Cambridge Assessment International Education

Cambridge International AS & A Level

CANDIDATE NAME

CENTRE NUMBER

CANDIDATE NUMBER

3731431728

CHEMISTRY **9701/42**

Paper 4 A Level Structured Questions **May/June 2020**

2 hours

You must answer on the question paper.

You will need: Data booklet

INSTRUCTIONS

- Answer **all** questions.
- Use a black or dark blue pen. You may use an HB pencil for any diagrams or graphs.
- Write your name, centre number and candidate number in the boxes at the top of the page.
- Write your answer to each question in the space provided.
- Do **not** use an erasable pen or correction fluid.
- Do **not** write on any bar codes.
- You may use a calculator.
- You should show all your working, use appropriate units and use an appropriate number of significant figures.

INFORMATION

- The total mark for this paper is 100.
- The number of marks for each question or part question is shown in brackets [ ].

This document has **24** pages. Blank pages are indicated.

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Answer **all** the questions in the spaces provided.

1 $EDTA^{4-}$, is a polydentate ligand.

(a) (i) Explain what is meant by the term *polydentate ligand*.

.....

.....

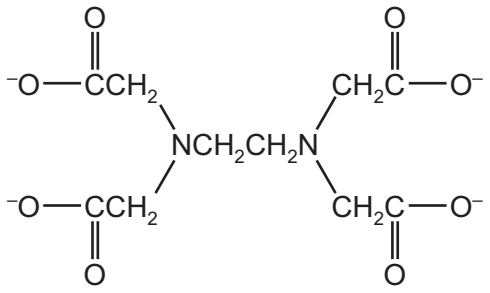
..... [2]

(ii) When a solution containing $EDTA^{4-}$ is added to a solution containing $[Cd(H_2O)_6]^{2+}$ a new complex is formed, $[CdEDTA]^{2-}$.

equilibrium **1** $[Cd(H_2O)_6]^{2+} + EDTA^{4-} \rightleftharpoons [CdEDTA]^{2-} + 6H_2O$

Circle, on the structure of $EDTA^{4-}$, the **six** atoms that form bonds with the metal ion.

$EDTA^{4-}$



[1]

(iii) Write an expression for the stability constant, K_{stab1}, for equilibrium **1**, and state its units.

K_{stab1} =

units = ...
[2]

(b) Cadmium ions form complexes with methylamine, CH_3NH_2, and with 1,2-diaminoethane, $H_2NCH_2CH_2NH_2$, as shown in equilibriums **2** and **3**. 1,2-diaminoethane is shown as en.

equilibrium **2** $[Cd(H_2O)_6]^{2+} + 4CH_3NH_2 \rightleftharpoons [Cd(CH_3NH_2)_4(H_2O)_2]^{2+} + 4H_2O \quad K_{stab2} = 3.60 \times 10^6$

equilibrium **3** $[Cd(H_2O)_6]^{2+} + 2en \rightleftharpoons [Cd(en)_2(H_2O)_2]^{2+} + 4H_2O \quad K_{stab3} = 4.20 \times 10^{10}$

An equilibrium is set up between these two complexes as shown in equilibrium **4**.

equilibrium **4** $[Cd(CH_3NH_2)_4(H_2O)_2]^{2+} + 2en \rightleftharpoons [Cd(en)_2(H_2O)_2]^{2+} + 4CH_3NH_2 \quad \Delta H^\ominus = +0.840\,kJ\,mol^{-1}$, $\Delta S^\ominus = +80.9\,J\,K^{-1}\,mol^{-1}$

(i) K_{eq4} is the equilibrium constant for equilibrium **4**.

Write an expression for K_{eq4} in terms of K_{stab2} and K_{stab3}.

K_{eq4} =

[1]

(ii) Calculate the value of the standard Gibbs free energy change, $\Delta G^\ominus$, for equilibrium **4** at 298 K.

$\Delta G^\ominus$ = ... $kJ\,mol^{-1}$ [2]

(iii) State how the value of $\Delta G^\ominus$ changes as the temperature increases. Explain your answer.

.....

.....

..... [1]

[Total: 9]

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[Turn over

2 **(a)** Describe and explain how the solubility of the Group 2 sulfates varies down the group.

.....

.....

.....

.....

.....

..... [4]

(b) The trend in the decomposition temperatures of Group 2 peroxides, MO_2, is similar to that of Group 2 carbonates.

Suggest which of barium peroxide, BaO_2, and calcium peroxide, CaO_2, will decompose at the **lower** temperature. Explain your answer.

.....

.....

..... [2]

(c) Magnesium iodate(V), $Mg(IO_3)_2$, decomposes when heated to form magnesium oxide, oxygen and iodine.

Construct an equation for this reaction.

..... [1]

(d) Calcium iodate(V), $Ca(IO_3)_2$, is sparingly soluble in water.
The concentration of its saturated solution is 5.6×10^{-3} mol dm^{-3} at 298 K.

(i) Write an expression for the solubility product, K_{sp}, of $Ca(IO_3)_2$, and state its units.

K_{sp} =

units = ... [2]

(ii) Calculate the numerical value for K_{sp} $Ca(IO_3)_2$ at 298 K.

K_{sp} = ... [1]

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(iii) When a few cm^3 of concentrated $Ca(NO_3)_2(aq)$ is added to a saturated solution of $Ca(IO_3)_2$ a white precipitate forms.

Identify the white precipitate and give an explanation for this observation.

.....

.....

..... [2]

(e) Iodised salt is sodium chloride mixed with a small amount of sodium iodate(V), $NaIO_3$.

- 50.00 g of iodised salt is dissolved in distilled water and the solution made up to 250 cm^3 in a volumetric flask with distilled water.
- 50.0 cm^3 of this solution is pipetted into an excess of aqueous acidified potassium iodide.

$$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O$$

- The iodine produced requires 12.40 cm^3 of 0.00200 mol dm^{-3} aqueous sodium thiosulfate solution for complete reaction.

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

Calculate the mass of sodium iodate(V) present in 50.00 g of iodised salt.

mass of $NaIO_3$ = ... g [3]

(f) The half-equation for the reduction of iodate(V) ions is shown.

$$IO_3^- + 6H^+ + 5e^- \rightarrow \tfrac{1}{2}I_2 + 3H_2O \qquad E^\ominus = +1.19\,V$$

Use data from the *Data Booklet* to predict whether a reaction is feasible when aqueous solutions of acidified iodate(V) ions and bromide ions are mixed. Explain your answer.

.....

..... [1]

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(g) Iodate(V) ions react with sulfite ions in acidic solution at pH 5.00 as shown.

$$IO_3^- + 3SO_3^{2-} \rightarrow I^- + 3SO_4^{2-}$$

The initial rate of reaction was found to be first order with respect to IO_3^-, first order with respect to SO_3^{2-} and first order with respect to H^+.

(i) Write the rate equation for this reaction, stating the units of the rate constant, *k*.

rate = ... $mol\,dm^{-3}\,s^{-1}$

units of *k* = ...

[2]

(ii) The rate of reaction depends on the pH of the solution. Assume all other concentrations remain the same.

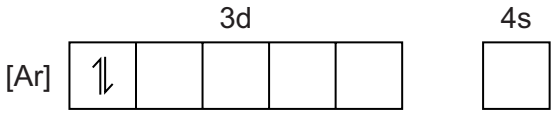
Use the expression $x = \frac{\text{rate at pH 5.00}}{\text{rate at pH 4.00}}$ to calculate the value of x.

x = ... [1]

[Total: 19]

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3 **(a)** Complete the electronic configuration of an isolated gaseous nickel(II) ion, Ni^{2+}.



[1]

(b) Explain the origin of colour in transition element complexes.

.....

.....

.....

.....

.....

..... [4]

(c) Hexaaquanickel(II) ions are green. They form a green precipitate with hydroxide ions, OH^-, in equilibrium **1** and a blue complex with ammonia, NH_3, in equilibrium **2**.

equilibrium **1** $[Ni(H_2O)_6]^{2+} + 2OH^- \rightleftharpoons Ni(OH)_2 + 6H_2O$
green ppt.

equilibrium **2** $[Ni(H_2O)_6]^{2+} + 6NH_3 \rightleftharpoons [Ni(NH_3)_6]^{2+} + 6H_2O$
blue

Use Le Chatelier's principle to suggest explanations for the following observations.

(i) Explain why when aqueous NH_3 is added dropwise to $[Ni(H_2O)_6]^{2+}$ a green precipitate is formed.

.....

.....

..... [1]

(ii) Explain why when a large excess of aqueous NH_3 is added to $[Ni(H_2O)_6]^{2+}$, the green precipitate dissolves and a blue solution is formed.

.....

.....

..... [1]

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[Turn over

(d) The complex ion $[NiBr_2(CN)_2]^{2-}$ shows stereoisomerism.

Draw diagrams to show the two isomers of $[NiBr_2(CN)_2]^{2-}$. Name the type of stereoisomerism.

isomer 1	isomer 2

type of stereoisomerism .....

[2]

[Total: 9]

4 (a) (i) When benzene undergoes nitration a nitro group substitutes at a carbon atom.

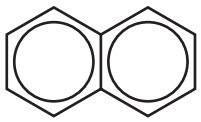
State the shape (geometry) around the substituted carbon atom

- in the benzene molecule, ...
- in the intermediate complex, ...
- in the nitrobenzene product. .....

[2]

(ii) Naphthalene, $C_{10}H_8$, is an arene hydrocarbon.

naphthalene



When naphthalene undergoes nitration, a mixture of two organic compounds is formed. Each compound contains **one** nitro group.

Suggest the structures of these compounds.

structure 1	structure 2

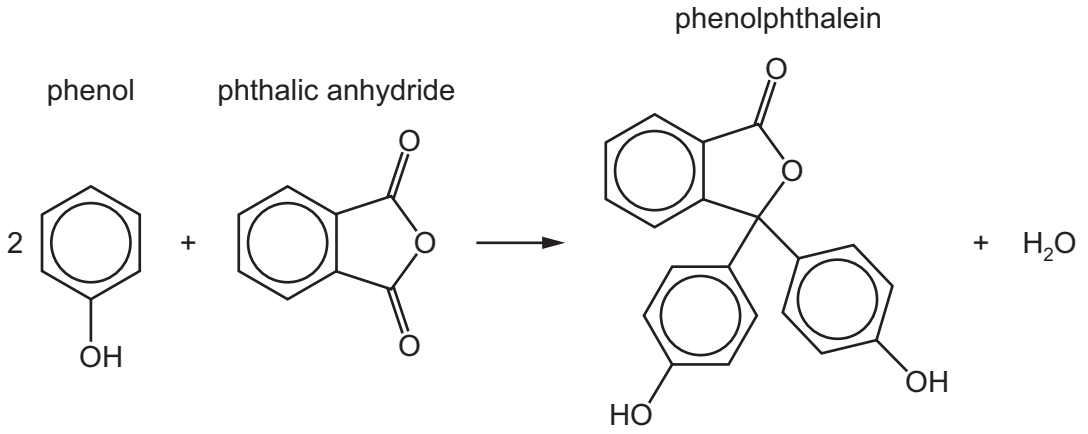
[1]

(b) Naphthalene can be oxidised under certain conditions to phthalic anhydride, $C_8H_4O_3$, carbon dioxide and water.

Construct an equation for this reaction. Use [O] to represent an atom of oxygen from the oxidising agent.

..... [1]

(c) The indicator, phenolphthalein, can be synthesised from phthalic anhydride and phenol under certain conditions.



Deduce the *type of reaction* shown by this equation.

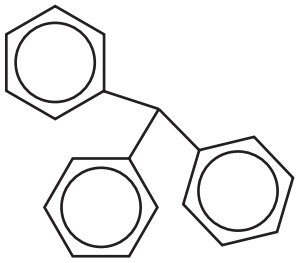
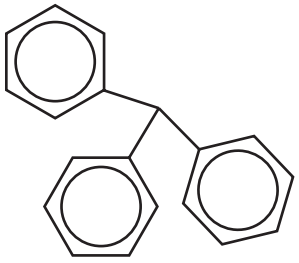
..... [1]

(d) (i) Name the functional groups, in addition to the benzene ring, present in a phenolphthalein molecule.

..... [1]

(ii) Phenolphthalein reacts separately with the two reagents shown in the table.

Complete the table by:
- drawing the structures of the organic products formed (part of the structure has been given for you)
- stating the types of reaction.

reagent	organic product structure	type of reaction
an **excess** of hot NaOH(aq)		
an **excess** of Br_2(aq)		

[4]

(e) Phenolphthalein is an indicator and is represented by the formula HIn.
Phenolphthalein, HIn, is a weak acid.

$$HIn \rightleftharpoons H^+ + In^-$$

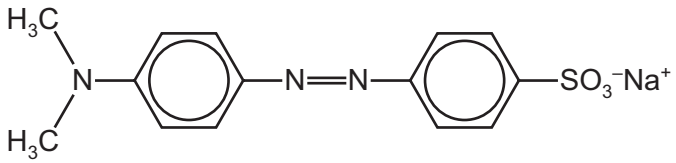
The K_a value for phenolphthalein is 5.0×10^{-10} mol dm^{-3} at 298 K. This indicator changes colour at a pH of approximately 8.8.

Calculate the ratio $\frac{[In^-]}{[HIn]}$ at pH 8.8.

ratio $\frac{[In^-]}{[HIn]}$ = ... [2]

(f) Methyl orange is another acid-base indicator. Its structure in aqueous solution at pH 4.4 is shown.

methyl orange



(i) On the structure of methyl orange, **circle** the bond or bonds that make this compound a dye. [1]

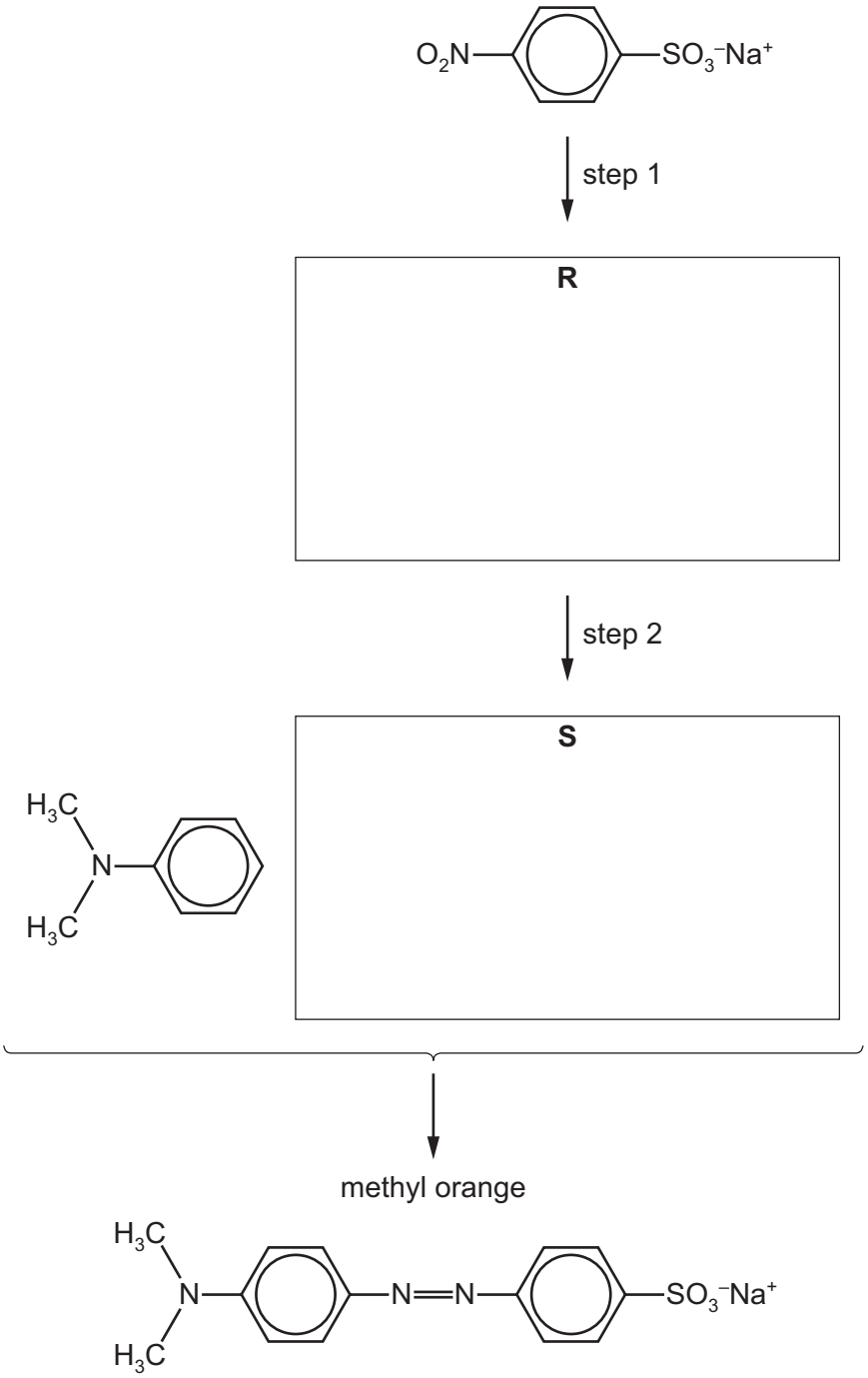
The colour of this indicator changes between pH 3.2 and pH 4.4.

(ii) Suggest the structure of methyl orange at pH 3.0. Assume the $-SO_3^-Na^+$ group is unreactive.

[1]

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(g) Methyl orange can be synthesised as shown.



(i) Deduce the identities of compounds **R** and **S** and draw their structures in the boxes. [2]

(ii) Suggest reagents and conditions for step 1 and step 2.

step 1 .....

step 2 .....

[3]

[Total: 19]

5 **(a)** Define the term *partition coefficient,* K_{pc}.

.....

.....

..... [2]

(b) K_{pc} of benzoic acid between octan-1-ol and water is 79.4.

(i) A solution of 0.400 g of benzoic acid in 25.0 cm^3 octan-1-ol is shaken with 125 cm^3 of water.

Calculate the mass of benzoic acid extracted into the water layer.

mass of benzoic acid extracted = ... g [2]

(ii) K_{pc} of benzophenone, $C_6H_5COC_6H_5$, between octan-1-ol and water is different from the value of K_{pc} of benzoic acid given in **(b)(i)**.

Explain why.

.....

.....

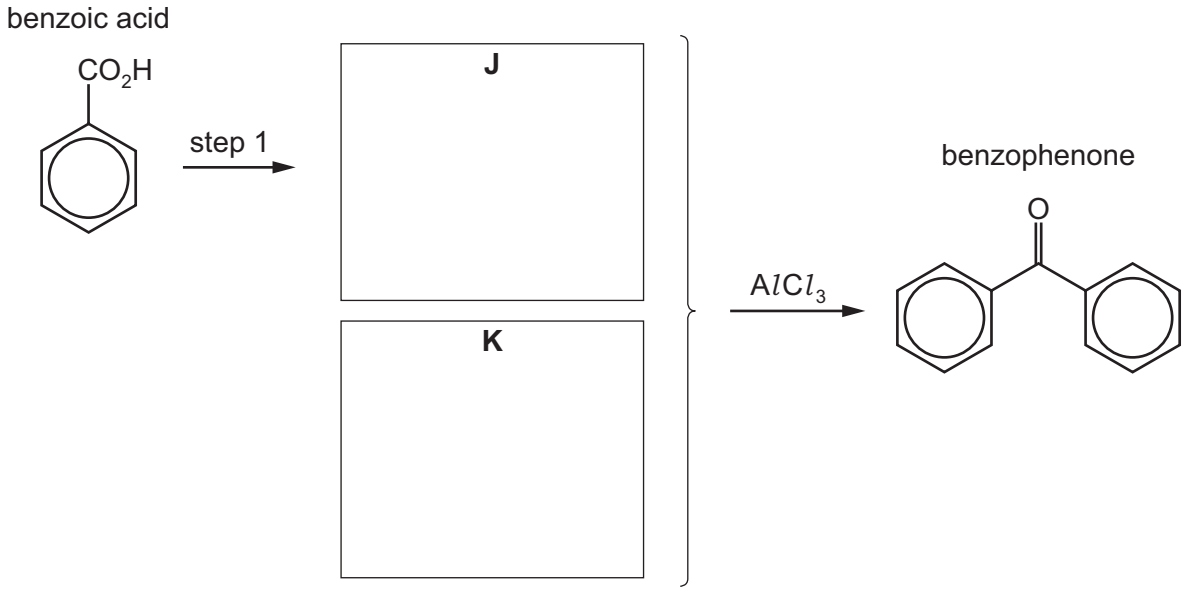
..... [1]

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(c) Benzophenone can be synthesised from benzoic acid in two steps as shown.

In step 1 compound **J**, a reactive reaction intermediate, is formed.

Compound **J** then reacts with an organic compound, **K**, to form benzophenone.

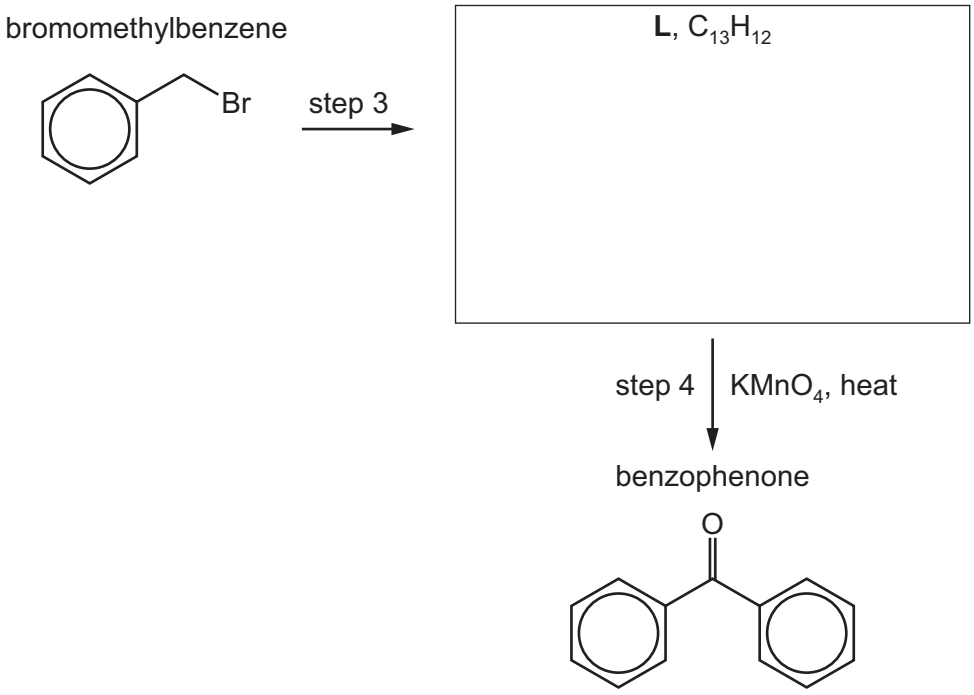


(i) Deduce the identities of organic compounds **J** and **K** and draw their structures in the boxes. [2]

(ii) Suggest reagents and conditions for step 1.

..... [1]

(d) Benzophenone can also be synthesised in two steps from bromomethylbenzene.



(i) Deduce the identity of compound **L** and draw its structure in the box. [1]

(ii) Name the mechanism of step 3 and suggest reagents and conditions for step 3.

mechanism of step 3 .....

reagents and conditions .....

[2]

(iii) Deduce the *type of reaction* in step 4.

..... [1]

(e) (i) Deduce the number of peaks that would be present in the carbon-13 NMR spectrum of benzophenone.

number of peaks ..... [1]

(ii) Identify **two** different environments of carbon atom that would result in different chemical shift ranges in this carbon-13 NMR spectrum of benzophenone.

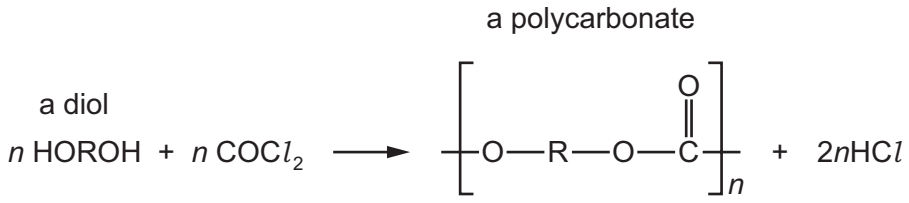
environment of carbon atom	chemical shift range (δ)

[2]

[Total: 15]

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6 The class of polymers called polycarbonates are made by the reaction of carbonyl dichloride, $COCl_2$, with a diol.

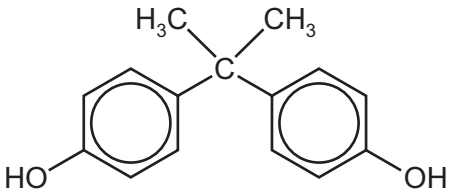


(a) (i) Deduce the *type of polymerisation* shown here.

..... [1]

Nalgene® is a polycarbonate formed from the diol **P** and $COCl_2$.

P



(ii) Draw **one** repeat unit of Nalgene®.

[1]

(iii) Nalgene® is a strong and tough polymer.

Identify **two** types of intermolecular force that are responsible for these properties of Nalgene®.

1 .....

2 .....

[1]

(b) Proteins are polymers of amino acids.

Complete the table to show how the secondary and tertiary structures of proteins are stabilised.

	one intermolecular force responsible	groups involved
secondary structure		
tertiary structure		

[2]

(c) Explain the significance of hydrogen bonding in DNA in relation to the accurate replication of genetic information.

.....

.....

..... [2]

(d) Many polymers are degradable.

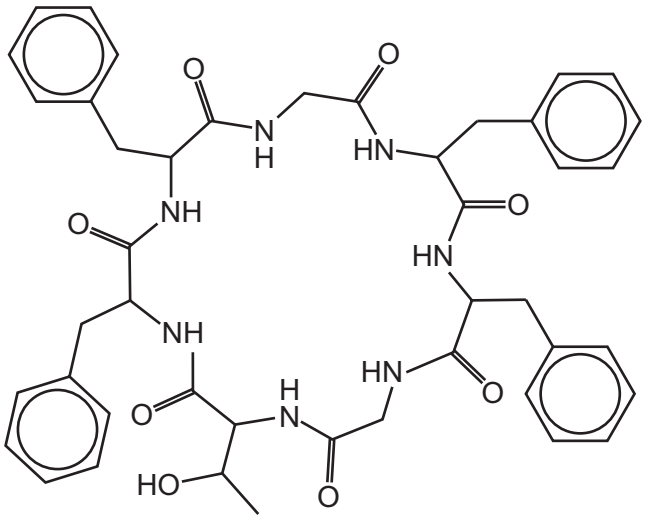
State **two** different processes by which some polymers can be degraded.

.....

..... [1]

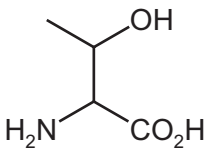
(e) The cyclic peptide **B** is shown.

B



Cyclic peptide **B** is broken into its monomers by heating under reflux with dilute hydrochloric acid. The amino acid threonine, Thr, and two other organic products are formed.

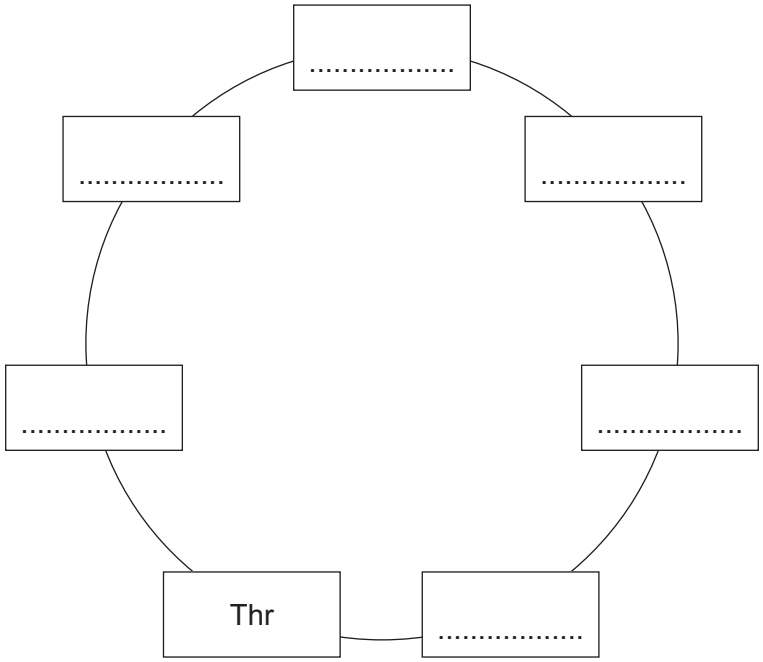
threonine



(i) Draw the structures of the two other organic products formed.

[2]

(ii) Using the 3-letter abbreviations for the amino acids as given in the *Data Booklet*, complete the sequence for the cyclic peptide, **B**.



[1]

(iii) Name **two** analytical techniques that could be used to separate these amino acids.

..... and ..... [1]

[Total: 12]

7 **(a)** **(i)** Define the term *electron affinity*.

.....

.....

..... [2]

(ii) Define the term *lattice energy*.

.....

.....

..... [2]

(b) Use the following data and relevant data from the *Data Booklet* to calculate a value for the enthalpy change of formation of zinc bromide, $ZnBr_2(s)$.

You might find it helpful to construct an energy cycle.

electron affinity of Br(g)	= –325 kJ mol^{-1}
enthalpy change of atomisation of Zn(s)	= +131 kJ mol^{-1}
enthalpy change of vaporisation of $Br_2(l)$	= +31 kJ mol^{-1}
lattice energy of $ZnBr_2(s)$	= –2678 kJ mol^{-1}

enthalpy change of formation of $ZnBr_2(s)$ = ... kJ mol^{-1} [4]

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(c) The lattice energies of $ZnBr_2$, $ZnCl_2$ and ZnO are shown.

compound	lattice energy / kJ mol^{-1}
$ZnBr_2$	–2678
$ZnCl_2$	–2734
ZnO	–3971

(i) Explain why there is a difference between the lattice energies of $ZnBr_2$ and $ZnCl_2$.

.....

..... [1]

(ii) Explain why there is a difference between the lattice energies of $ZnCl_2$ and ZnO.

.....

..... [1]

[Total: 10]

8 (a) (i) Define the term *standard cell potential*.

.....

.....

..... [2]

An electrochemical cell is set up to measure the standard electrode potential of a cell, $E^{\ominus}_{cell}$, made of a Co^{3+}/Co^{2+} half-cell and a Cl_2/Cl^- half-cell.

(ii) Complete the table with the substance used to make the electrode in each of these half-cells.

half-cell	electrode
Co^{3+}/Co^{2+}	
Cl_2/Cl^-	

[1]

(iii) Use data from the *Data Booklet* to calculate the $E^{\ominus}_{cell}$.

$E^{\ominus}_{cell}$ = ... V [1]

(iv) Write the equation for the overall cell reaction.

..... [1]

(b) A fuel cell is an electrochemical cell that can be used to generate electrical energy.
A methanol-oxygen fuel cell can be used as an alternative to a hydrogen-oxygen fuel cell. When the cell operates, the carbon atoms in the methanol molecules are converted into carbon dioxide.

$$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$$

Calculate the volume of CO_2, in cm^3, formed when a current of 2.5A is delivered by the cell for 30 minutes. Assume the cell is operated at room conditions.

volume of CO_2 = ... cm^3 [2]

[Total: 7]

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