X012/701

NATIONAL QUALIFICATIONS 2004

WEDNESDAY, 2 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

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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SECTION A

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

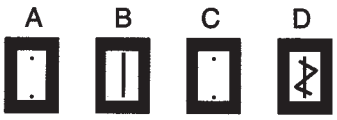
B chromatography

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. According to the aufbau principle, electrons fill orbitals in the order

   A 1s 2s 2p 3s 3p 4s 4p 3d

   B 1s 2s 2p 3s 3d 3p 4s 4p

   C 1s 2s 2p 3s 3p 3d 4s 4p

   D 1s 2s 2p 3s 3p 4s 3d 4p.

2. A Lewis base may be regarded as a substance which is capable of donating an unshared pair of electrons to form a covalent bond.

   Which of the following could act as a Lewis base?

   A BCl_3

   B NH_4^+

   C PH_3

   D Co^{3+}

3. Which of the following statements referring to the structures of sodium chloride and caesium chloride is correct?

   A There are eight chloride ions surrounding each sodium ion.

   B There are eight chloride ions surrounding each caesium ion.

   C The chloride ions are arranged tetrahedrally round the sodium ions.

   D The chloride ions are arranged tetrahedrally round the caesium ions.

4. Which of the following is the best term to describe aluminum oxide?

   A Basic

   B Acidic

   C Neutral

   D Amphoteric

5. Which of the following compounds contains hydride ions?

   A NH_3

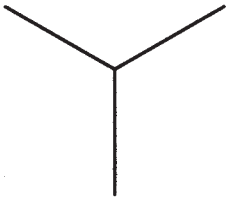
   B HCl

   C H_2S

   D CaH_2

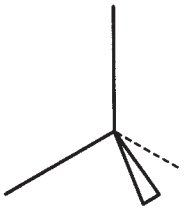
Questions 6 and **7** refer to the following diagrams which indicate different arrangements of **electron pairs**.

A



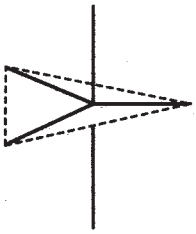
trigonal planar

B



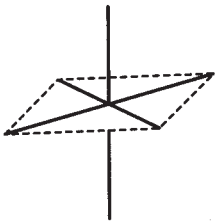
tetrahedral

C



trigonal bipyramidal

D



octahedral

Which arrangement of electron pairs will be found in the following molecules?

6. NF_3

7. ClF_3

[Turn over

8. The number of unpaired electrons in a gaseous Ni^{2+} ion is

A 0

B 2

C 4

D 6.

9. Which of the following ions is **least** likely to be coloured?

A $Ti(H_2O)_6^{3+}$

B $Cr(NH_3)_6^{3+}$

C $Ni(H_2O)_6^{2+}$

D $Zn(NH_3)_4^{2+}$

10. $ClO_3^-(aq) + 6H^+(aq) + ne^- \rightarrow Cl^-(aq) + 3H_2O(\ell)$

What value of n is required to balance the above equation?

A 4

B 5

C 6

D 7

11. What volume of 0·5 mol l^{-1} sodium carbonate is required to make, by dilution with water, one litre of a solution with a $\mathbf{Na^+(aq)}$ concentration of 0·2 mol l^{-1}?

A 100 cm^3

B 200 cm^3

C 300 cm^3

D 400 cm^3

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

The above reaction can be said to have reached equilibrium when

A the equilibrium constant K is equal to 1

B the concentrations of the products equal those of the reactants

C the reaction between the acid and the alcohol has stopped

D the rate of production of ethyl ethanoate equals its rate of hydrolysis.

13. $C_2H_6(g) \rightleftharpoons C_2H_4(g) + H_2(g)$ $\Delta H° = +157 kJ\ mol^{-1}$

The conditions favouring the highest equilibrium yield of ethene in the above reaction are

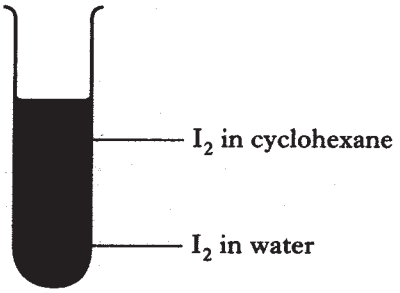
A low pressure and high temperature

B low pressure and low temperature

C high pressure and high temperature

D high pressure and low temperature.

14.



The partition coefficient for the above system can be altered by

A adding more cyclohexane

B adding more iodine

C changing the temperature

D shaking the mixture thoroughly.

15. $\frac{1}{2}N_2(g) + O_2(g) \rightarrow NO_2(g)$

$\Delta G° = +51·8 kJ\ mol^{-1}$

$N_2(g) + 2O_2(g) \rightarrow N_2O_4(g)$

$\Delta G° = +97·7 kJ\ mol^{-1}$

What is the free energy change $\Delta G°$, in kJ mol^{-1}, for the conversion of nitrogen dioxide to one mole of dinitrogen tetroxide?

A −45·9

B −5·9

C +5·9

D +45·9

16. The standard enthalpy of formation of strontium chloride is the enthalpy change for which of the following reactions?

A $Sr(g) + Cl_2(g) \rightarrow SrCl_2(s)$

B $Sr(s) + Cl_2(g) \rightarrow SrCl_2(s)$

C $Sr^{2+}(g) + 2Cl^-(g) \rightarrow SrCl_2(s)$

D $Sr^{2+}(aq) + 2Cl^-(aq) \rightarrow SrCl_2(s)$

17. The mean bond enthalpy of a C — F bond is $486\,kJ\ mol^{-1}$.

In which of the processes is ΔH approximately equal to $+1944\,kJ\ mol^{-1}$?

A $CF_4(g) \rightarrow C(s) + 2F_2(g)$

B $CF_4(g) \rightarrow C(g) + 4F(g)$

C $CF_4(g) \rightarrow C(g) + 2F_2(g)$

D $CF_4(g) \rightarrow C(s) + 4F(g)$

18. $$Cr(g) \rightarrow Cr^{3+}(g) + 3e^-$$

The energy required for this change is

A $1977\,kJ\ mol^{-1}$

B $3000\,kJ\ mol^{-1}$

C $5259\,kJ\ mol^{-1}$

D $9000\,kJ\ mol^{-1}$.

19. A Born-Haber cycle can be used to calculate the lattice enthalpy of sodium chloride. Which of the following is **not** required in the calculation?

A The first ionisation energy of chlorine

B The enthalpy of formation of sodium chloride

C The first ionisation energy of sodium

D The bond enthalpy of chlorine

20. The enthalpy change for the reaction

$Li^+(g) + Br^-(g) \rightarrow Li^+(aq) + Br^-(aq)$

is

A the enthalpy of formation of lithium bromide

B the enthalpy of solution of lithium bromide

C the sum of the hydration enthalpies of lithium and bromide ions

D the sum of the first ionisation energy of lithium and the electron affinity of bromine.

21. In which of the following are the molecules likely to have the lowest degree of disorder?

A $H_2O(g)$

B $Br_2(g)$

C $H_2O(\ell)$

D $Br_2(\ell)$

22. For a certain reaction

$\Delta H° = +7{\cdot}3\,kJ\ mol^{-1}$ and $\Delta S° = -200\,J\,K^{-1}\ mol^{-1}$.

This reaction will

A never be thermodynamically feasible

B be thermodynamically feasible above a certain temperature

C be thermodynamically feasible below a certain temperature

D be thermodynamically feasible at all temperatures.

23. The equilibrium constant for the reaction

$$Zn(s) + Cu^{2+}(aq) \rightleftharpoons Zn^{2+}(aq) + Cu(s)$$

at 298 K has a numerical value of 2×10^{37}.

Which of the following statements about the reaction is correct?

A The free energy change associated with the reverse reaction has a large negative value.

B The free energy change associated with the forward reaction has a small negative value.

C The reverse reaction does not occur to any appreciable extent.

D The value of the equilibrium constant is not dependent on temperature.

24. $Ti^{3+}(aq) + e^- \rightleftharpoons Ti^{2+}(aq) \quad E° = -0{\cdot}37\,V$

$V^{3+}(aq) + e^- \rightleftharpoons V^{2+}(aq) \quad E° = -0{\cdot}26\,V$

Which line in the table is true for the reaction represented below?

$$V^{3+}(aq) + Ti^{2+}(aq) \rightleftharpoons V^{2+}(aq) + Ti^{3+}(aq)$$

	$\Delta G°$	K
A	negative	>1
B	positive	>1
C	negative	<1
D	positive	<1

[Turn over

25. For a cell in which the following reaction occurs

$$X(s) + 2Y^+(aq) \rightarrow X^{2+}(aq) + 2Y(s)$$

the E° value is 1·5 V.

$\Delta G°$ for the reaction, per mole of X, is

A $-289{\cdot}5\ kJ\ mol^{-1}$

B $-144{\cdot}8\ kJ\ mol^{-1}$

C $+144{\cdot}8\ kJ\ mol^{-1}$

D $+289{\cdot}5\ kJ\ mol^{-1}$.

26. A cell consists of inert electrodes in half cells whose Standard Reduction Potentials are shown below.

$$MnO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightleftharpoons MnO_2(s) + 2H_2O(\ell) \qquad E° = 2{\cdot}26\ V$$

$$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq) \qquad E° = 0{\cdot}77\ V$$

Under standard conditions the emf of the cell would be

A 0·72 V

B 1·49 V

C 3·03 V

D 3·80 V.

27. A suggested mechanism for the reaction

$$2A + B \rightarrow A_2B$$

is a two-step process

$$A + B \rightarrow AB \text{ (slow)}$$

$$AB + A \rightarrow A_2B \text{ (fast)}$$

This mechanism is consistent with the rate equation

A rate = $k[A]^2[B]$

B rate = $k[A][B]$

C rate = $k[A][A_2B]$

D rate = $k[AB]$.

28. Which of the following equations does **not** represent a nucleophilic substitution?

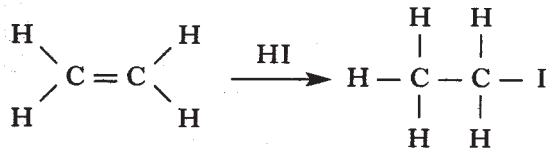
A $C_3H_7Br + KOH \xrightarrow{\text{ethanol}} C_3H_6 + KBr + H_2O$

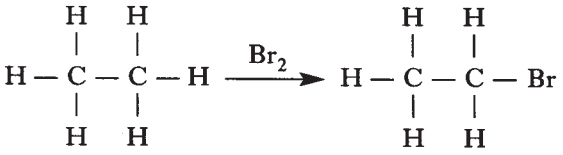
B $C_3H_7Br + KCN \xrightarrow{\text{ethanol}} C_3H_7CN + KBr$

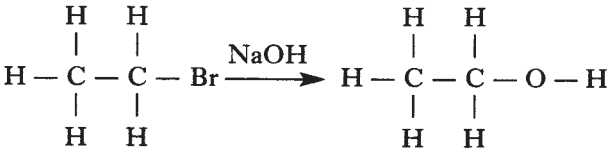
C $C_2H_5Cl + C_2H_5ONa \xrightarrow{\text{ethanol}} C_2H_5OC_2H_5 + NaCl$

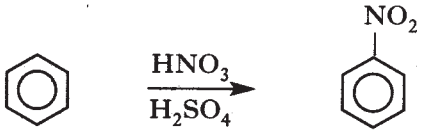
D $C_2H_5Br + NaOH \xrightarrow{\text{water}} C_2H_5OH + NaBr$

Questions 29 and **30** refer to the following.

A 

B 

C 

D 

29. Which of the above involves homolytic fission?

30. Which of the above involves electrophilic substitution?

31. Which of the following is most reactive as a nucleophile?

A NH_3

B NH_4^+

C Br_2

D CH_3I

32. Which formula represents 2-methylpentan-3-ol?

A $CH_3CH(CH_3)CH(OH)CH_2CH_3$

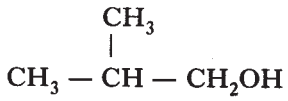
B $CH_3CH(OH)CH(CH_3)CH_2CH_3$

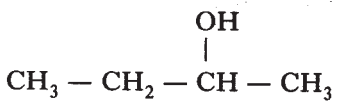
C $CH_3CH(CH_3)CH(OH)CH_3$

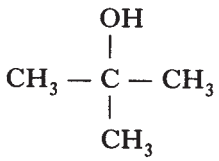
D $CH_3CH_2C(CH_3)_2CH_2CH_2OH$

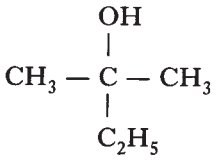
33. An alcohol, **X**, does **not** react with acidified dichromate solution, but gives an alkene when dehydrated with hot concentrated sulphuric acid. This alkene reacts with bromine water to form 1,2-dibromo-2-methylpropane.

Which of the following is **X**?

A


B


C


D


Questions 34 and **35** refer to the following.

An organic compound is sometimes identified by the preparation of a crystalline derivative.

34. To help in identification, a derivative **must**

A decompose at its melting point

B have a low relative molecular mass

C have a sharp boiling point

D have a sharp melting point.

35. Which of the following can be distinguished by making 2,4-dinitrophenylhydrazone derivatives?

A Propan-1-ol and propan-2-ol

B Ethanoic acid and benzoic acid

C Methoxyethane and ethoxyethane

D Ethanal and propanal

36. What would be the products formed when $CH_3COOCH_2CH_2OOCCH_3$ is warmed with aqueous sodium hydroxide solution?

A $CH_3COONa + HOCH_2CH_2OH$

B $CH_3COOH + NaOCH_2CH_2ONa$

C $CH_3COONa + C_2H_5OOCCH_3$

D $CH_3COOCH_3 + H_2O$

37. Which of the following compounds would dissolve in water to give an alkaline solution?

A CH_3COCH_3

B CH_3CH_2CN

C CH_3CH_2CHO

D $CH_3CH_2NH_2$

38. Which of the following molecules is planar?

A Chlorobenzene

B Methylbenzene (toluene)

C Cyclohexane

D Hexane

39. Which of the following analytical techniques depends on the vibrations within molecules?

A Nuclear magnetic resonance spectroscopy

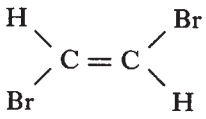
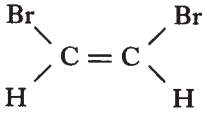
B Atomic emission spectroscopy

C Infra-red spectroscopy

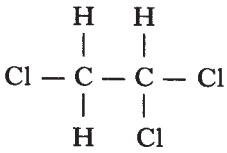
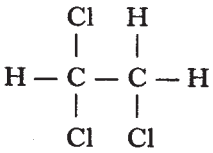
D Mass spectrometry

40. Which of the following represent the same chemical substance?

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

B  and 

C $CH_3 - CH_2 - \underset{\displaystyle CH_3}{\underset{|}{CH}} - CH_3$ and $CH_3 - \underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}} - CH_3$

D  and 

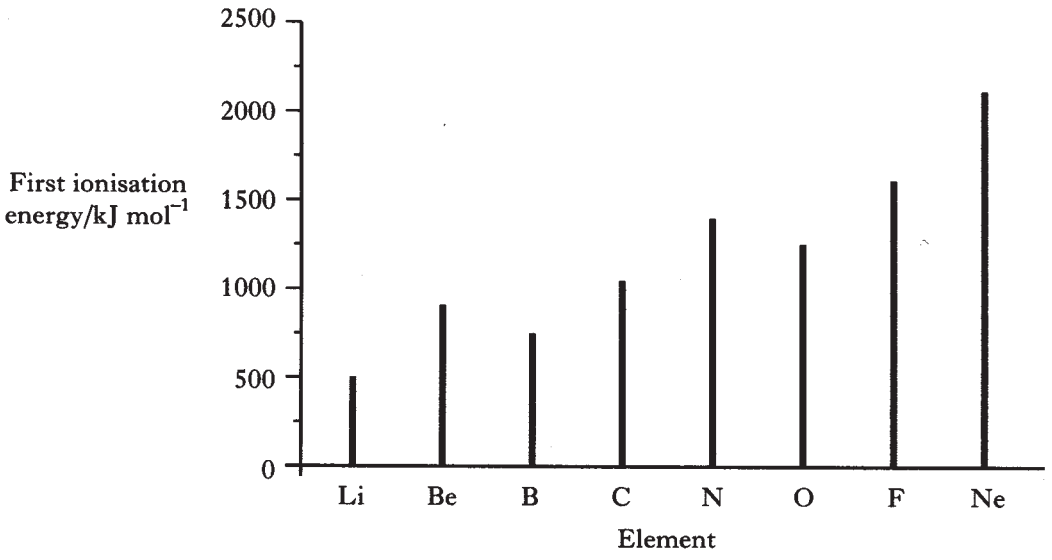
[END OF SECTION A]

Candidates are reminded that the answer sheet for Section A must be placed inside the front cover of your answer book.

SECTION B

Marks

1. The graph below shows the first ionisation energies for the elements of the second period in the Periodic Table.



(*a*) (i) Why does the first ionisation energy tend to increase across the period? **1**

(ii) Give a reason why the first ionisation energy of nitrogen is higher than that of oxygen. **1**

(*b*) Explain why the **second** ionisation energy of lithium is the highest in this period. **1**

(3)

2. (*a*) Using bond enthalpy values from the **Data Booklet**, calculate the enthalpy change for the following reaction.

$$C_2H_2(g) + 2H_2(g) \longrightarrow C_2H_6(g)$$ **3**

(*b*) The enthalpy change for the reaction above can also be calculated using standard enthalpies of combustion.

Why might this value be different from the answer to (*a*)? **1**

(4)

[Turn over

Marks

3. (*a*) Using the data from the table below calculate the standard enthalpy change, in kJ mol^{-1}, for the following reaction.

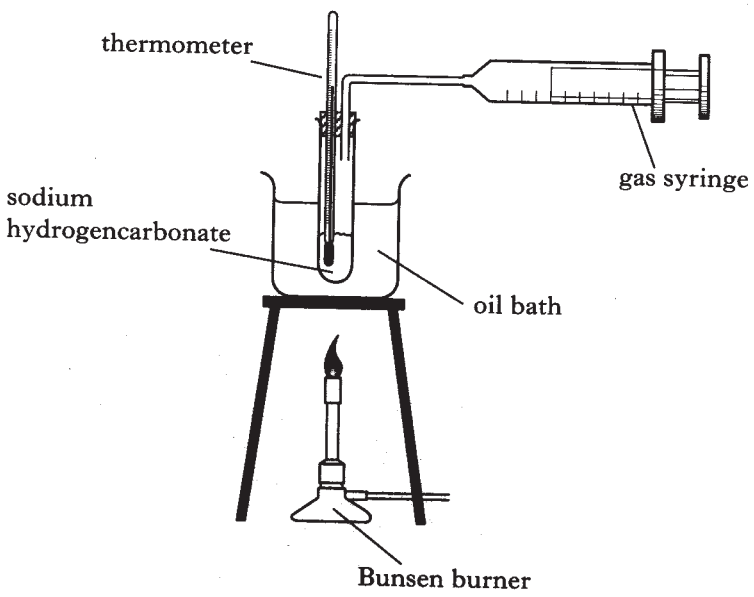
$$2NaHCO_3(s) \rightarrow Na_2CO_3(s) + CO_2(g) + H_2O(g)$$

Compound	Standard enthalpy of formation/kJ mol^{-1}
$NaHCO_3(s)$	−948
$Na_2CO_3(s)$	−1131
$H_2O(g)$	−242
$CO_2(g)$	−394

1

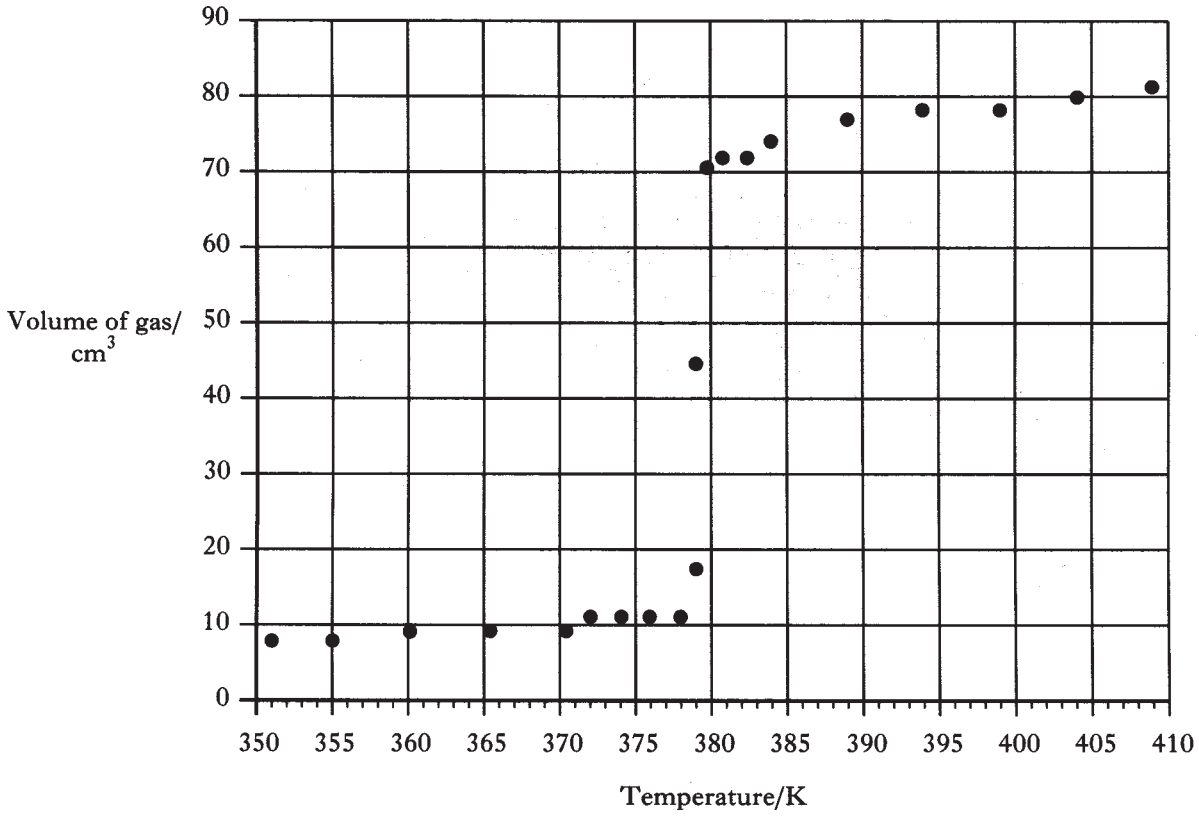
(*b*) Given that the entropy change for the reaction is +335 J K^{-1} mol^{-1}, calculate the temperature at which the reaction just becomes feasible. **2**

(*c*) A student set up an experiment to measure the temperature at which sodium hydrogencarbonate begins to decompose on heating, using the apparatus below.



3. (*c*) (continued)

From the student's results below, what is the experimental value for the temperature at which the sodium hydrogencarbonate begins to decompose?



1

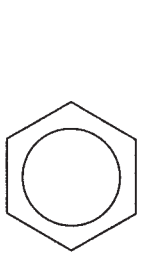
(*d*) Suggest a reason why the calculated and experimental decomposition temperatures may be different. **1**

(5)

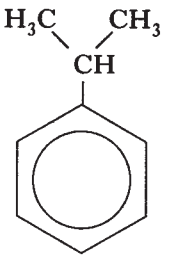
[Turn over

Marks

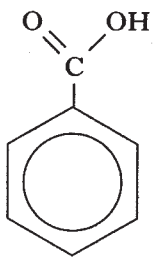
4. The structural formulae of three aromatic compounds are shown below.



benzene



2-phenylpropane



benzoic acid

The relative formula masses and boiling points of these compounds are shown in the table below.

Compound	Relative formula mass	Boiling point/°C
benzene	78·1	80
2-phenylpropane	120·2	152
benzoic acid	122·1	250

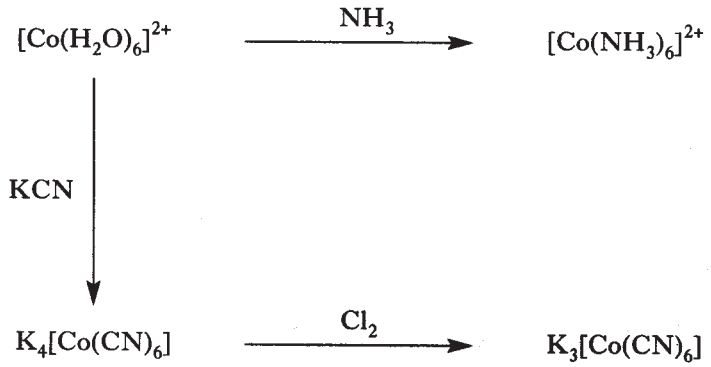
(*a*) In terms of bonding, why does 2-phenylpropane have a higher boiling point than benzene? **1**

(*b*) Benzoic acid and 2-phenylpropane molecules are of similar size and shape. Why is the boiling point of benzoic acid higher than that of 2-phenylpropane? **1**

(*c*) What would benzene be reacted with to form 2-phenylpropane? **1**

(3)

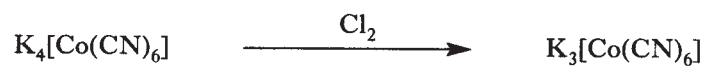
5. Consider the following reactions.



(*a*) Write the electronic configuration of the cobalt(II) ion in terms of s, p and d orbitals. **1**

(*b*) Name the $[Co(NH_3)_6]^{2+}$ ion. **1**

(*c*) What is the function of the chlorine in the following reaction?



1

(*d*) There is a colour change when NH_3 is added to $[Co(H_2O)_6]^{2+}$.
Why does this change of ligand result in different wavelengths of light being absorbed? **1**

(*e*) The $[Co(H_2O)_6]^{2+}$ ion absorbs at 550 nm.
Calculate the energy, in kJ mol l^{-1}, corresponding to this absorption. **3**

(7)

Marks

6. A 1·11 g sample of steel containing manganese was dissolved in nitric acid. The manganese(II) ions formed were then oxidised to permanganate ions. The resulting purple solution was made up to 100 cm^3 in a standard flask.

In a titration, a 25·0 cm^3 portion of the permanganate solution was reduced by 30·1 cm^3 of 0·0020 mol l^{-1} iron(II) sulphate solution.

(*a*) Using information from the Data Booklet, write a redox equation for the reaction between the permanganate ions and iron(II) ions. **1**

(*b*) (i) Calculate the number of moles of permanganate ions in the 25·0 cm^3 portion titrated. **2**

(ii) Calculate the percentage by mass of manganese in the original sample of steel. **2**

(*c*) What other method could be used to determine the manganese content of the purple solution? **1**

(6)

7. Ozone, O_3, is one of the earth's key defences against damaging ultra-violet radiation.

(*a*) Ozone can be described in terms of resonance structures.

Draw the **two** resonance structures for ozone. **1**

(*b*) Ozone can be broken down by nitrogen monoxide gas produced by high flying aircraft.

Reaction 1 $NO(g) + O_3(g) \longrightarrow NO_2(g) + O_2(g)$

The nitrogen dioxide formed can then react with oxygen atoms.

Reaction 2 $NO_2(g) + O(g) \longrightarrow NO(g) + O_2(g)$

(i) Write an equation for the overall reaction. **1**

(ii) From the equations, what part does the nitrogen monoxide play in the overall reaction? **1**

(*c*) The following table shows how the initial rate of **reaction 2** varies with changing concentrations of $NO_2(g)$ and O(g) at a fixed temperature.

[O]/mol l^{-1}	[NO_2]/mol l^{-1}	Initial rate/mol l^{-1} s^{-1}
$9{\cdot}20 \times 10^{-15}$	$1{\cdot}11 \times 10^{-12}$	$6{\cdot}10 \times 10^{-17}$
$1{\cdot}81 \times 10^{-14}$	$1{\cdot}11 \times 10^{-12}$	$1{\cdot}20 \times 10^{-16}$
$1{\cdot}81 \times 10^{-14}$	$2{\cdot}23 \times 10^{-12}$	$2{\cdot}41 \times 10^{-16}$

(i) Determine the overall order of this reaction. **1**

(ii) Calculate a value for the rate constant, k, including appropriate units. **3**

(7)

8. Before a pH electrode can be used to measure the pH of a solution it must be calibrated by placing it in a series of buffer solutions of known pH.

One buffer solution used to calibrate a pH electrode was made by dissolving 2·24 g of potassium propanoate, C_2H_5COOK, in 250 cm^3 of 0·20 mol l^{-1} propanoic acid.

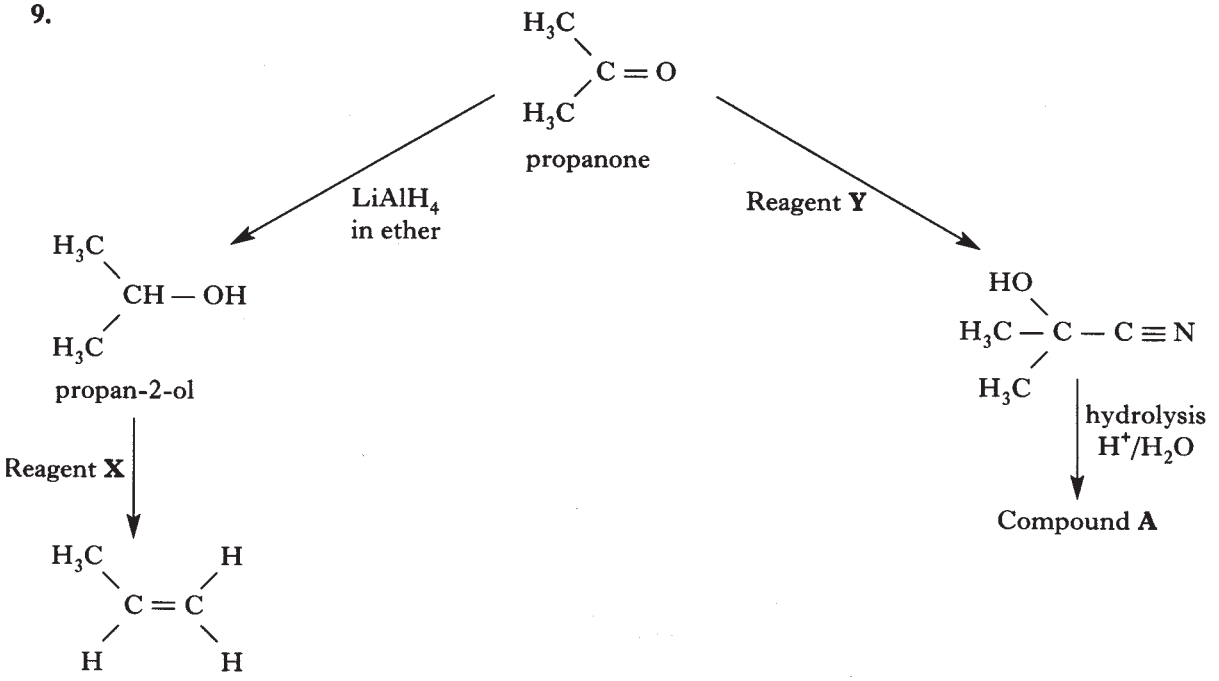
(*a*) What property of buffer solutions makes them ideal for calibrating pH electrodes? **1**

(*b*) Calculate the pH of the buffer solution described above. **3**

(4)

Marks

9.



(*a*) Identify:

(i) reagent **X**; **1**

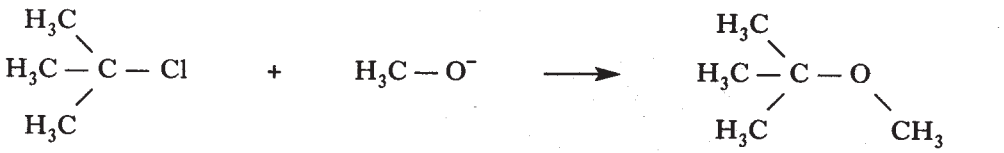
(ii) reagent **Y**. **1**

(*b*) Draw a structural formula for compound **A**. **1**

(c) Name the type of reaction involved in the conversion of propanone to propan-2-ol. **1**

(4)

10. 2-Methoxy-2-methylpropane is a compound added to unleaded petrol as a "knock inhibitor". It can be synthesised by the reaction of methoxide ions with 2-chloro-2-methylpropane.



(*a*) To which class of organic compounds does 2-methoxy-2-methylpropane belong? **1**

(*b*) How can the methoxide ion be prepared from methanol? **1**

(*c*) The preparation of the 2-methoxy-2-methylpropane proceeds by a S_N1 mechanism.

(i) Clearly showing the electron shifts, outline the step(s) involved. **2**

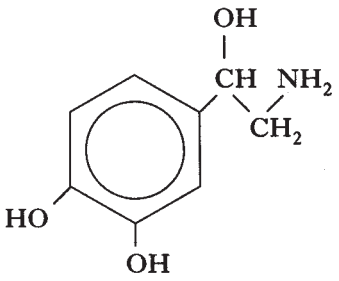
(ii) Suggest why this reaction is more likely to proceed by a S_N1 mechanism rather than a S_N2. **1**

(*d*) 2-Methoxy-2-methylpropane does not display optical isomerism. Draw the structural formula of an isomer of this compound which does display optical isomerism. **1**

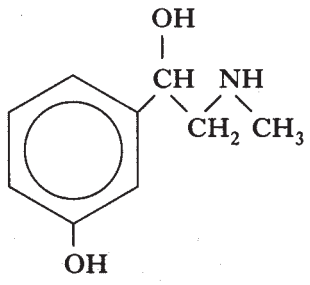
(6)

Marks

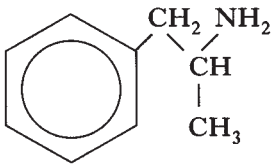
11. The three molecules shown below can all increase blood pressure if introduced into the human body.



noradrenaline



phenylephrine



amphetamine

Noradrenaline is produced naturally by the adrenal gland in times of stress. It activates sites called adrenoreceptors that cause many changes in the body including increased blood pressure.

Phenylephrine has been found to stimulate the same receptors producing very similar effects.

Amphetamine is classed as an indirectly acting agonist. Instead of acting directly on adrenoreceptors it causes certain nerve terminals in the body to produce noradrenaline thus raising blood pressure.

(*a*) What is meant by the term "agonist"? **1**

(*b*) Draw the structural formula for the pharmacophore acting on the adrenoreceptors. **1**

(*c*) Amines can be classified as primary, secondary or tertiary. To which class of amine does phenylephrine belong? **1**

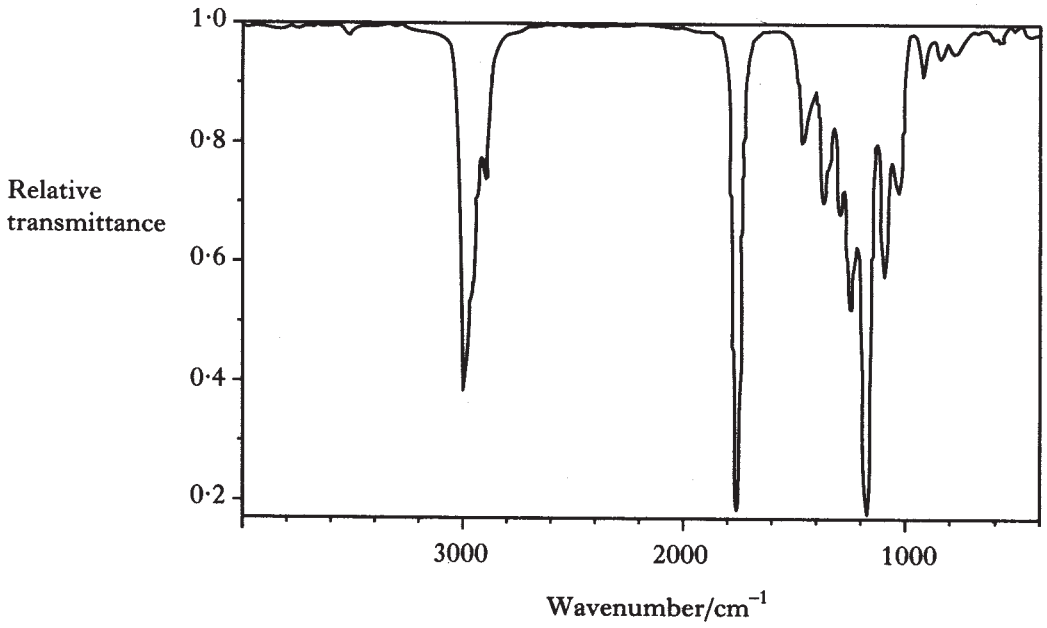
(3)

[Turn over

Marks

12. A chemist used a variety of techniques to identify a sweet-smelling compound, **X**.

(*a*) The infra-red spectrum of **X** is shown below.



(i) Which bond is responsible for the strong absorption at 1745 cm^{-1}? **1**

(ii) To which class of organic compounds does **X** belong? **1**

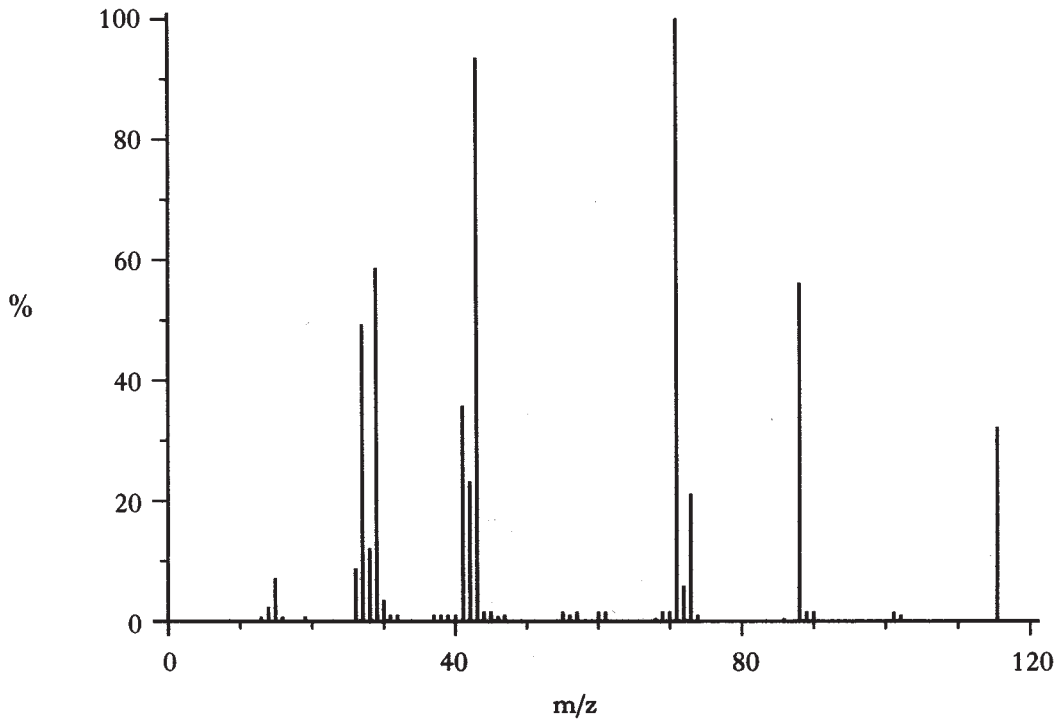
(*b*) Compound **X** was subjected to elemental analysis. Complete combustion of 0·210 g of **X** gave 0·478 g of carbon dioxide and 0·196 g of water. No other product was formed.

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

(ii) Calculate the empirical formula for compound **X**. **1**

12. (continued)

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



(i) From the mass spectrum, what is the relative molecular mass of compound **X**? **1**

(ii) What is the molecular formula for compound **X**? **1**

(*d*) Compound **X** was hydrolysed producing ethanol and another compound.
Considering all the evidence, name **X**. **1**

(8)

[*END OF QUESTION PAPER*]