X012/701

NATIONAL QUALIFICATIONS 2008

FRIDAY, 30 MAY 9.00 AM – 11.30 AM

CHEMISTRY ADVANCED HIGHER

Reference may be made to the Chemistry Higher and Advanced Higher Data Booklet.

SECTION A – 40 marks

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

For this section of the examination you must use an **HB pencil**.

SECTION B – 60 marks

All questions should be attempted.

Answers must be written clearly and legibly in ink.

SECTION A

Read carefully

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

2 For this section of the examination you must use an **HB pencil** and, where necessary, an eraser.

3 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.

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

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

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

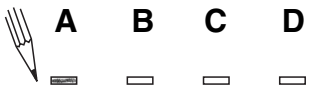
A chromatography

B fractional distillation

C fractional crystallisation

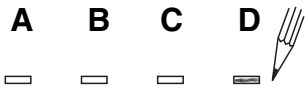
D filtration.

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



Changing an answer

If you decide to change your answer, carefully erase your first answer and using your pencil, fill in the answer you want. The answer below has been changed to **D**.



1. An atom has the electronic configuration

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

What is the charge of the most likely ion formed from this atom?

A -1

B $+1$

C $+2$

D $+3$

2. The electronic configurations, **X** and **Y**, for two uncharged atoms of sodium 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 **X** is an excited state.

B Both **X** and **Y** have vacant 2d orbitals.

C Energy is absorbed in changing **Y** to **X**.

D Less energy is required to ionise **Y** compared to **X**.

3. 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 Co^{3+}

B PH_3

C BCl_3

D NH_4^+

4. Silicon can be converted into an n-type semiconductor by adding

A boron

B carbon

C arsenic

D aluminium.

5. 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.

6. The transition metal salts, MnF_2, FeF_2 and CoF_2, have identical crystal structures because the metal ions have

A similar radii

B similar colours

C the same nuclear charge

D the same number of d electrons.

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

8. Sodium hydride reacts with sodium sulphate as shown.

$$4NaH + Na_2SO_4 \rightarrow 4NaOH + Na_2S$$

This reaction demonstrates sodium hydride acting as

A a base

B an acid

C a reducing agent

D an oxidising agent.

[Turn over

9. Three elements, **X**, **Y** and **Z**, are in the same period of the Periodic Table.

The oxide of **X** is amphoteric, the oxide of **Y** is basic and the oxide of **Z** is acidic.

Which of the following shows the elements arranged in order of increasing atomic number?

A **Y**, **X**, **Z**

B **Y**, **Z**, **X**

C **Z**, **X**, **Y**

D **X**, **Y**, **Z**

10. Which of the following involves oxidation?

A $MnO_4^- \rightarrow MnO_4^{2-}$

B $Ag^+ \rightarrow [Ag(NH_3)_2]^+$

C $[Fe(CN)_6]^{4-} \rightarrow [Fe(CN)_6]^{3-}$

D $[Ni(H_2O)_6]^{2+} \rightarrow [Ni(CN)_4]^{2-}$

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

A 0

B 2

C 4

D 6.

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

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

Which of the following is true?

A The value of $\Delta S°$ must be positive.

B The value of $\Delta G°$ must be positive.

C Adding a catalyst will change the equilibrium constant.

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

13.

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

The above reaction can be said to have reached equilibrium when

A the equilibrium constant K is equal to 1

B the reaction between the acid and the alcohol has stopped

C the concentrations of the products equal those of the reactants

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

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 temperature increases
A	+	decreases
B	+	increases
C	–	decreases
D	–	increases

15. 500 cm^3 of 0·022 $mol\,l^{-1}$ hydrochloric acid is mixed with 500 cm^3 of 0·020 $mol\,l^{-1}$ sodium hydroxide solution. The pH of the resulting solution will be

A 2

B 3

C 4

D 5.

16. The Bronsted-Lowry definition of a base is a substance which acts as a

A proton donor to form a conjugate acid

B proton donor to form a conjugate base

C proton acceptor to form a conjugate acid

D proton acceptor to form a conjugate base.

17. The mean bond enthalpy of the N–H bond is equal to one third of the value of ΔH for which change of the following changes?

A $NH_3(g) \rightarrow N(g) + 3H(g)$

B $2NH_3(g) \rightarrow N_2(g) + 3H_2(g)$

C $NH_3(g) \rightarrow \frac{1}{2}N_2(g) + 1\frac{1}{2}H_2(g)$

D $2NH_3(g) + 1\frac{1}{2}O_2(g) \rightarrow N_2(g) + 3H_2O(g)$

18. The entropy of a perfect crystal is zero at

A 0 K

B 25 K

C 273 K

D 298 K.

19. Which of the following reactions results in a **decrease** in entropy?

A $N_2O_4(g) \rightarrow 2NO_2(g)$

B $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

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

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

20. Which of the following is **not** a required condition for measuring standard electrode potentials?

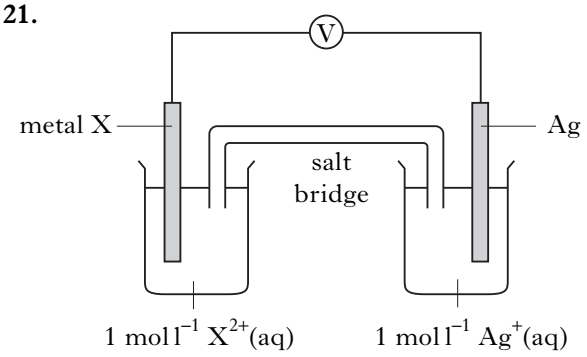
A Volume of 1 litre

B Temperature of 298 K

C Concentration of 1 mol l^{-1}

D Pressure of 1 atmosphere

21.



The E° values are

$X^{2+}(aq) + 2e^- \rightarrow X(s)$ $\quad E° = -0{\cdot}23\ V$

$Ag^+(aq) + e^- \rightarrow Ag(s)$ $\quad E° = 0{\cdot}80\ V$

In the above cell, which of the following is reduced?

A X(s)

B Ag(s)

C $X^{2+}(aq)$

D $Ag^+(aq)$

22. Under standard conditions, the emf of the cell

$$Al(s) \,|\, Al^{3+}(aq) \,||\, Cu^{2+}(aq) \,|\, Cu(s)$$

would be

A 1·34 V

B 2·02 V

C 2·34 V

D 4·38 V.

23. 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}

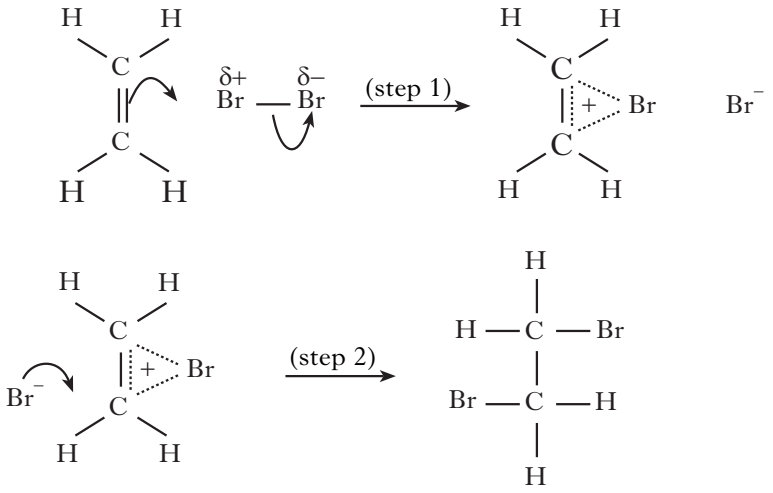
B $-144{\cdot}8$ kJ mol^{-1}

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

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

[Turn over

24.



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

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

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

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

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

25. In the homologous series of alkanols, increase in chain length from CH_3OH to $C_{10}H_{21}OH$ is accompanied by

A increased volatility and increased solubility in water

B increased volatility and decreased solubility in water

C decreased volatility and decreased solubility in water

D decreased volatility and increased solubility in water.

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

A The low density of ice compared to water

B The solubility of methoxymethane in water

C The higher boiling point of methanol compared to ethane

D The higher melting point of hydrogen compared to helium

27. A compound C_3H_8O does **not** react with sodium and is **not** reduced by lithium aluminium hydride. It is likely to be an

A acid

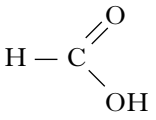
B ether

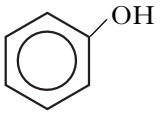
C alcohol

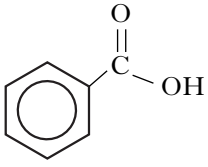
D aldehyde.

28. Which of the following is least acidic?

A CH_3OH

B 

C 

D 

29. Which statement about ethanol and its isomeric ether is true?

They

A have similar volatilities

B have similar infra-red spectra

C form the same products when burned in excess oxygen

D form the same products when reacted with acidified dichromate.

30. When 2-bromobutane is reacted with potassium cyanide and the compound formed is hydrolysed with dilute acid, the final product is

A butanoic acid

B pentanoic acid

C 2-methylbutanoic acid

D 2-methylpropanoic acid.

31. Which of the following compounds would liberate one mole of hydrogen gas if one mole of it reacts with excess sodium?

A C_2H_5OH

B CH_3CHO

C CH_3COOH

D $HOCH_2CH_2OH$

32. Two isomeric esters, **X** and **Y**, have the molecular formula $C_4H_8O_2$. Ester **X** on hydrolysis with sodium hydroxide solution gives CH_3CH_2COONa, and ester **Y** on similar treatment gives CH_3CH_2OH.

Which line in the table shows the correct names of **X** and **Y**?

	X	**Y**
A	propyl methanoate	ethyl ethanoate
B	methyl propanoate	ethyl ethanoate
C	methyl propanoate	ethyl methanoate
D	propyl methanoate	methyl propanoate

33. A white crystalline compound, soluble in water, was found to react with both dilute hydrochloric acid and sodium hydroxide solution.

Which of the following might it have been?

A C_6H_5OH

B $C_6H_5NH_2$

C C_6H_5COOH

D H_2NCH_2COOH

34. Which of the following amines has the lowest boiling point?

A $C_4H_9NH_2$

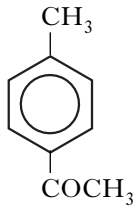
B $C_3H_7NHCH_3$

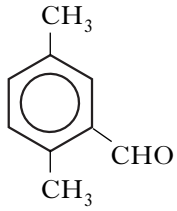
C $C_2H_5NHC_2H_5$

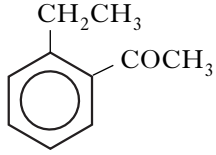
D $C_2H_5N(CH_3)_2$

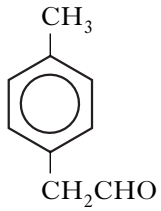
35. Spectral studies of an organic compound indicated the presence of a di-substituted benzene ring, two methyl groups and a molecular weight of 134.

Which of the following is a possible structure for the compound?

A 

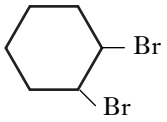
B 

C 

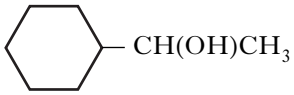
D 

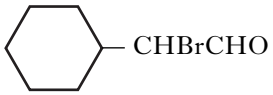
[Turn over

36. Which of the following molecules does **not** exhibit optical isomerism?

A 

B 

C 

D 

37. Which of the following could **not** exist in isomeric forms?

A C_2F_4

B C_3H_6

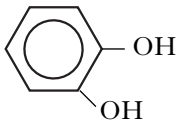
C C_3H_7Br

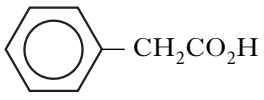
D $C_2H_4Cl_2$

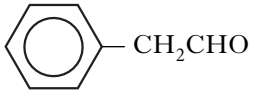
38. Elemental analysis of an organic compound showed it contained 70·6 % carbon, 23·5 % oxygen and 5·9 % hydrogen by mass.

The structural formula of the compound could be

A CH_2CHCH_2COOH

B 

C 

D 

39. An organic compound with empirical formula, C_2H_4O, has major peaks at 1715 cm^{-1} and 3300 cm^{-1} in its infrared spectrum.

The structural formula of the compound could be

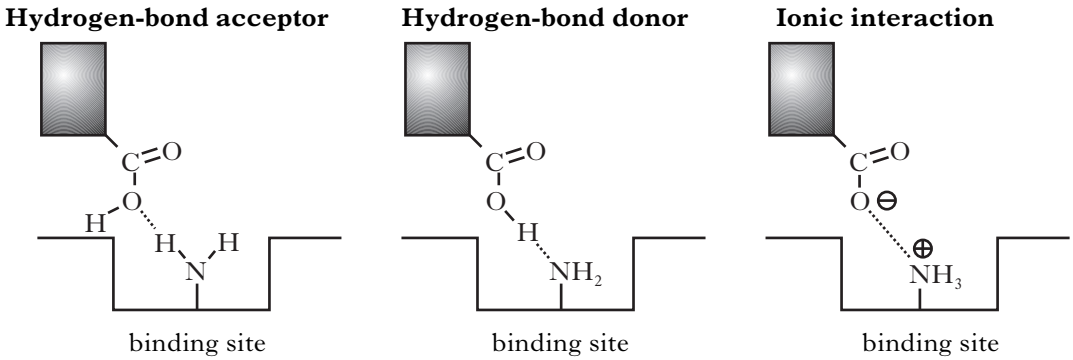
A CH_3CHO

B CH_3COOH

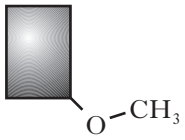
C $CH_3COOCH_2CH_3$

D $CH_3CH_2CH_2COOH$.

40. A drug containing a carboxyl group can bind to an amino group on a receptor site in three different ways.



The drug with the following structure



could bind to the same site

A only by ionic interaction

B only as a hydrogen-bond donor

C only as a hydrogen-bond acceptor

D both as a hydrogen-bond donor and acceptor.

[*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.

[Turn over for SECTION B on *Page ten*

SECTION B

60 marks are available in this section of the paper.

All answers must be written clearly and legibly in ink.

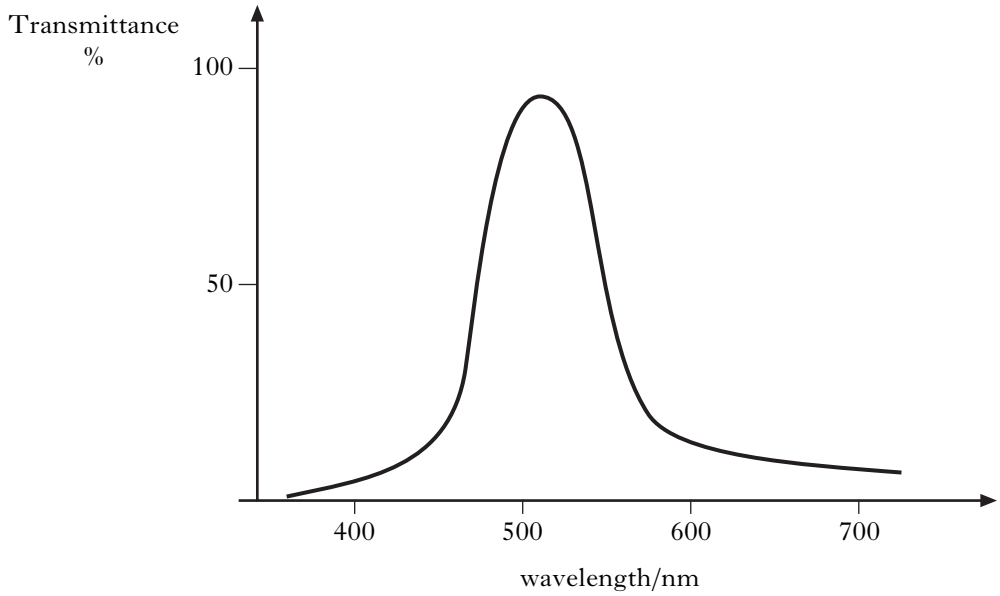
Marks

1. (*a*) What is the arrangement of the **electron pairs** around the iodine atom in an IF_5 molecule? **1**

(*b*) By considering the electron pairs, explain why the bond angle in BF_3 is greater than the bond angle in NF_3. **1**

(2)

2. An aqueous solution of the compound $[CoCl_2(NH_3)_4]Cl$ gave the following **transmittance** spectrum.



(*a*) From the above spectrum, deduce the colour of the solution. **1**

(*b*) The solution contains the complex ion $[CoCl_2(NH_3)_4]^+$.

(i) What is the oxidation number of cobalt in this complex ion? **1**

(ii) Name this complex ion. **1**

(iii) Write down the electronic configuration of cobalt in this complex ion in terms of s, p and d orbitals. **1**

(4)

3. Some metal salts emit light when heated in a Bunsen flame.

Lithium nitrate changes the flame colour to crimson.

Magnesium nitrate has no effect on the flame colour.

(*a*) Explain, in terms of electrons, why some metal salts emit light when heated in a Bunsen flame. **1**

(*b*) Suggest why magnesium nitrate has no effect on the flame colour. **1**

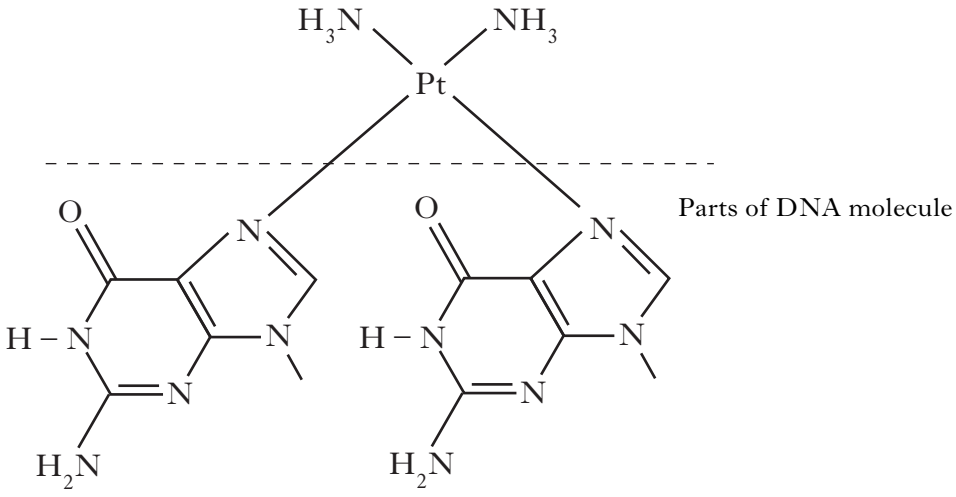
(*c*) Calculate the energy, in kJ mol^{-1}, associated with crimson light of wavelength 671 nm. **2**

(4)

Marks

4. *cis*-Platin is a highly successful anti-cancer drug. The formula for *cis*-platin is $[Pt(NH_3)_2Cl_2]$.

(*a*) *cis*-Platin works by forming a complex with parts of a DNA molecule. These parts of the DNA form bonds through nitrogen atoms to $Pt(NH_3)_2$ as shown below.



(i) Explain why DNA can be classified as a bidentate ligand in this complex. **1**

(ii) What feature of the DNA makes it suitable as a ligand? **1**

(*b*) Draw a possible structure for the geometric isomer of *cis*-platin. **1**

(3)

5. The equation for the decomposition of ammonium dichromate is

$$(NH_4)_2Cr_2O_7(s) \longrightarrow N_2(g) + 4H_2O(\ell) + Cr_2O_3(s)$$

Consider the following data for the reaction at 298 K.

Substance	$\Delta H_f°$/kJ mol^{-1}	S°/J K^{-1} mol^{-1}
$(NH_4)_2Cr_2O_7(s)$	–1806	336
$N_2(g)$	0	192
$H_2O(\ell)$	–286	70
$Cr_2O_3(s)$	–1140	81

(*a*) For the decomposition of $(NH_4)_2Cr_2O_7$, calculate

(i) $\Delta H°$ **1**

(ii) $\Delta S°$ **1**

(iii) $\Delta G°$. **2**

(*b*) Chromium burns in excess oxygen to form chromium(III) oxide. From the information in the table, deduce a value for the enthalpy of combustion of chromium. **1**

(5)

[Turn over

Marks

6. Sodium hypochlorite, NaClO, is the active ingredient in household bleach. The concentration of the hypochlorite ion, ClO^-, can be determined in two stages.

In stage 1, an acidified iodide solution is added to a solution of the bleach and iodine is formed.

$$ClO^-(aq) + 2I^-(aq) + 2H^+(aq) \rightarrow I_2(aq) + Cl^-(aq) + H_2O(\ell)$$

In stage 2, the iodine formed is titrated with sodium thiosulphate solution.

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

$10{\cdot}0\,cm^3$ of a household bleach was diluted to $250\,cm^3$ in a standard flask.

$25{\cdot}0\,cm^3$ of this solution was added to excess acidified potassium iodide solution.

The solution was then titrated with $0{\cdot}10\ mol\,l^{-1}$ sodium thiosulphate using an appropriate indicator.

The volume of thiosulphate solution required to reach the end point of the titration was $20{\cdot}5\,cm^3$.

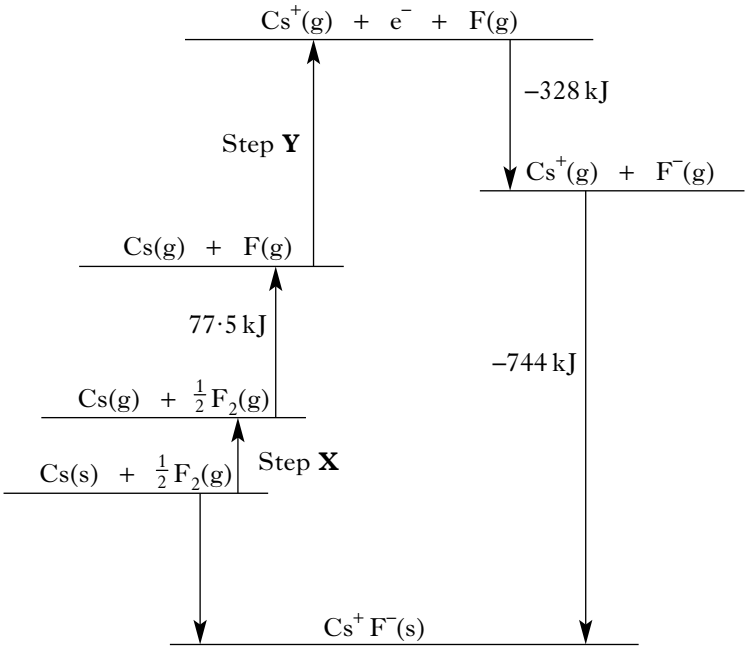
(*a*) Calculate the number of moles of **iodine** which reacted in the titration. **1**

(*b*) Calculate the concentration, in $mol\,l^{-1}$, of the ClO^- in the original household bleach. **2**

(3)

7. Consider the Born-Haber cycle below which represents the formation of caesium fluoride.

$$Cs(s) + \tfrac{1}{2}F_2(g) \longrightarrow Cs^+F^-(s)$$



(*a*) Use the Data Booklet to find the enthalpy values for Step **X** and Step **Y**. **2**

(*b*) Name the enthalpy change that has the value –744 kJ in this cycle. **1**

(*c*) Use this Born-Haber cycle to calculate the enthalpy of formation of caesium fluoride in $kJ\ mol^{-1}$. **1**

(4)

Marks

8. In a PPA, a student added 50 cm^3 of an aqueous iodine solution to 50 cm^3 of cyclohexane in a separating funnel. After shaking thoroughly, the funnel was left until the following equilibrium was established.

$$I_2(\text{aqueous}) \rightleftharpoons I_2(\text{cyclohexane})$$

Two layers were formed, each containing dissolved iodine. 10·0 cm^3 of each layer was titrated with sodium thiosulphate solution until the end point was reached.

The cyclohexane layer required 18·8 cm^3 of 0·025 mol l^{-1} sodium thiosulphate.

The aqueous layer required 10·5 cm^3 of 0·050 mol l^{-1} sodium thiosulphate.

(*a*) Which indicator is used to show that the end point has been reached? **1**

(*b*) Calculate the concentration of iodine in

(i) the cyclohexane layer **1**

(ii) the aqueous layer. **1**

(*c*) Calculate the partition coefficient for iodine between the two solvents. **1**

(*d*) If 100 cm^3 of cyclohexane had been used instead of the 50 cm^3, what effect would this have on

(i) the concentration of iodine in the aqueous layer **1**

(ii) the value of the partition coefficient? **1**

(6)

[Turn over

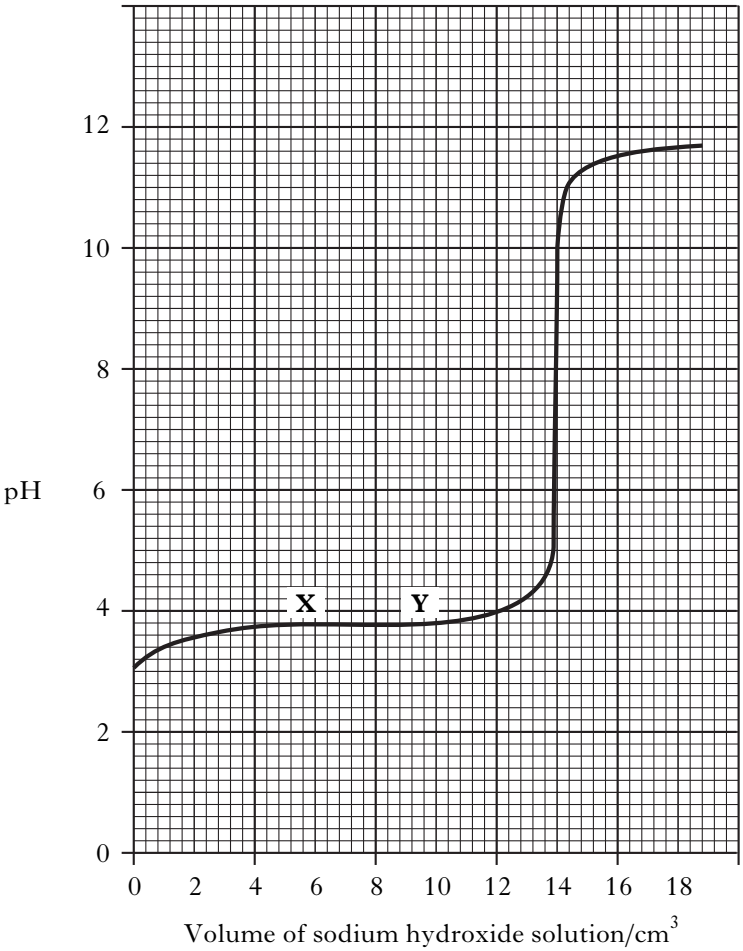
Marks

9. Hydrofluoric acid, HF, is a weak acid.

$$HF(aq) + H_2O(\ell) \rightleftharpoons H_3O^+(aq) + F^-(aq)$$

A student neutralised 25 cm^3 of hydrofluoric acid solution with sodium hydroxide solution and followed the reaction by measuring the pH.

The graph obtained for this reaction is shown below.



(*a*) Write the expression for the dissociation constant, K_a, of hydrofluoric acid. **1**

(*b*) When exactly half the acid has been neutralised, $pK_a = pH$.
Using only information from the graph, deduce pK_a and thus calculate K_a for hydrofluoric acid. **2**

(*c*) The region **XY** on the graph is sometimes referred to as the buffer region.
Apart from HF, what else is present in the solution which enables it to act as a buffer? **1**

(*d*)

Indicator	pK_{In}
Methyl orange	3·7
Alizarin red	6·6
Cresol red	8·0
Alizarin yellow	11·1

Which of the above indicators could be used to detect the end point of this neutralisation reaction? **1**

(5)

Marks

10. A mixture of butan-1-ol and butan-2-ol can be synthesised from 1-bromobutane in a two stage process.

$$CH_3CH_2CH_2CH_2Br \xrightarrow[\textbf{Stage 1}]{KOH/C_2H_5OH} CH_3CH_2CH{=}CH_2 \xrightarrow[\textbf{Stage 2}]{H_2O/H^+} \begin{matrix}\text{butan-1-ol}\\+\\\text{butan-2-ol}\end{matrix}$$

(*a*) What type of reaction is taking place in **Stage 1**? **1**

(*b*) The bonding in but-1-ene can be described in terms of sp^2 and sp^3 hybridisation and sigma and pi bonds.

(i) What is meant by sp^2 hybridisation? **1**

(ii) What is the difference in the way atomic orbitals overlap to form sigma and pi bonds? **1**

(*c*) Draw a structural formula for the major product of **Stage 2**. **1**

(*d*) 1-Bromobutane reacts with hydroxide ions in a nucleophilic substitution reaction to produce butan-1-ol. The following results were obtained for this reaction.

Experiment	[1-Bromobutane]/mol l^{-1}	$[OH^-]$/mol l^{-1}	Initial rate/mol l^{-1} s^{-1}
1	0·25	0·10	$3{\cdot}3 \times 10^{-6}$
2	0·50	0·10	$6{\cdot}6 \times 10^{-6}$
3	0·50	0·20	$1{\cdot}3 \times 10^{-5}$

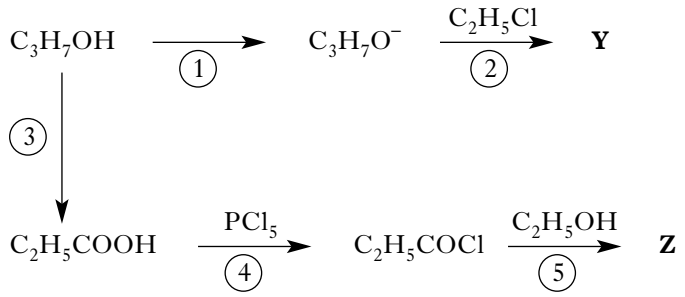
(i) What is the overall order of this reaction? **1**

(ii) Calculate a value for the rate constant of this reaction, giving the appropriate units. **2**

(iii) Outline the mechanism for this nucleophilic substitution reaction using structural formulae. **2**

(9)

11. A student devised the following reaction sequence starting from propan-1-ol, C_3H_7OH.



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

(i) Step (1)

(ii) Step (3). **2**

(*b*) Name **Y**. **1**

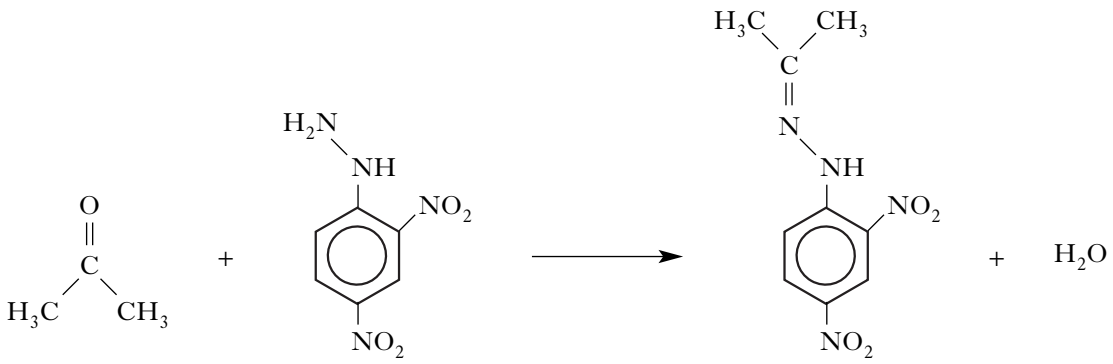
(*c*) Draw a structural formula for **Z**. **1**

(4)

[Turn over

Marks

12. In a PPA, propanone reacts with 2,4-dinitrophenylhydrazine to make the 2,4-dinitrophenylhydrazone derivative as shown below.



propanone 2,4-dinitrophenylhydrazine 2,4-dinitrophenylhydrazone derivative

(*a*) What type of reaction is this? **1**

(*b*) The 2,4-dinitrophenylhydrazone derivative formed in the reaction is impure.

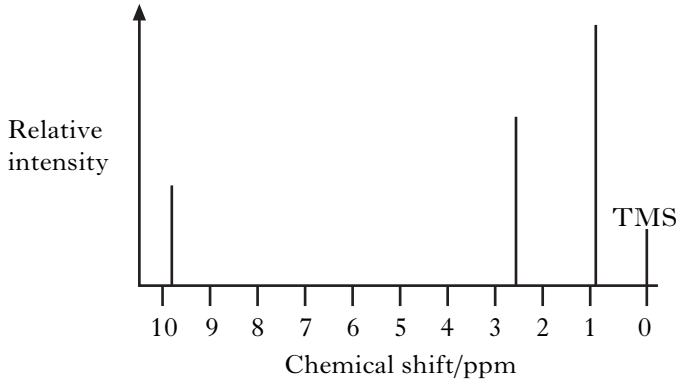
(i) How would the derivative be purified? **1**

(ii) How can the technique of derivative formation be used to identify an unknown ketone? **1**

(*c*) Propanone has an isomer. The shortened structural formula of this isomer is CH_3CH_2CHO.

(i) Which chemical reagent could be used to distinguish between propanone and this isomer and what would be the result? **1**

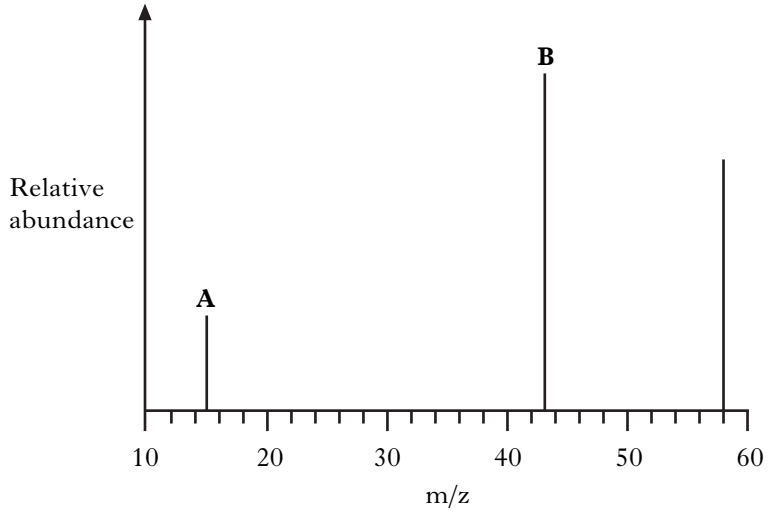
(ii) Nuclear magnetic resonance spectroscopy can also be used to distinguish between these two isomers. The proton nmr spectrum for CH_3CH_2CHO is shown.



Sketch the proton nmr spectrum you would obtain for propanone. **1**

12. (*c*) (continued)

(iii) A simplified mass spectrum for propanone is shown below.



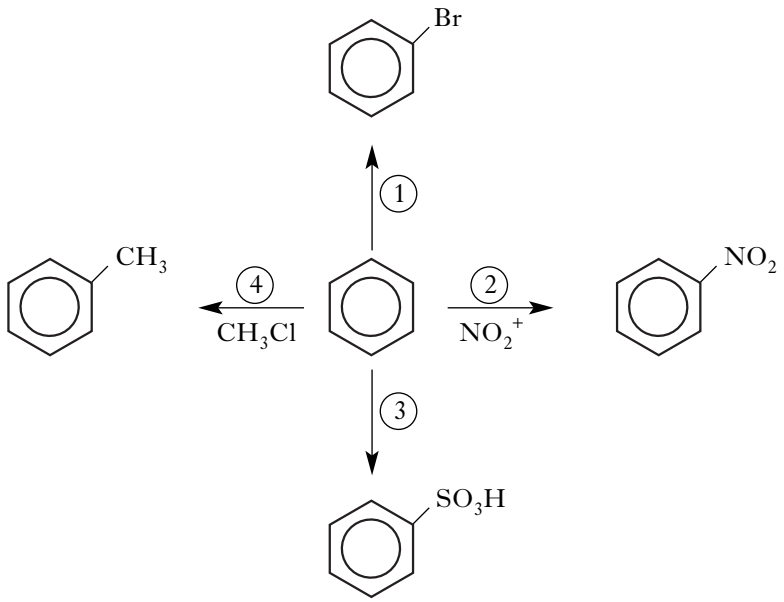
Identify the ion fragments responsible for peaks **A** and **B**. **1**

(6)

[Turn over for Question 13 on *Page eighteen*

Marks

13. A student devised the following reaction scheme starting with benzene.



(*a*) What type of reaction does benzene undergo in reactions (1) – (4)? **1**

(*b*) Name a suitable reagent and catalyst for reaction (1). **1**

(*c*) Reaction (2) involves nitration of benzene.
Which reagents are used to produce the NO_2^+ ion? **1**

(*d*) What is the molecular formula for the product of reaction (3)? **1**

(*e*) The product of reaction (4) was reacted with bromine in the presence of light.
Draw a structural formula for an organic product of this reaction. **1**

(5)

[*END OF QUESTION PAPER*]

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