced by $LiAlH_4$.

It can be said **with certainty** that the compound

A   can be oxidised to an acid

B   contains a carbonyl group

C   is an alkene

D   is an alkanone.

40.

$$CH = CHCOOH$$
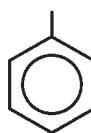
The above compound should **not** react with

A   ethanol

B   bromine water

C   copper(II) oxide

D   a mixture of concentrated nitric and sulphuric acids.

[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.
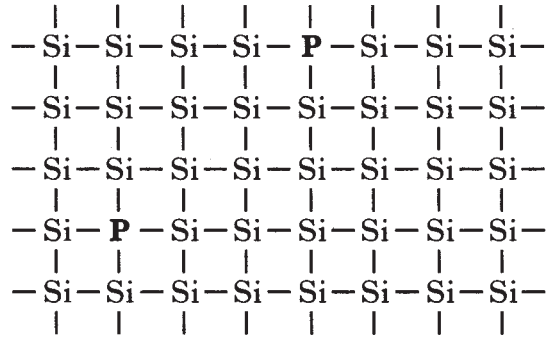
Marks

1. Superconductors and semiconductors are important modern materials.

   (*a*) Superconductor A and semiconductor B are cooled by immersing them in liquid nitrogen. As the temperature falls, what happens to the electrical conductivity of

       (i) superconductor A

       (ii) semiconductor B?

   2

   (*b*) A semiconductor was produced by doping silicon with phosphorus atoms as shown below.

$$
\begin{array}{cccccccc}
| & | & | & | & | & | & | & | \\
-\mathrm{Si}-\mathrm{Si}-\mathrm{Si}-\mathrm{Si}-\mathbf{P}-\mathrm{Si}-\mathrm{Si}-\mathrm{Si}- \\
| & | & | & | & | & | & | & | \\
-\mathrm{Si}-\mathrm{Si}-\mathrm{Si}-\mathrm{Si}-\mathrm{Si}-\mathrm{Si}-\mathrm{Si}-\mathrm{Si}- \\
| & | & | & | & | & | & | & | \\
-\mathrm{Si}-\mathrm{Si}-\mathrm{Si}-\mathrm{Si}-\mathrm{Si}-\mathrm{Si}-\mathrm{Si}-\mathrm{Si}- \\
| & | & | & | & | & | & | & | \\
-\mathrm{Si}-\mathbf{P}-\mathrm{Si}-\mathrm{Si}-\mathrm{Si}-\mathrm{Si}-\mathrm{Si}-\mathrm{Si}- \\
| & | & | & | & | & | & | & | \\
-\mathrm{Si}-\mathrm{Si}-\mathrm{Si}-\mathrm{Si}-\mathrm{Si}-\mathrm{Si}-\mathrm{Si}-\mathrm{Si}- \\
| & | & | & | & | & | & | & |
\end{array}
$$

   **Explain** which type of semiconductor has been formed.

   2

   (4)

[Turn over

2. Silicon dioxide reacts with alkalis, magnesium oxide reacts with acids and aluminium oxide reacts with both acids and alkalis.

 (*a*) What term is used to describe the behaviour of aluminium oxide?   **1**

 (*b*) What type of bonding structure is present in silicon dioxide?   **1**

 (*c*) Aluminium metal can be produced from its oxide by heating it with magnesium.
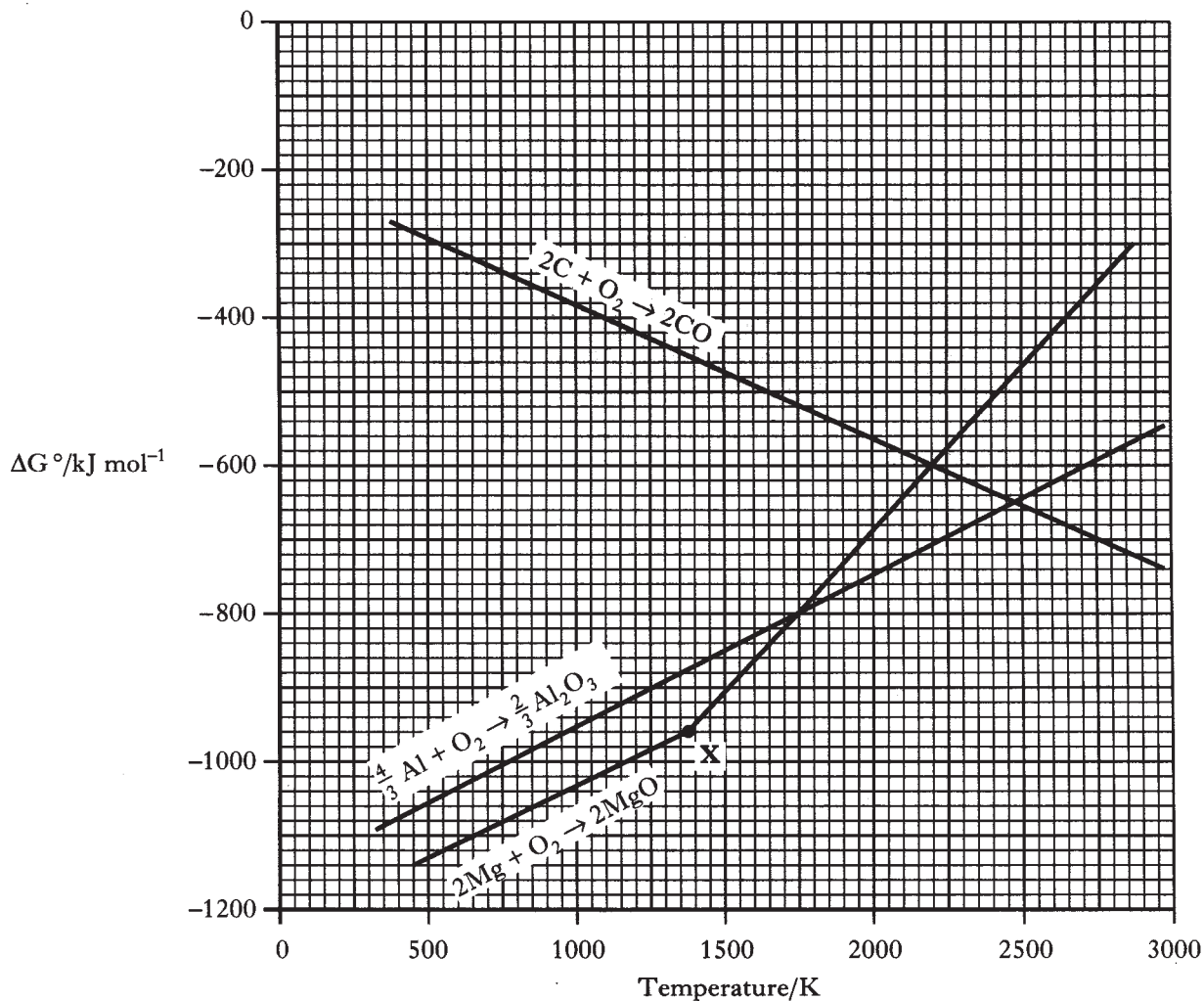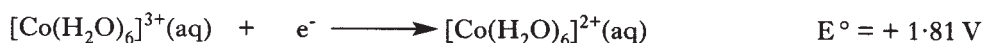

  (i) Using the Ellingham diagram, determine a temperature range in which the reduction of aluminium oxide by magnesium is feasible.   **1**

  (ii) Suggest what causes the change in the gradient of the line at point **X**.   **1**

                                (4)

3. Different ligands may affect the redox properties of metal ions.

$$[Co(NH_3)_6]^{3+}(aq) + e^- \longrightarrow [Co(NH_3)_6]^{2+}(aq) \qquad E° = +0·11\,V$$

$$[Co(H_2O)_6]^{3+}(aq) + e^- \longrightarrow [Co(H_2O)_6]^{2+}(aq) \qquad E° = +1·81\,V$$

(a) Why can ammonia and water molecules act as ligands? **1**

(b) Write the electronic configuration of the Co^{3+} ion in terms of s, p and d orbitals. **1**

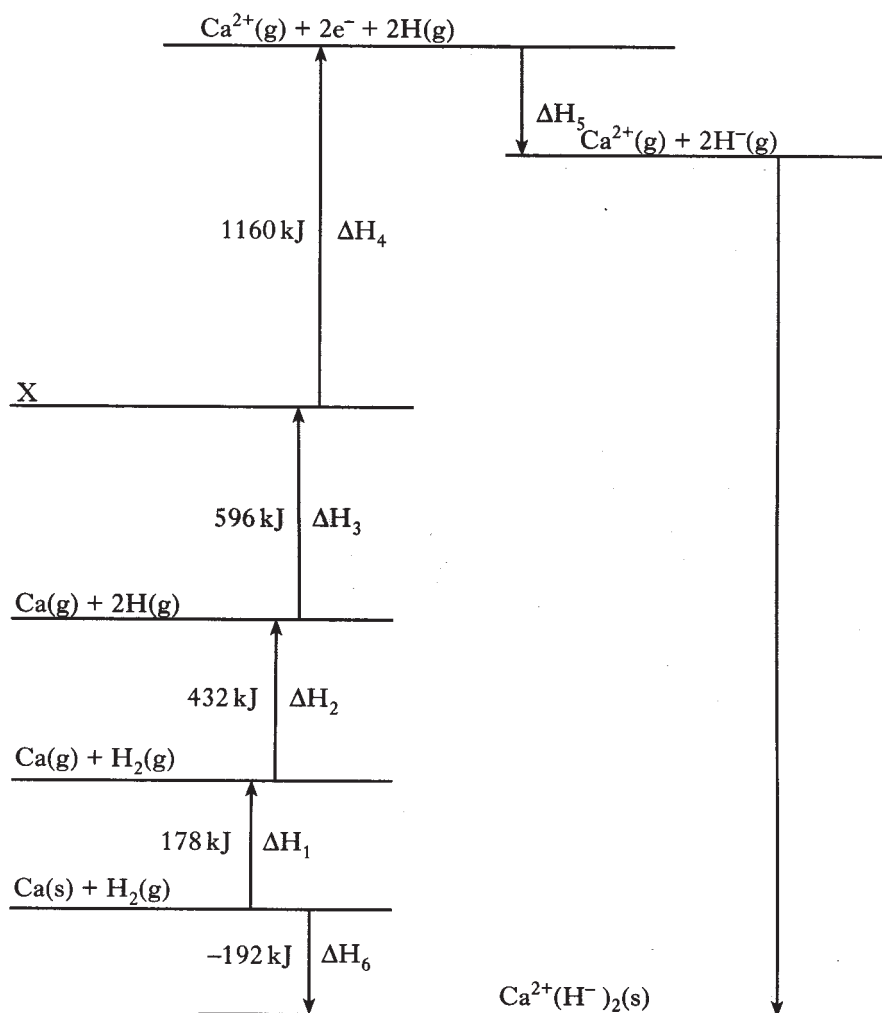(c) $[Co(H_2O)_6]^{3+}$ can be used to oxidise water into oxygen gas.

   (i) Write the ion-electron equation for the oxidation of water into oxygen. **1**

   (ii) The emf value for the reaction between $[Co(H_2O)_6]^{3+}$ and water under standard conditions is $0·58\,V$.

   Calculate the standard free energy change, in $kJ\,mol^{-1}$, for this reaction. **3**

   (6)

4. Consider the following thermochemical cycle (which is not drawn to scale) describing the steps involved in the enthalpy of formation of calcium hydride.

$$Ca^{2+}(g) + 2e^- + 2H(g)$$

$$\Delta H_5$$
$$Ca^{2+}(g) + 2H^-(g)$$

$$1160\,kJ \quad \Delta H_4$$

X

$$596\,kJ \quad \Delta H_3$$

$$Ca(g) + 2H(g)$$

$$432\,kJ \quad \Delta H_2$$

$$Ca(g) + H_2(g)$$

$$178\,kJ \quad \Delta H_1$$

$$Ca(s) + H_2(g)$$

$$-192\,kJ \quad \Delta H_6$$

$$Ca^{2+}(H^-)_2(s)$$

(a) What should be written on line X? **1**

(b) Calculate ΔH_5 using information from the Data Booklet. **1**

(c) Calculate the lattice enthalpy, in $kJ\,mol^{-1}$, of calcium hydride. **1**

(d) Identify the two products formed when calcium hydride reacts with excess water. **1**

   (4)

5. Solvent extraction is a technique used in the extraction of platinum from its ore. This extraction makes use of the fact that platinum complexes have different solubilities in aqueous hydrochloric acid and in organic solvents.

(a) When platinum complexes are extracted, an equilibrium is established.

$$[PtCl_6]^{2-}(aq) \rightleftharpoons [PtCl_6]^{2-}(organic)$$
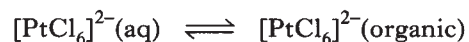
   (i) Name the $[PtCl_6]^{2-}$ ion.   **1**

    (ii) Write the expression for the partition coefficient, K, for this system.   **1**

    (iii) If more organic solvent was added, what effect would this have on the value of K?   **1**

(b) The organic solvents used to extract platinum contain an amine.

There are three types of amine, primary, secondary and tertiary.

The diagram shows how three amines affect the partition coefficient at different concentrations of hydrochloric acid.
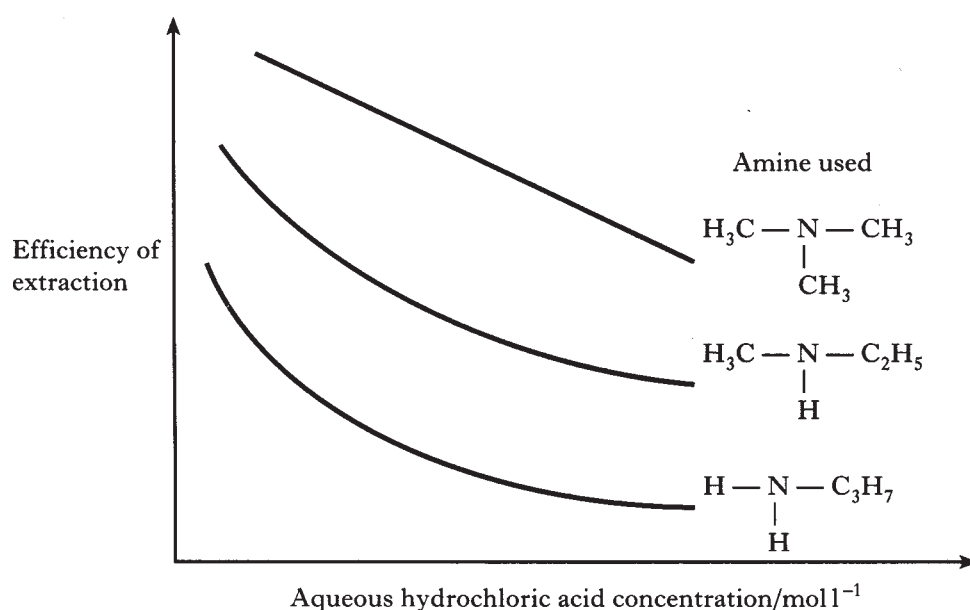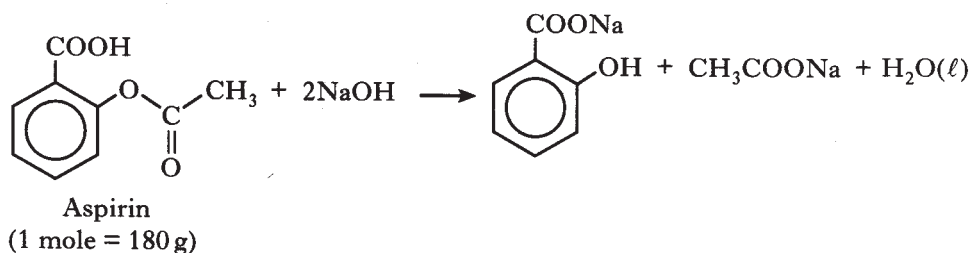

Which **type** of amine is most efficient at extracting $[PtCl_6]^{2-}$?   **1**

    (4)

6. As well as the active ingredient, aspirin tablets contain other substances.

In a PPA experiment the aspirin content was determined by the method indicated in steps 1 and 2 below.

Step 1 Crushed tablets were simmered in excess sodium hydroxide solution.

Aspirin
(1 mole = 180 g)

Step 2 The excess sodium hydroxide was determined by back titration with a standard solution of sulphuric acid.

$$2NaOH + H_2SO_4 \longrightarrow Na_2SO_4 + 2H_2O$$

Three aspirin tablets were added to $25 \cdot 0\,cm^3$ of $1 \cdot 00$ $mol\,l^{-1}$ sodium hydroxide solution and simmered for 30 minutes. When cooled the reaction mixture was diluted to exactly $250\,cm^3$ in a standard flask.

$25 \cdot 0\,cm^3$ samples were then titrated with $0 \cdot 0500$ $mol\,l^{-1}$ sulphuric acid until concordant results were obtained. The average titre was $15 \cdot 2\,cm^3$.

(*a*) (i) Calculate the number of moles of sulphuric acid in the average titre.   **1**

(ii) Calculate the number of moles of excess sodium hydroxide in the **standard flask**.   **1**

(iii) Calculate the number of moles of sodium hydroxide which reacted with the aspirin.   **1**

(iv) Calculate the average mass of pure aspirin in each tablet.   **2**

(*b*) Why does a back titration technique have to be used to determine the mass of aspirin?   **1**

(*c*) In a separate PPA experiment a sample of aspirin was prepared and then purified by recrystallisation.

What test could be carried out in the laboratory to confirm its purity?   **1**

(7)

[Turn over

7. The bromate ion, BrO_3^-, is a useful oxidising agent.

   (a) Calculate the oxidation number of bromine in the bromate ion. **1**

   (b) The following table of results was obtained for the reaction between bromate ions and bromide ions under acidic conditions.

   $$BrO_3^-(aq) + 5Br^-(aq) + 6H^+(aq) \longrightarrow 3Br_2(aq) + 3H_2O(\ell)$$
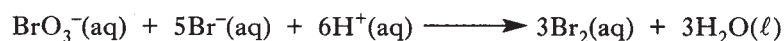
Experiment	$[BrO_3^-]/$ $mol\,l^{-1}$	$[Br^-]/$ $mol\,l^{-1}$	$[H^+]/$ $mol\,l^{-1}$	Initial rate/ $mol\,l^{-1}s^{-1}$
1	0·05	0·05	0·05	$5·0 \times 10^{-5}$
2	0·10	0·05	0·05	$1·0 \times 10^{-4}$
3	0·10	0·10	0·05	$2·0 \times 10^{-4}$
4	0·05	0·05	0·10	$2·0 \times 10^{-4}$

   (i) Deduce the order of reaction with respect to each of the three reactants. **1**

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

   (iii) Calculate the rate constant for this reaction giving the appropriate units. **2**

   (5)

8. Hypochlorous acid is a weak acid which dissociates in water as shown.

   $$HClO(aq) + H_2O(\ell) \rightleftharpoons H_3O^+(aq) + ClO^-(aq)$$
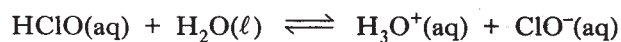
   (a) What is the conjugate base of hypochlorous acid? **1**

   (b) Write the expression for the dissociation constant, K_a, of hypochlorous acid. **1**

   (c) Given that the K_a for hypochlorous acid is $3·98 \times 10^{-8}$ and that the solution has a pH of 5·4, calculate the following ratio.

   $$\frac{[ClO^-(aq)]}{[HClO(aq)]}$$ **2**

   (4)

9. A student designed the following reaction sequence based on ethanol, C_2H_5OH.
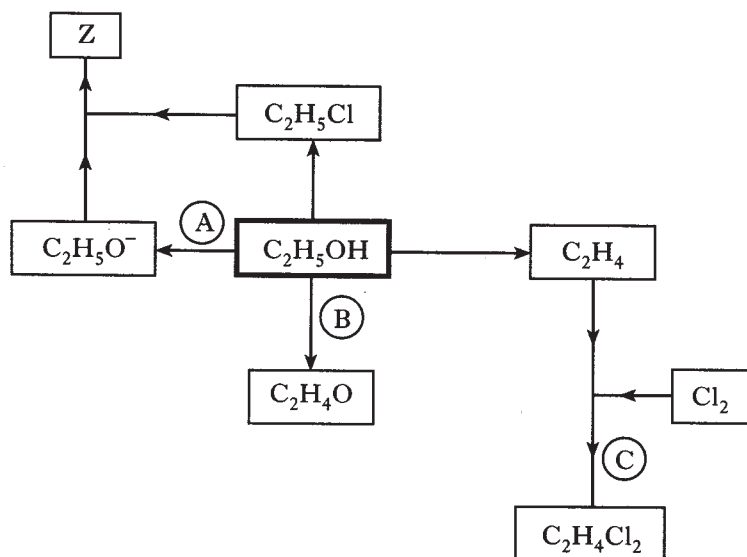
(a) Suggest a suitable reagent to carry out

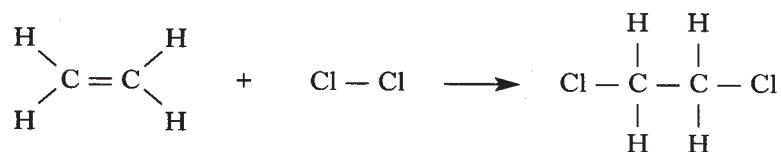 (i) Step Ⓐ   **1**

  (ii) Step Ⓑ .   **1**

(b) Draw a structural formula for **Z**.   **1**

(c) Using bond enthalpy values from the Data Booklet, calculate ΔH for reaction Ⓒ:

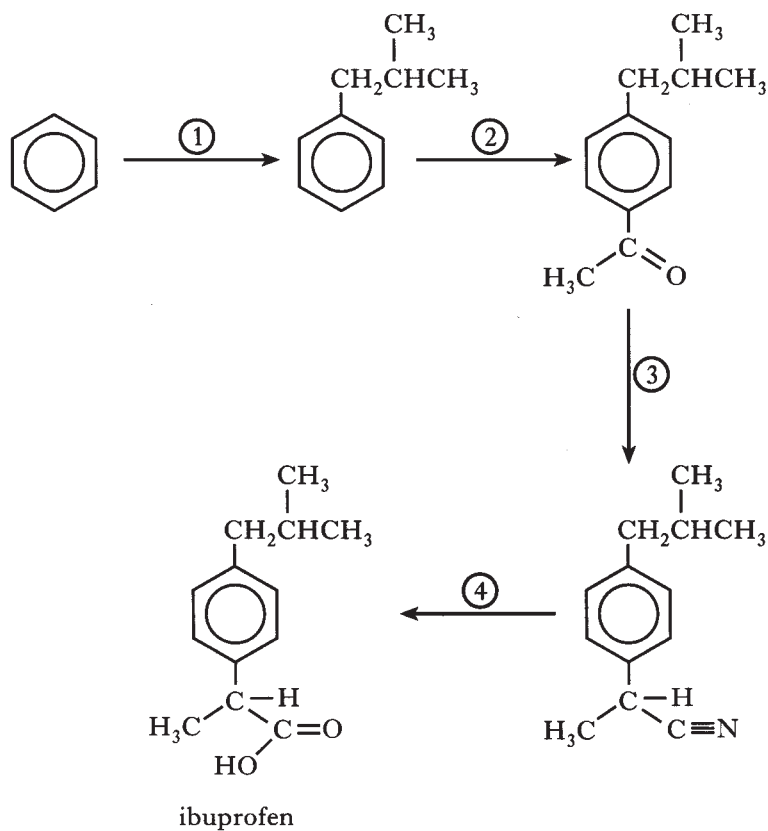   **2**
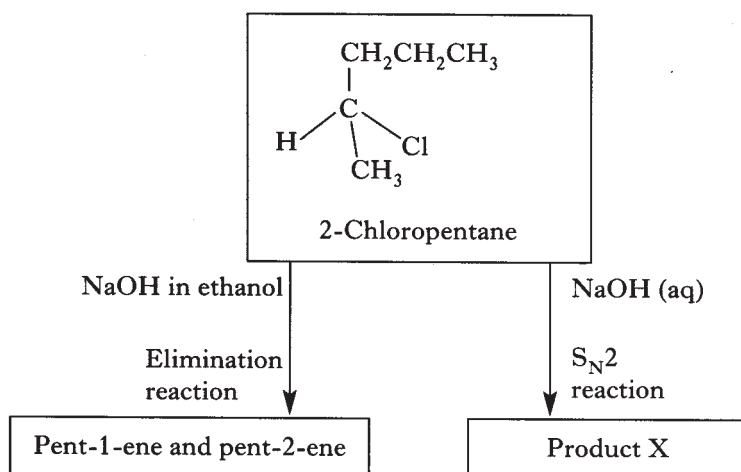
                                                                                (5)

[Turn over

10. Ibuprofen is an anti-inflammatory agent which can be synthesised from benzene as shown below.

ibuprofen

(*a*) Name the type of reaction taking place in steps ① and ②.   **1**

(*b*) Suggest a suitable reagent to carry out step ④.   **1**

(*c*) Copy the structure of ibuprofen and circle a chiral carbon atom.   **1**

(3)

11. In the reaction sequence shown below, 2-chloropentane reacts with sodium hydroxide in different ways depending on the solvent used.

$$CH_2CH_2CH_3$$
$$|$$
$$C$$
$$H \diagup \quad \diagdown Cl$$
$$CH_3$$

2-Chloropentane

NaOH in ethanol

Elimination reaction

Pent-1-ene and pent-2-ene

NaOH (aq)

S_N2 reaction

Product X

(a) Outline the mechanism for the S_N2 reaction using structural formulae.　　2

(b) One of the alkenes formed in the elimination reaction is present as two **geometric** isomers. Draw the structures of both geometric isomers and name each one.　　2
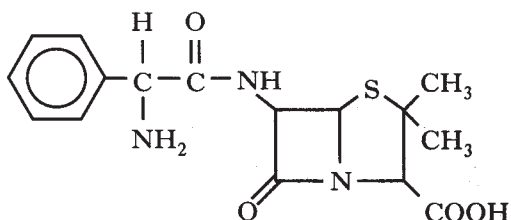
(4)

[Turn over

12. Penicillins are well tried families of drugs that bind to proteins in the cell walls of bacteria and inhibit bacterial wall synthesis. New forms of penicillin with different pharmacaphores are constantly being developed.
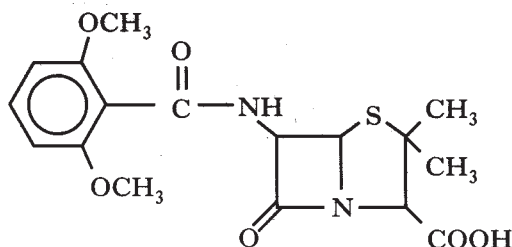
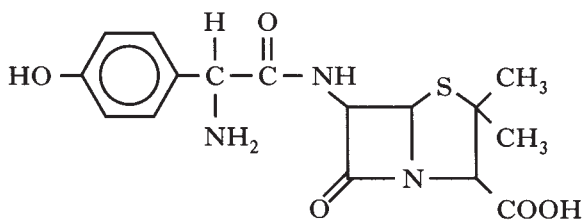The structures of four penicillin molecules are shown.
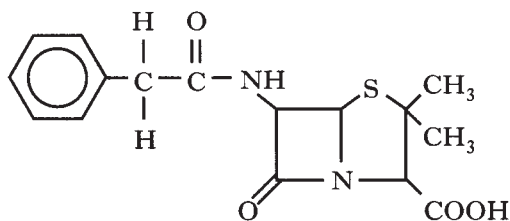
penicillin G


ampicillin

methicillin

amoxicillin

(a) Using information from the passage, explain whether these penicillin molecules are acting as agonists or antagonists with regard to the bacteria.

1

(b) Draw the structure of the pharmacaphore that is shared by these four penicillin molecules.

1

(2)

13. A soluble white solid, **X**, does **not** react with 2,4-dinitrophenylhydrazine (Brady's Reagent).

(*a*) The infra red spectrum of **X** is shown.
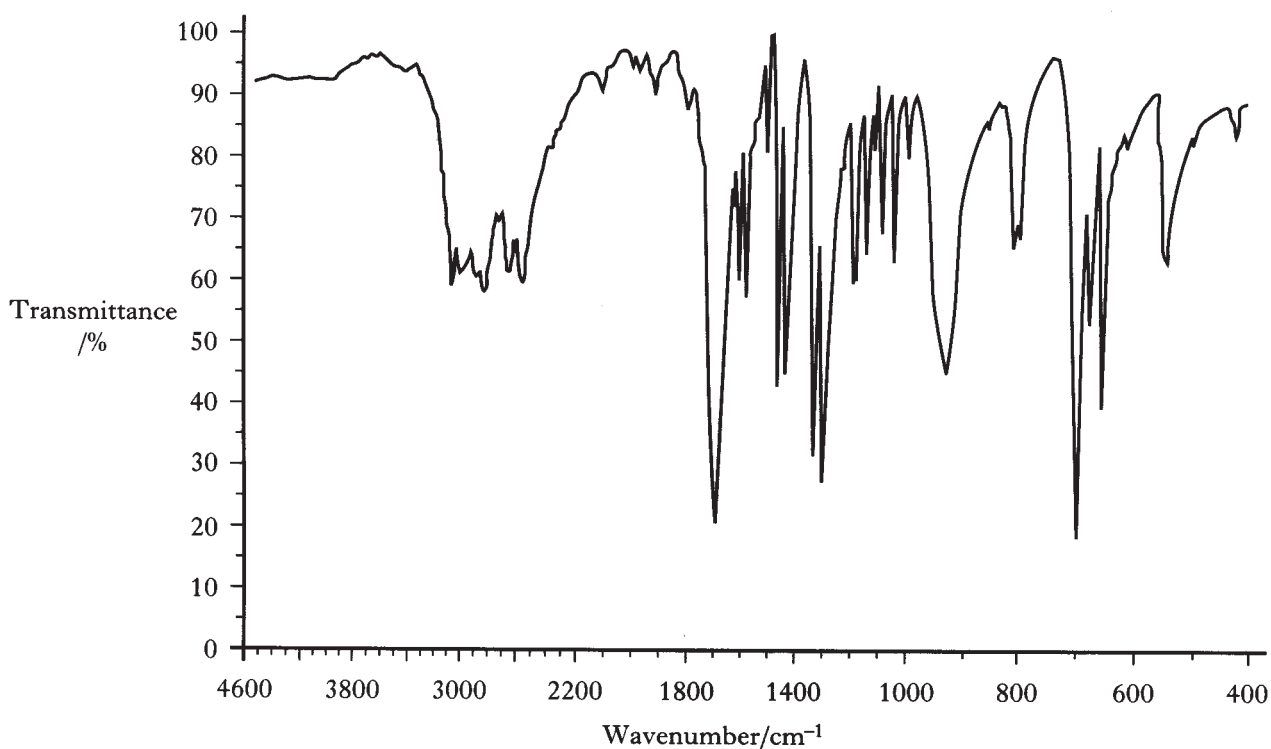
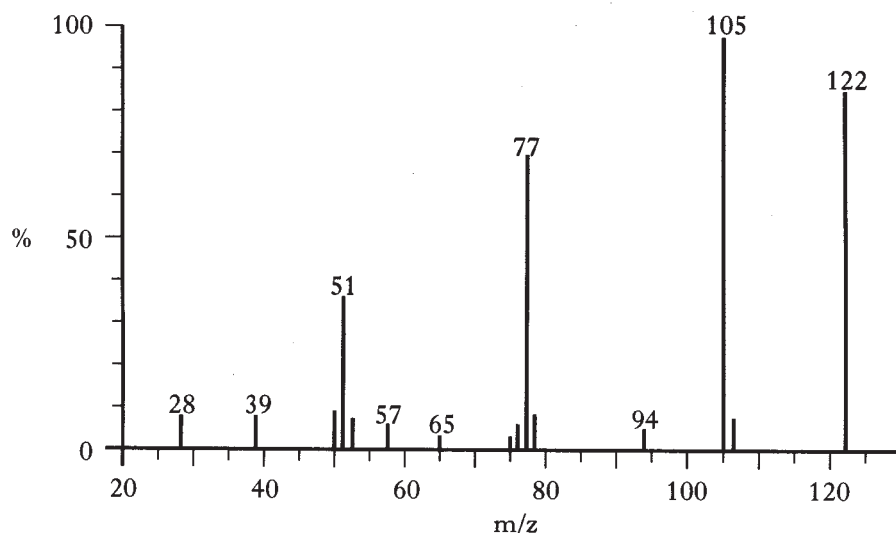Which bond causes the absorption peak at 1685 cm^{-1}?

1

(*b*) Microanalysis shows that compound **X** has a composition, by mass, of 68·9% C, 4·9% H and 26·2% O.

Show by calculation that the empirical formula for compound **X** is $C_7H_6O_2$.

1

(*c*) The mass spectrum for compound **X** is shown below.

(i) What is the molecular formula for compound **X**?

1

(ii) Identify a possible ion fragment responsible for the peak at m/z 77 in the mass spectrum.

1

(*d*) From the information above, draw a structural formula for compound **X**.

1

(*e*) Calculate the energy, in kJ mol^{-1}, corresponding to the absorption peak at **wavenumber** 1685 cm^{-1} in the infra red spectrum.

3

[END OF QUESTION PAPER]

(8)