X012/701

NATIONAL 2010

WEDNESDAY, 2 JUNE QUALIFICATIONS 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 examination, 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 \mathbf{D} .



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1. An atom of iron contains 26 electrons.

Which of the following diagrams below correctly represents the distribution of electrons in the 3d and 4s orbitals in an atom of iron in its ground state?

	3d	4s
A	$\uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \uparrow \downarrow $	
В	$\boxed{\uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \uparrow \uparrow}$	
С	$\uparrow \downarrow \uparrow \downarrow \uparrow \uparrow \uparrow \uparrow \uparrow$	↑
D	$\uparrow \downarrow \uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \uparrow$	↑ ↓

2. An atom has the electronic configuration

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

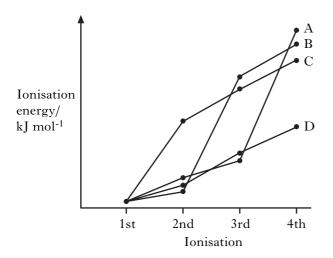
What is the charge on the most probable ion formed by this element?

- A +1
- B +2
- C +3
- D +4

3. 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.

4. Which line in the graph represents the trend in successive ionisation energies of a Group 2 element?

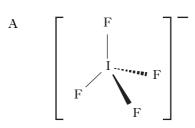


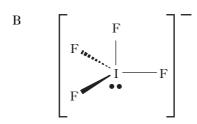
5. Which of the following statements about atomic emission spectroscopy is **incorrect**?

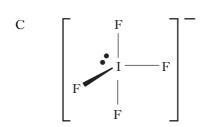
- A Each element provides a characteristic spectrum.
- B Visible light is used to promote electrons to higher energy levels.
- C The lines arise from electron transitions between one energy level and another.
- D The quantity of the element can be determined from the intensity of radiation transmitted.

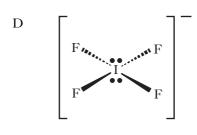
6. Which of the following diagrams best represents the arrangement of atoms in the IF_4 -ion?

Note: a lone pair of electrons is represented by ullet









[Turn over

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- 7. Which of the following solids is likely to have the same type of crystal lattice structure as caesium chloride?
 - A Ba²⁺O²⁻
 - ${
 m B} {
 m Fe^{2+}O^{2-}}$
 - C Ag⁺I⁻
 - D Ni²⁺O²⁻
- 8. An ionic hydride is added to water.

Which line in the table correctly describes the gas produced and the type of solution formed?

	Gas produced	Type of solution formed
A	hydrogen	acidic
В	hydrogen	alkaline
С	oxygen	acidic
D	oxygen	alkaline

9. An element forms an oxide which is a gas at room temperature.

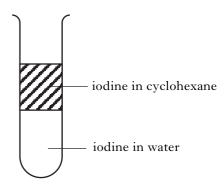
Which type of bonding is likely to be present in the element?

- A Ionic
- B Metallic
- C Polar covalent
- D Non-polar covalent
- **10.** Which of the following oxides would produce the solution with the greatest conductivity when 0·1 mol is added to 250 cm³ of water?
 - A SO₂
 - B CO,
 - C Na₂O
 - D Al₂O₃
- 11. $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g) \Delta H^\circ = 92 \text{ kJ mol}^{-1}$

The conditions favouring the decomposition of ammonia are

- A low pressure and low temperature
- B high pressure and low temperature
- C low pressure and high temperature
- D high pressure and high temperature.

12. An aqueous solution of iodine was shaken with cyclohexane until equilibrium was established.



Some solid iodine was added to the test tube and the contents shaken until equilibrium was re-established.

Which line in the table shows the effects caused by the addition of the solid iodine?

	Concentration of iodine in water	Concentration of iodine in cyclohexane	Partition coefficient
A	increases	increases	no change
В	increases	increases	increases
С	no change	increases	no change
D	increases	no change	increases

- **13.** An acid is a substance which
 - A donates a proton leaving a conjugate acid
 - B donates a proton leaving a conjugate base
 - C accepts a proton leaving a conjugate acid
 - D accepts a proton leaving a conjugate base.
- **14.** The pH ranges over which some indicators change colour are shown below.

Which line in the table shows the indicator most suitable for the titration of hydrochloric acid with ammonia solution?

	Indicator	pH range
A	Methyl orange	4.2 - 6.3
В	Bromothymol blue	6.0 - 7.6
С	Phenol red	6.8 - 8.4
D	Phenolphthalein	8.3 – 10.0

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

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

$${\rm B} \quad {\rm Mg^{2+}(g) + 2Br^{-}(g) \to Mg^{2+}(Br^{-})_2(g)}$$

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

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

16. The standard enthalpy of combustion of hydrogen is -286 kJ mol⁻¹.

The standard enthalpy of formation of water, in kJ mol⁻¹, is

- **17.** Which of the following enthalpy changes can be measured directly by experiment?
 - A Bond enthalpy of C-H bond
 - B Enthalpy of formation of ethane
 - C Lattice enthalpy of magnesium oxide
 - D Enthalpy of solution of potassium chloride
- **18.** In which of the following does X represent the bond enthalpy for the O–H bond in water?

A
$$H_2O(g) \rightarrow O(g) + H_2(g)$$
 $\Delta H = 2X$

B
$$H_2O(g) \rightarrow O(g) + 2H(g) \Delta H = 2X$$

C
$$H_2O(g) \rightarrow O(g) + H_2(g) \Delta H = X$$

D
$$H_2O(g) \rightarrow O(g) + 2H(g) \Delta H = X$$

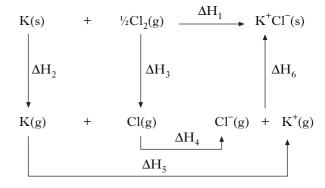
19. The enthalpy change for

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

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.

Questions 20 and 21 refer to the Born-Haber cycle below.



- **20.** The enthalpy change which requires the input of most energy is
 - A ΔH_2
 - B ΔH_3
 - $C \Delta H_4$
 - D ΔH_5 .
- 21. The main enthalpy term which ensures that ΔH_1 is exothermic is
 - A ΔH_3
 - B ΔH_4
 - C ΔH₅
 - D ΔH_6 .
- 22. Which line in the table shows the correct signs of ΔG° and E° for a feasible reaction occurring under standard conditions?

	ΔG°	E°
A	+	+
В	+	_
С	_	+
D	_	_

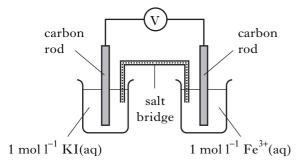
23. For the following cell

$$Ni(s)$$
 $Ni^{2+}(aq)$ $Cu^{2+}(aq)$ $Cu(s)$

the species being reduced is

- A Ni(s)
- B Ni²⁺(aq)
- $C \quad Cu^{2+}(aq)$
- D Cu(s).

24.



In the electrochemical cell shown above, operating under standard conditions, the emf produced would be

- A 0.23 V
- B 0.58 V
- C 1.00 V
- D 2.88 V.

25.
$$C_3H_7C1 + C_2H_5O^- \rightarrow C_3H_7OC_2H_5 + CI^-$$

The above reaction is

- A an elimination reaction
- B a nucleophilic addition reaction
- C a nucleophilic substitution reaction
- D an electrophilic substitution reaction.
- **26.** Which of the following does **not** occur in the reaction between methane and chlorine?
 - A A chain reaction
 - B Homolytic fission
 - C Free radical formation
 - D An addition reaction

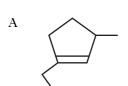
27. Which of the following compounds is likely to be the most soluble in water?

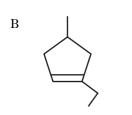
- **28.** The sideways overlap of two parallel atomic orbitals lying perpendicular to the axis of the bond is known as
 - A hybridisation
 - B a pi bond
 - C a sigma bond
 - D a double bond.

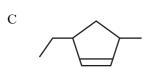
29. If the structure of 3-methylcyclobutene can be represented by

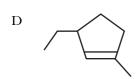


then the structure of 1-ethyl-3-methylcyclopentene will be represented by









30. Caryophyllene $(C_{15}H_{24})$ is an unsaturated cyclic hydrocarbon.

Complete hydrogenation of caryophyllene gives a saturated hydrocarbon $\rm C_{15}H_{28}.$

Which line in the table shows the correct numbers of double bonds and rings in caryophyllene?

	Number of double bonds	Number of rings
A	2	1
В	2	2
С	4	2
D	4	4

- **31.** Which of the following is most reactive as a nucleophile?
 - A Br₂
 - B CH₂I
 - C NH₄+
 - D NH₃
- 32. Hydrogen bonding occurs in
 - A CH₃I
 - B CH₃OH
 - C CH₃OCH₃
 - D CH₃CH₂CHO.
- **33.** Cinnamaldehyde, which can be extracted from cinnamon, has the structure:

Cinnamaldehyde will not react with

- A sodium metal
- B bromine solution
- C lithium aluminium hydride
- D acidified potassium dichromate.
- **34.** Which of the following compounds would be produced by passing ammonia gas into dilute ethanoic acid?
 - A CH₃CONH₂
 - B CH₃COO⁻NH₄⁺
 - C NH₂CH₂COOH
 - D CH₃CH₂NH₃⁺Cl⁻

[Turn over

35. Secondary amines react with carbonyl compounds to form unsaturated amines known as enamines as shown

$$\begin{array}{c} R \\ NH + H \\ H_{3}C \\ H \end{array} = 0 \longrightarrow \begin{array}{c} R \\ N-C \\ H_{3}C \\ H_{3}C \\ \end{array}$$

an enamine

Which carbonyl compound would react with (CH₃)₂NH to form the enamine with the following structure?

$$H_3C$$
 $N-C$
 $C-H$
 H_3C

- A Propanal
- B Propanone
- C Butanal
- D Butanone

36.
$$\frac{\text{HNO}_3 / \text{H}_2 \text{SO}_4}{} \longrightarrow \text{Product } \mathbf{X}$$

Which line in the table is correct for the reaction above?

		Type of reaction	Product X
	A	electrophilic substitution	${\bigcap^{\mathrm{NO}_2}}$
]	В	electrophilic substitution	SO_3H
•	С	nucleophilic substitution	${\bigcap}^{\mathrm{NO}_2}$
]	D	nucleophilic substitution	SO ₃ H

- **37.** Which of the following statements about the benzene molecule is **not** true?
 - A It is planar.
 - B It has empirical formula CH.
 - C It is readily attacked by bromine.
 - D Its C—C bonds are equal in length.
- **38.** Which of the following could **not** exist in isomeric forms?
 - A C_3H_6
 - $B C_3H_8$
 - C C₃H₇Br
 - $D C_2H_4Cl_2$
- **39.** Which of the following causes the separation of the ions in a mass spectrometer?
 - A A magnetic field
 - B A vacuum pump
 - C An ionisation chamber
 - D Electron bombardment
- **40.** Which of the following compounds is most likely to show an infra-red absorption at 2725 cm⁻¹?

$$\begin{array}{ccc} \mathbf{A} & & \mathbf{C}\mathbf{H}_3 - \mathbf{C} - \mathbf{C}\mathbf{H}_3 \\ & & & & \\ \mathbf{O} & & & \\ \end{array}$$

B
$$HOCH_2CH = CH_2$$

$$C \quad CH_3 - CH_2 - C \\ \begin{matrix} \\ \end{matrix} \\ H$$

$$\mathbf{D} \quad \mathbf{CH_3} - \mathbf{O} - \mathbf{CH} = \mathbf{CH_2}$$

SECTION B

60 marks are available in this section of the paper.

All answers must be written clearly and legibly in ink.

Marks

- 1. The first argon compound was prepared by shining light of wavelength 160 nm onto a mixture of argon and hydrogen fluoride at a temperature of 7.5 K. The hydrogen fluoride reacted with the argon to form HArF.
 - (a) Calculate the energy, in kJ mol⁻¹, associated with light of wavelength 160 nm.

2

- (b) Supposing HArF is covalent,
 - (i) predict the total number of electron pairs, bonding and non-bonding, which surround the Ar atom in the HArF molecule.

1

(ii) what shape do the electron pairs around the Ar atom in an HArF molecule adopt?

1 (4)

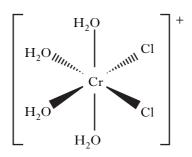
- **2.** Complex ions **A** and **B** are isomeric and have the formula $[Cr(H_2O)_4Cl_2]^+$.
 - (a) Calculate the oxidation number of chromium in the complex ion.

1

(b) Name the complex ion.

1

(c) The structural formula for complex ion \mathbf{A} is



Draw the structural formula for complex ion **B**.

1

(3)

[Turn over

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3. The Thermit process can be used to extract iron from iron(III) oxide.

$$2\mathrm{Al}(\mathrm{s}) + \mathrm{Fe_2O_3}(\mathrm{s}) \rightarrow 2\mathrm{Fe}(\mathrm{s}) + \mathrm{Al_2O_3}(\mathrm{s})$$

Substance	Substance Standard enthalpy of formation, $\Delta H^{\circ}/kJ$ mol ⁻¹	
Al(s)	0	28.0
Fe ₂ O ₃ (s)	-824	87.0
Fe(s)	0	27.0
Al ₂ O ₃ (s)	-1676	51.0

For the Thermit process, use the data in the table to calculate

(a) the standard enthalpy change, ΔH°

(b) the standard entropy change, ΔS°

1

1

(c) the standard free energy change, ΔG° .

2 (4)

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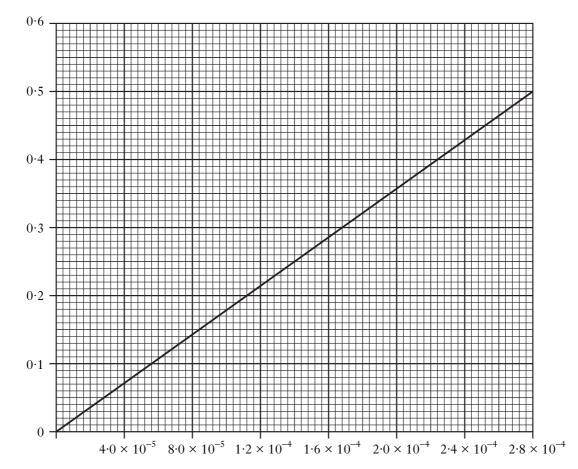
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4. In a PPA, a sample of steel was treated in a sequence of reactions to determine the manganese content.

$$\operatorname{Mn}(s) \xrightarrow{\hspace{1cm} \operatorname{HNO}_3 \hspace{1cm}} \operatorname{Mn}^{2+}(\operatorname{aq}) \xrightarrow{\hspace{1cm} \operatorname{KIO}_4 \hspace{1cm}} \operatorname{MnO}_4^-(\operatorname{aq})$$

The absorbance of a sample of the permanganate solution formed was analysed using a colorimeter fitted with a 520 nm filter. Optically matched cuvettes were used throughout.

- (a) (i) Apart from the steel dissolving in the hot nitric acid, what would have been observed at step one?
 - (ii) In step two, $\mathrm{Mn}^{2+}(\mathrm{aq})$ is converted into $\mathrm{MnO_4}^-(\mathrm{aq})$. What is the role of the potassium periodate, $\mathrm{KIO_4}$?
 - (iii) Why was a 520 nm filter used?
- (b) A series of standard permanganate solutions were used to produce the calibration graph below.



Concentration of permanganate solution/mol l⁻¹

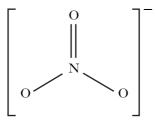
The results of the experiment are shown below.

Absorbance

Mass of steel used $= 0.19 \,\mathrm{g}$ Absorbance of permanganate solution = 0.25Total volume of permanganate solution $= 100 \,\mathrm{cm}^3$

Use the graph and the results to calculate the percentage, by mass, of manganese in the sample of steel.

5. The nitrate ion has three equivalent resonance structures. One of these structures is shown below.



- (a) Draw a similar diagram to show one of the other two resonance structures.
- (b) The formal charge on an atom in a resonance structure can be found using the expression

Formal charge =
$$\begin{pmatrix} Group & in \\ Periodic & Table \end{pmatrix} - \begin{pmatrix} Number & of lone & pair \\ electrons \end{pmatrix} - \frac{1}{2} \begin{pmatrix} Number & of bonding \\ electrons \end{pmatrix}$$
.

Use this expression to find the formal charge on atoms (b), (c) and (d) shown in the table below.

Resonance structure	Atom	Formal charge
[(b) O] -	(a)	+1
(a) N	(b)	?
	(c)	?
L	(d)	?

2

(3)

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1 2

(6)

1

1

(5)

1

3

(4)

6. The formula of potassium hydrogen oxalate can be written as $K_xH_v(C_2O_4)_z$.

In an experiment to determine the values of \mathbf{x} , \mathbf{y} and \mathbf{z} , $4.49\,\mathrm{g}$ of this compound was dissolved in water and the solution made up to one litre.

(a) $20 \cdot 0 \text{ cm}^3$ of the solution was pipetted into a conical flask and then titrated with $0 \cdot 0200 \text{ mol l}^{-1}$ acidified potassium permanganate at $60 \,^{\circ}\text{C}$. The average titre volume was $16 \cdot 5 \, \text{cm}^3$.

The equation for the reaction taking place in the conical flask is

$$5C_2O_4^{2-} + 16H^+ + 2MnO_4^- \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O_3$$

- (i) What colour change would indicate the end point of the titration?
- From the titration result, calculate the number of moles of oxalate ions, $C_2O_4^{2-}$, in 20.0 cm^3 of the solution.
- (iii) Calculate the mass of oxalate ions in one litre of the solution.
- (iv) Using another analytical procedure, 4·49 g of potassium hydrogen oxalate was found to contain 0·060 g of hydrogen.

Use this information with the answer to (a)(iii) to calculate the mass of potassium in this sample.

- (b) Calculate the values of \mathbf{x} , \mathbf{y} and \mathbf{z} .
- 7. The expression for the equilibrium constant of an esterification reaction is

$$\mathrm{K}\text{=}\frac{[\mathrm{CH_{3}COOCH_{2}CH_{3}}]\,[\mathrm{H_{2}O}]}{[\mathrm{CH_{3}COOH}]\,[\mathrm{CH_{3}CH_{2}OH}]}$$

- (a) Write the chemical equation for this esterification reaction.
- (b) In an experiment to determine the value of the equilibrium constant, 0.70 moles of ethanoic acid and 0.68 moles of ethanol were mixed in a conical flask. The flask was stoppered to prevent the contents escaping and then placed in a water bath at 50 °C.

At equilibrium the mixture contained 0.24 moles of ethanoic acid.

- (i) Why is it important to prevent the contents of the flask escaping?
- (ii) Calculate K at 50 °C.
- **8.** Nicotinic acid is used in the treatment of high cholesterol levels. A structural formula for nicotinic acid is

- (a) Write an equation to show the dissociation of nicotinic acid in water.
- (b) The K_a value of nicotinic acid is 1.4×10^{-5} .

 Calculate the concentration of a nicotinic acid solution which has a pH of 3.77.

1

2

(5)

9. The rate equation for the reaction between nitrogen dioxide and fluorine is

Rate =
$$k[NO_2][F_2]$$

A proposed reaction mechanism is

Step one $NO_2 + F_2 \rightarrow NO_2F + F$

Step two $NO_2 + F \rightarrow NO_2F$.

- (a) Which step in the proposed reaction mechanism would be **faster**?
- (b) Write a balanced equation for the overall reaction.
- (c) What is the overall order of the reaction?

(d)	Experiment	$[NO_2]/mol\ l^{-1}$	$[F_2]/\text{mol } l^{-1}$	Initial rate/ mol l ⁻¹ s ⁻¹
	1	0.001	0.003	1.2×10^{-4}
	2	0.006	0.001	2.4×10^{-4}
	3	0.002	0.004	3.2×10^{-4}

Use the data in the table to calculate a value for the rate constant, k, including the appropriate units.

10. Alkenes can be prepared from alcohols.

In a PPA, 22·56 g of cyclohexanol was dehydrated using an excess of concentrated phosphoric acid. The reaction mixture was then distilled. The crude cyclohexene was added to a separating funnel containing a solution which was used to wash the cyclohexene and improve the separation of the aqueous and organic layers. The organic layer was separated and treated with anhydrous calcium chloride before it was distilled to yield 6·52 g of pure cyclohexene.

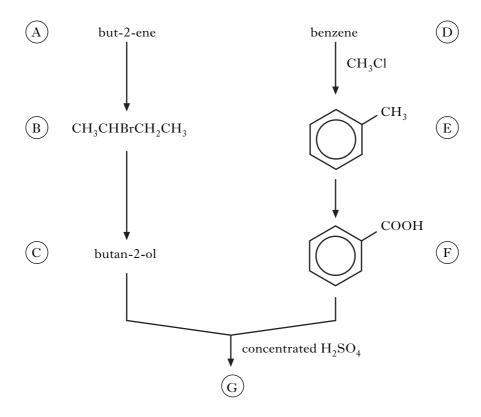
- (a) Why was concentrated phosphoric acid used as the dehydrating agent rather than concentrated sulphuric acid?
- (b) Name the solution that the crude cyclohexene was added to in the separating funnel.
- (c) What was the function of the anhydrous calcium chloride?
- (d) The relative formula masses of cyclohexanol and cyclohexene are 100 and 82 respectively. Calculate the percentage yield of cyclohexene.

2 (5)

1

[X012/701] Page fourteen

11. Consider the following reaction scheme.



(a) Explain why but-2-ene exhibits geometric isomerism yet its structural isomer but-1-ene does not.

1

(b) But-2-ene undergoes electrophilic addition to form B.
Draw a structure for the carbocation intermediate formed in this electrophilic addition reaction.

1

(c) Name a reagent used to convert B to C .

1

(d) Name a catalyst required in converting \bigodot to \bigodot .

1

1

(e) Draw a structural formula for ester \widehat{G} .

(5)

[Turn over

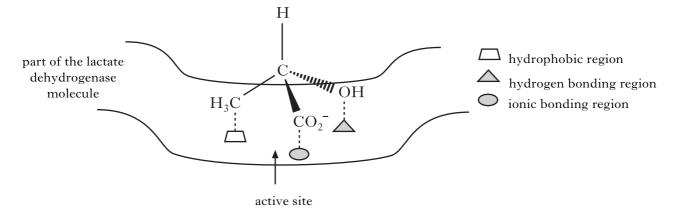
[X012/701] Page fifteen

12. Consider the following reaction sequence.

A
$$\xrightarrow{\text{HCN}}$$
 $H_3C - \overset{\text{OH}}{C} - \overset{\text{H}_2\text{O}/\text{H}^+}{H_2\text{O}/\text{H}^+}$ $H_3C - \overset{\text{OH}}{C} - \overset{\text{I}}{H_2\text{O}/\text{H}^+}$ $H_3C - \overset{\text{OH}}{C} - \overset{\text{I}}{H_2\text{O}/\text{H}^+}$ $H_3C - \overset{\text{OH}}{H_2\text{O}/\text{H}^+}$ $H_3C -$

- (a) Name compound **A**.
- (b) To which class of organic compounds does compound **B** belong?
- (c) Name the type of reaction taking place in converting compound **B** into lactic acid.
- (d) Lactic acid in the form of lactate ions is dehydrogenated in the liver by the enzyme, lactate dehydrogenase.

The diagram shows how one of the optical isomers of the lactate ion binds to an active site of lactate dehydrogenase.



- (i) Which type of intermolecular force is involved when the methyl group of the lactate ion binds to the hydrophobic region of the active site?
- (ii) Draw a structure for the other optical isomer of the lactate ion.
- (iii) Explain why this other optical isomer of the lactate ion cannot bind as efficiently to the active site of lactate dehydrogenase.

1 (6)

1

[X012/701] Page sixteen

- **13.** Compound **A** has molecular formula $C_4H_{10}O$.
 - (a) To which two classes of organic compounds could A belong?

1 1

(4)

(b) Compound $\bf A$ reacts with acidified potassium dichromate solution to form $\bf B$ which has molecular formula C_4H_8O .

The proton nmr spectrum of ${\bf B}$ shows three peaks. Analysis of this spectrum produces the following data.

Peak	Chemical shift/ppm	Relative area under peak
1	0.95	3
2	2.05	3
3	2.35	2

Considering all the evidence above:

(i)	draw a structural formula for ${f B}$;	
(::)		

(ii) name **A**.

 $[END\ OF\ QUESTION\ PAPER]$

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