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CHEMISTRY

9701/41

Paper 4 A Level Structured Questions

May/June 2017

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your Centre number, candidate number and name on all the work you hand in.

Write in dark blue or black pen.

You may use an HB pencil for any diagrams or graphs.

Do not use staples, paper clips, glue or correction fluid.

DO **NOT** WRITE IN ANY BARCODES.

Answer **all** questions.

Electronic calculators may be used.

You may lose marks if you do not show your working or if you do not use appropriate units.

A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.

The number of marks is given in brackets [] at the end of each question or part question.

This document consists of **16** printed pages.

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

- 1 (a) Describe and explain the variation in the solubilities of the hydroxides of the Group 2 elements.

.....

.....

.....

.....

.....

..... [4]

The table lists the standard enthalpy changes of formation, $\Delta H_f^\ominus$, for some compounds and aqueous ions.

species	$\Delta H_f^\ominus / \text{kJ mol}^{-1}$
$\text{Ba}^{2+}(\text{aq})$	–538
$\text{OH}^-(\text{aq})$	–230
$\text{CO}_2(\text{g})$	–394
$\text{BaCO}_3(\text{s})$	–1216
$\text{H}_2\text{O}(\text{l})$	–286

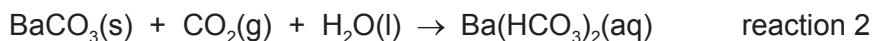
- (b) (i) Reaction 1 occurs when $\text{CO}_2(\text{g})$ is bubbled through an aqueous solution of $\text{Ba}(\text{OH})_2$.

Use the data in the table to calculate the standard enthalpy change for reaction 1, $\Delta H_{r1}^\ominus$.



$$\Delta H_{r1}^\ominus = \dots\dots\dots \text{kJ mol}^{-1} \quad [2]$$

If $\text{CO}_2(\text{g})$ is bubbled through an aqueous solution of $\text{Ba}(\text{OH})_2$ for a long time, the precipitated $\text{BaCO}_3(\text{s})$ dissolves, as shown in reaction 2.



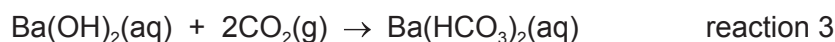
The standard enthalpy change for reaction 2, $\Delta H_{\text{r}2}^\ominus = -26 \text{ kJ mol}^{-1}$.

- (ii) Use this information and the data in the table to calculate the standard enthalpy change of formation of the $\text{HCO}_3^-(\text{aq})$ ion.

$$\Delta H_{\text{f}}^\ominus \text{HCO}_3^-(\text{aq}) = \dots\dots\dots \text{ kJ mol}^{-1} \quad [2]$$

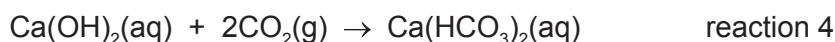
- (iii) The overall process is shown by reaction 3.

Use your answer to (ii), and the data given in the table, to calculate the standard enthalpy change for reaction 3, $\Delta H_{\text{r}3}^\ominus$.



$$\Delta H_{\text{r}3}^\ominus = \dots\dots\dots \text{ kJ mol}^{-1} \quad [1]$$

- (iv) How would the value of $\Delta H_{\text{r}3}^\ominus$ compare with the value of $\Delta H_{\text{r}4}^\ominus$ for the similar reaction with $\text{Ca}(\text{OH})_2(\text{aq})$ as shown in reaction 4? Explain your answer.



.....

 [2]

- (c) The standard entropy change for reaction 1 is $\Delta S_{\text{r}1}^\ominus$.

Suggest, with a reason, how the standard entropy change for reaction 3 might compare with $\Delta S_{\text{r}1}^\ominus$.

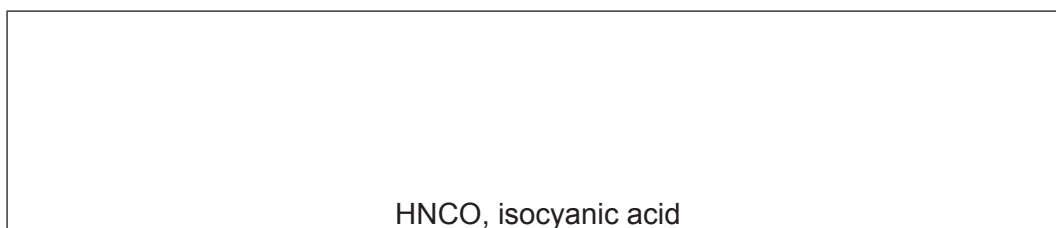
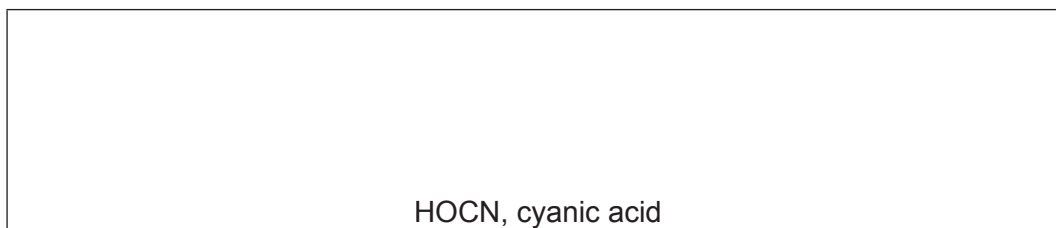
.....

 [2]

[Total: 13]

- 2 (a) One atom of each of the four elements H, C, N and O can bond together in different ways. Two examples are molecules of cyanic acid, HOCN, and isocyanic acid, HNCO. The atoms are bonded in the order they are written.

(i) Draw 'dot-and-cross' diagrams of these two acids, showing outer shell electrons only.



[3]

(ii) Suggest the values of the bond angles HNC and NCO in **isocyanic acid**.

HNC NCO

[1]

(iii) Suggest which acid, cyanic or isocyanic, will have the **shorter** C–N bond length. Explain your answer.

.....
 [1]

(b) (i) Isocyanic acid is a weak acid.



Calculate the pH of a 0.10 mol dm^{-3} solution of isocyanic acid.

pH = ... [2]

(ii) Sodium cyanate, NaNCO, is used in the production of isocyanic acid. Sodium cyanate is prepared commercially by reacting urea, $(\text{NH}_2)_2\text{CO}$, with sodium carbonate. Other products in this reaction are carbon dioxide, ammonia and steam.

Write an equation for the production of NaNCO by this method.

..... [1]

- (c) Barium hydroxide, $\text{Ba}(\text{OH})_2$, is completely ionised in aqueous solutions. During the addition of 30.0 cm^3 of 0.100 mol dm^{-3} $\text{Ba}(\text{OH})_2$ to 20.0 cm^3 of 0.100 mol dm^{-3} isocyanic acid, the pH was measured.

(i) Calculate the $[\text{OH}^-]$ at the end of the addition.

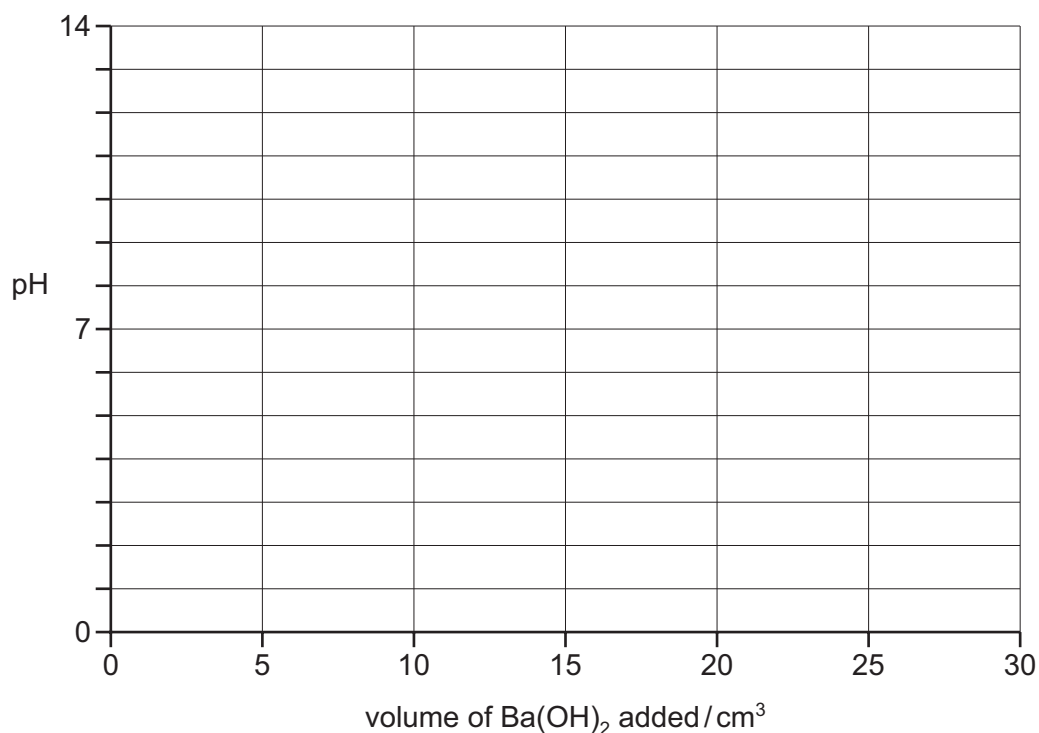
$$[\text{OH}^-] = \dots\dots\dots \text{mol dm}^{-3} \quad [2]$$

(ii) Use your value in (i) to calculate $[\text{H}^+]$ and the pH of the solution at the end of the addition.

$$\text{final } [\text{H}^+] = \dots\dots\dots \text{mol dm}^{-3}$$

$$\text{final pH} = \dots\dots\dots \quad [2]$$

(iii) On the following axes, sketch how the pH changes during the addition of a total of 30.0 cm^3 of 0.100 mol dm^{-3} $\text{Ba}(\text{OH})_2$ to 20.0 cm^3 of 0.100 mol dm^{-3} isocyanic acid.



[3]

(d) The cyanate ion, NCO^- , can act as a *monodentate ligand*.

(i) State what is meant by the terms

monodentate, ...

.....

ligand.

.....

[2]

Silver ions, Ag^+ , react with cyanate ions to form a linear complex.

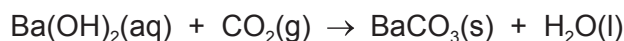
(ii) Suggest the formula of this complex, including its charge.

..... [2]

(e) When heated with $\text{HCl}(\text{aq})$, organic isocyanates, RNCO , are hydrolysed to the amine salt, RNH_3Cl , and CO_2 .



A 1.00 g sample of an organic isocyanate, RNCO , was treated in this way, and the CO_2 produced was absorbed in an excess of aqueous $\text{Ba}(\text{OH})_2$ according to the equation shown. The solid BaCO_3 precipitated weighed 1.66 g.



(i) Calculate the number of moles of BaCO_3 produced.

moles of BaCO_3 = ... [1]

(ii) Hence calculate the M_r of the organic isocyanate RNCO .

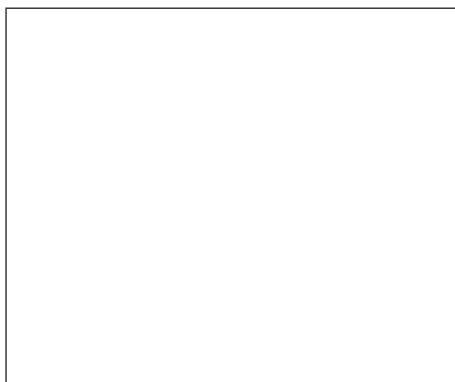
M_r of RNCO = ... [1]

The R group in RNCO and RNH_3Cl contains carbon and hydrogen only.

- (iii) Use your M_r value calculated in (ii) to suggest the molecular formula of the organic isocyanate RNCO .

molecular formula of RNCO [1]

- (iv) Suggest a possible structure of the amine RNH_2 , which forms the amine salt, RNH_3Cl .



[1]

[Total: 23]

- 3 Bubbling air through different aqueous mixtures of CoCl_2 , NH_4Cl and NH_3 produces various complex ions with the general formula $[\text{Co}(\text{NH}_3)_{6-n}\text{Cl}_n]^{3-n}$.

(a) (i) Determine the oxidation state of the cobalt in these complex ions.

..... [1]

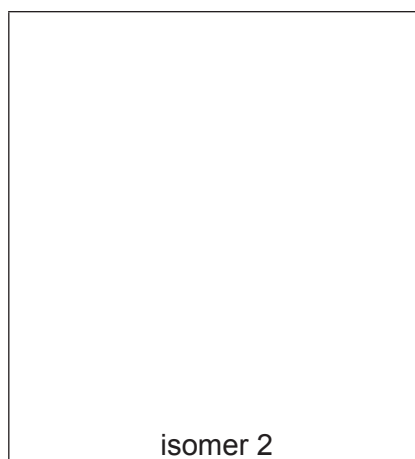
(ii) Name the **two** types of reaction undergone by the cobalt ions during the formation of these complex ions.

.....

..... [2]

(iii) The complex $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ shows isomerism.

Draw three-dimensional structures of the two isomers, and suggest the type of isomerism shown here.



type of isomerism [3]

(b) (i) What is meant by the term *co-ordination number*?

.....

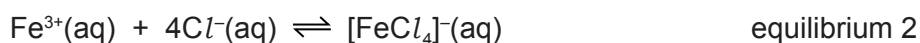
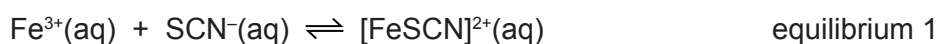
..... [1]

- (ii) Complete the table by predicting appropriate co-ordination numbers, formulae and charges for the complexes **C**, **D**, **E** and **F**.

complex	metal ion	ligand	co-ordination number	formula of complex	charge on complex
C	Cr^{3+}	CN^-			3–
D	Ni^{2+}	$\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$	6		
E	Pt^{2+}	Cl^-			2–
F	Fe^{3+}	$^-\text{O}_2\text{C}-\text{CO}_2^-$		$[\text{Fe}(\text{O}_2\text{CCO}_2)_3]$	

[6]

- (c) Iron(III) forms complexes in separate reactions with both SCN^- ions and Cl^- ions.



- (i) Write the expressions for the stability constants, K_{stab} , for these two equilibria. Include units in your answers.

$$K_{\text{stab1}} =$$

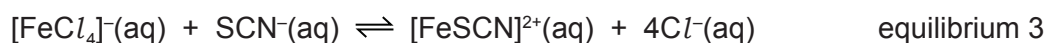
units = ...

$$K_{\text{stab2}} =$$

units = ...

[3]

- (ii) An equilibrium can be set up between these two complexes as shown in equilibrium 3.



Write an expression for K_{eq3} in terms of K_{stab1} and K_{stab2} .

$$K_{\text{eq3}} = \dots\dots\dots [1]$$

- (iii) The numerical values for these stability constants are shown.

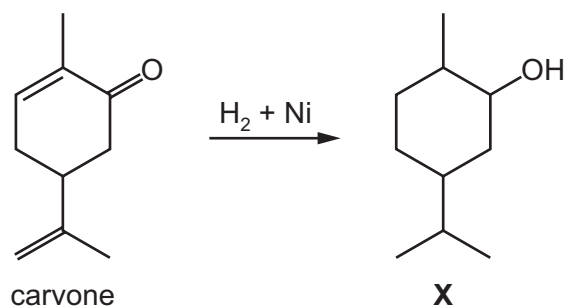
$$K_{\text{stab1}} = 1.4 \times 10^2 \quad K_{\text{stab2}} = 8.0 \times 10^{-2}$$

Calculate the value of K_{eq3} stating its units.

$$K_{\text{eq3}} = \dots\dots\dots \text{units} = \dots\dots\dots [2]$$

[Total: 19]

- 4 Carvone occurs in spearmint and a stereoisomer of carvone occurs in caraway seeds. Treating either isomer with hydrogen over a nickel catalyst produces a mixture of isomers with the structural formula **X**.



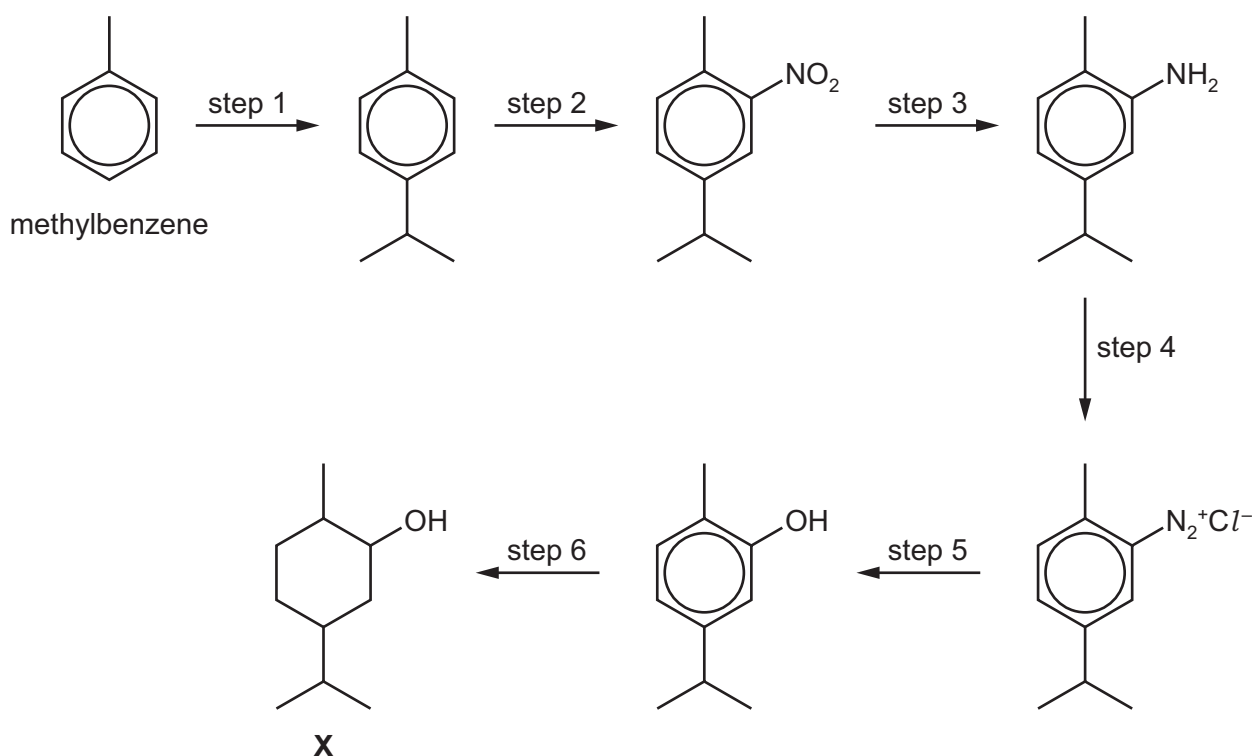
- (a) (i) State the type of stereoisomerism carvone can show. Explain your answer.

..... [1]

- (ii) Write an equation, using molecular formulae, for this conversion of carvone to **X**.

..... [2]

X can be synthesised from methylbenzene by the following route.



(b) (i) Name the mechanism in step 1.

..... [1]

(ii) What type of reaction is occurring in the following steps?

step 3

step 5 [2]

(iii) Suggest reagents and conditions for each of the following steps.

step 1

step 2

step 3

step 4 [6]

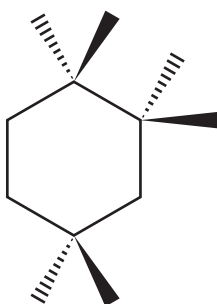
(c) During step 6, hydrogen is added to the benzene ring to produce the cyclohexane ring in **X**. The six hydrogen atoms are all added to the **same side** of the benzene ring.

(i) State the reagents and conditions needed for this reaction.

..... [1]

(ii) Complete the part structure to show the structure of the isomer of **X** that would most likely be obtained during this reaction.

X



[2]

[Total: 15]

- 5** Compounds **J**, **K**, **L** and **M** are isomers of each other with the molecular formula $C_9H_{11}NO$. All four isomers contain a benzene ring.
Two of the isomers contain a chiral centre.
 The results of six tests carried out on **J**, **K**, **L** and **M** are shown in the table.

test		observations with each isomer			
		J	K	L	M
1	add cold $HCl(aq)$	soluble	soluble	soluble	insoluble
2	add 2,4-DNPH reagent	orange ppt.	orange ppt.	orange ppt.	no reaction
3	add $NaOH(aq) + I_2(aq)$	pale yellow ppt.	no reaction	pale yellow ppt.	no reaction
4	warm with Fehling's solution	no reaction	red ppt.	no reaction	no reaction
5	heat with $NaOH(aq)$	no reaction	no reaction	no reaction	P (C_6H_7N) and Q ($C_3H_5O_2Na$) produced
6	diazotization and addition of alkaline phenol	no dye produced	orange dye produced	no dye produced	no dye produced

- (a) Use the experimental results in the table above to determine the group(s), in addition to the benzene ring, present in each of the four isomers **J**, **K**, **L** and **M**.

Complete the table below, identifying the group(s) present in each isomer.

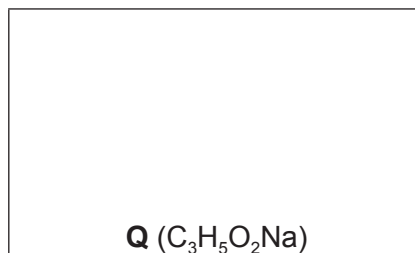
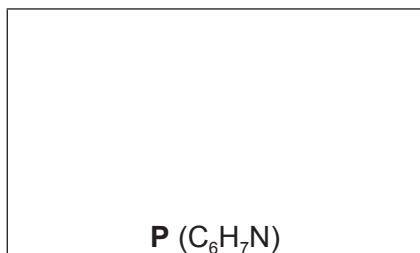
group(s) in compound			
J	K	L	M
.....			
.....			
.....			

[5]

- (b) (i) Name the *type of reaction* occurring in test 5 that converts **M** into **P** + **Q**.

..... [1]

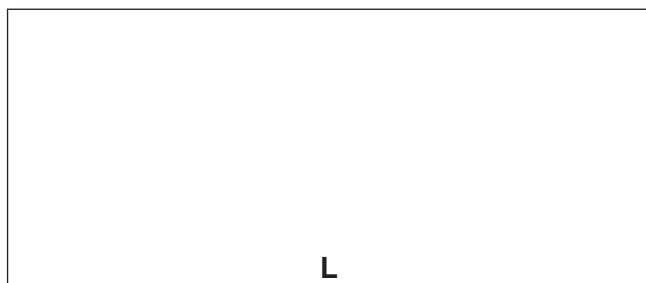
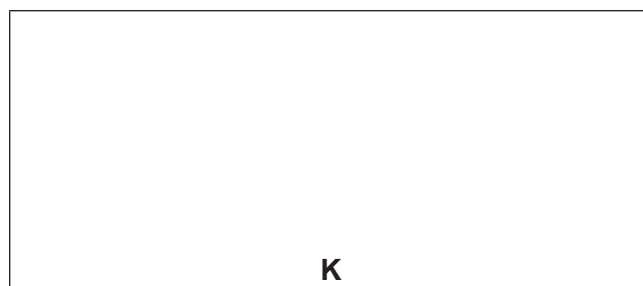
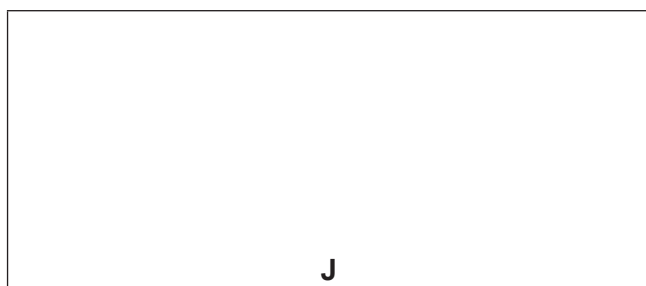
- (ii) Suggest structures for compounds **P** and **Q**.



[2]

- (c) Isomers **J**, **K**, **L** and **M** all have the molecular formula $\text{C}_9\text{H}_{11}\text{NO}$.

Use the information in (a) to suggest a structure for each of these isomers and draw these in the boxes. Draw **circles** around all chiral centres in **K** and **L**.



[5]

- (d) Compound **N** is another isomer which has the same molecular formula $\text{C}_9\text{H}_{11}\text{NO}$ and also contains a benzene ring.

N contains the same functional group as **M**.

When heated with NaOH(aq) , **N** produces ethylamine and a sodium salt **W**.

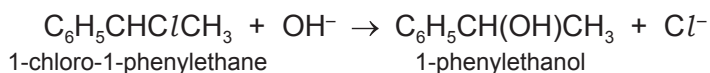
Suggest the structure of **W**.



[1]

[Total: 14]

- 6 The reaction between 1-chloro-1-phenylethane and hydroxide ions to produce 1-phenylethanol is:



The rate of this reaction can be studied by measuring the amount of hydroxide ions that remain in solution at a given time. The reaction can effectively be stopped if the solution is diluted with an ice-cold solvent.

- (a) Describe a suitable method for studying the rate of this reaction at a temperature of 40 °C, given the following.

- a solution of 0.10 mol dm⁻³ 1-chloro-1-phenylethane, labelled **A**
- a solution of 0.10 mol dm⁻³ sodium hydroxide, labelled **B**
- 0.10 mol dm⁻³ HCl
- volumetric glassware
- ice-cold solvent
- stopclock
- access to standard laboratory equipment and chemicals

.....

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.....

.....

.....

.....

.....

.....

..... [4]

- (b) The rate of this reaction was measured at different initial concentrations of the two reagents. The table shows the results obtained.

experiment	[C ₆ H ₅ CHClCH ₃] /mol dm ⁻³	[OH ⁻] /mol dm ⁻³	relative rate
1	0.05	0.10	0.5
2	0.10	0.20	1.0
3	0.15	0.10	1.5
4	0.20	0.15	to be calculated

- (i) Deduce the order of reaction with respect to each of [C₆H₅CHClCH₃] and [OH⁻]. Explain your reasoning.

order with respect to [C₆H₅CHClCH₃]

.....

order with respect to [OH⁻]

.....

[2]

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

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

units of k = ... [1]

- (iii) Calculate the relative rate for experiment 4.

relative rate for experiment 4 = ... [1]

- (c) (i) Use your answers in (b)(i) to help you to draw the mechanism for the reaction of 1-chloro-1-phenylethane with hydroxide ions, including the following.

- all relevant lone pairs and dipoles
- curly arrows to show the movement of electron pairs
- the structures of any transition state or intermediate

[3]

- (ii) This reaction was carried out using a single optical isomer of 1-chloro-1-phenylethane.

Use your mechanism in (i) to predict whether the product will be a single optical isomer or a mixture of two optical isomers. Explain your answer.

.....
 [1]

- (d) The proton NMR spectrum of a sample of 1-phenylethanol shows four peaks: a multiplet for the C_6H_5 protons and three other peaks as shown in the table. When the sample is shaken with D_2O and the proton NMR spectrum recorded, **fewer** peaks are seen.

Complete the table for the proton NMR spectrum of 1-phenylethanol, $\text{C}_6\text{H}_5\text{CH}(\text{OH})\text{CH}_3$.
Use of the *Data Booklet* might be helpful.

δ/ppm	number of ^1H atoms responsible for the peak	group responsible for the peak	splitting pattern	result on shaking with D_2O
1.4				
2.7				
4.0				
7.2-7.4	5	C_6H_5	multiplet	peak remains

[4]

[Total: 16]

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CHEMISTRY

9701/42

Paper 4 A Level Structured Questions

May/June 2017

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your Centre number, candidate number and name on all the work you hand in.

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Answer **all** questions.

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The number of marks is given in brackets [] at the end of each question or part question.

This document consists of **20** printed pages.

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

- 1 (a) (i) Describe and explain the variation in the thermal stabilities of the carbonates of the Group 2 elements.

.....

.....

.....

.....

..... [3]

- (ii) Suggest and explain a reason why sodium carbonate is more stable to heat than magnesium carbonate.

.....

.....

..... [1]

- (b) Sodium hydrogencarbonate, NaHCO_3 , and potassium hydrogencarbonate, KHCO_3 , decompose on heating to produce gases and the solid metal carbonate.

- (i) Write an equation for the decomposition of KHCO_3 .

..... [1]

- (ii) Predict which of NaHCO_3 or KHCO_3 will decompose at the **lower** temperature. Explain your answer.

.....

..... [1]

- (c) (i) Use the data in the table below, and relevant data from the *Data Booklet*, to calculate the lattice energy, $\Delta H_{\text{latt}}^{\ominus}$, of potassium oxide, $\text{K}_2\text{O}(\text{s})$.

energy change	value / kJ mol^{-1}
enthalpy change of atomisation of potassium, $\Delta H_{\text{at}}^{\ominus} \text{K}(\text{s})$	+89
electron affinity of $\text{O}(\text{g})$	–141
electron affinity of $\text{O}^-(\text{g})$	+798
enthalpy change of formation of potassium oxide, $\Delta H_{\text{f}}^{\ominus} \text{K}_2\text{O}(\text{s})$	–361

$$\Delta H_{\text{latt}}^{\ominus} = \dots\dots\dots \text{kJ mol}^{-1} \quad [3]$$

- (ii) State whether the lattice energy of Na_2O would be more negative, less negative or the same as that of K_2O . Give reasons for your answer.

.....
 [1]

[Total: 10]

- 2 (a) Complete the table to show how **both** $\text{AgNO}_3(\text{aq})$ and $\text{NH}_3(\text{aq})$ could be used to distinguish between solutions of $\text{NaCl}(\text{aq})$ and $\text{NaI}(\text{aq})$.

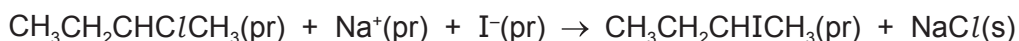
test performed	observation with NaCl	observation with NaI

[2]

Important information for this question

- In this question (pr) means 'a solution in propanone'.
- Sodium iodide is soluble in propanone giving $\text{Na}^+(\text{pr})$ and $\text{I}^-(\text{pr})$.
- Sodium chloride is insoluble in propanone.

The reaction between 2-chlorobutane and sodium iodide in propanone is shown.



The rate of this reaction can be investigated by measuring the electrical conductivity of the reaction mixture. The electrical conductivity changes as the reaction progresses due to the precipitation of the NaCl produced.

- (b) (i) Suggest how the electrical conductivity will change as the reaction proceeds. Explain your answer.

.....
 [1]

- (ii) Describe a suitable method for studying the rate of this reaction at a temperature of 40°C , using the following.

- an electrical conductance meter which measures the electrical conductivity of solutions
- solutions of known concentrations of 2-chlorobutane in propanone and sodium iodide in propanone
- stopclock
- access to standard laboratory equipment

.....

 [3]

- (c) The rate of this reaction was measured at different initial concentrations of the two reagents. The table shows the results obtained.

experiment	$[\text{CH}_3\text{CH}_2\text{CHClCH}_3]$ /mol dm ⁻³	$[\text{I}^-]$ /mol dm ⁻³	relative rate
1	0.06	0.03	3
2	0.10	0.03	5
3	0.06	0.05	5
4	0.08	0.04	to be calculated

- (i) Deduce the order of reaction with respect to each of $[\text{CH}_3\text{CH}_2\text{CHClCH}_3]$ and $[\text{I}^-]$. Explain your reasoning.

order with respect to $[\text{CH}_3\text{CH}_2\text{CHClCH}_3]$

.....

order with respect to $[\text{I}^-]$

.....

[2]

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

rate = ... mol dm⁻³ s⁻¹

units of k = ...

[1]

- (iii) Calculate the relative rate for experiment 4.

relative rate for experiment 4 = ... [1]

(d) (i) Suggest the mechanism for the reaction of 2-chlorobutane with iodide ions. Draw out the steps involved, including the following.

- all relevant lone pairs and dipoles
- curly arrows to show the movement of electron pairs
- the structure of any transition state or intermediate

[3]

(ii) This reaction was carried out using a single optical isomer of 2-chlorobutane.

Use your mechanism in (i) to predict whether the product will be a single optical isomer or a mixture of two optical isomers. Explain your answer.

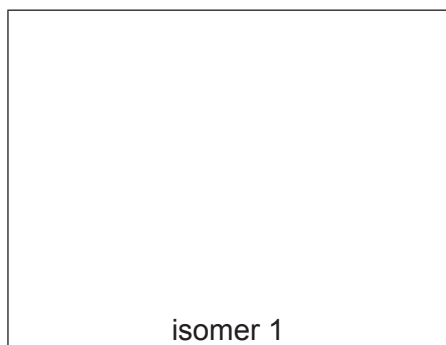
.....
 [1]

(e) (i) State the number of peaks that would be seen in the carbon-13 NMR spectrum of $\text{CH}_3\text{CH}_2\text{CHClCH}_3$.

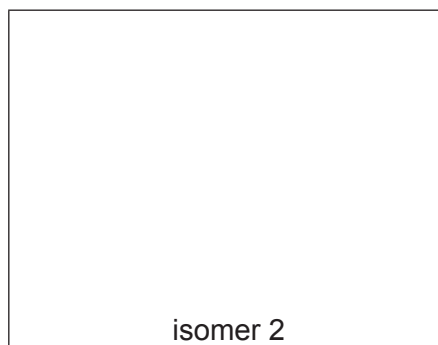
..... [1]

(ii) There are two isomers of $\text{CH}_3\text{CH}_2\text{CHClCH}_3$ that have **fewer** peaks in their carbon-13 NMR spectra than $\text{CH}_3\text{CH}_2\text{CHClCH}_3$.

Draw the structures of the isomers and state the number of peaks for each isomer.



number of peaks = ...



number of peaks = ...

[3]

[Total: 18]

Question 3 starts on the next page.

- 3 (a) In a molecule of SOCl_2 the sulfur atom has four bonds.

Draw a 'dot-and-cross' diagram of SOCl_2 . Show the outer shell electrons only.

[2]

- (b) When SOCl_2 is reacted with a carboxylic acid to produce an acyl chloride, two acidic gases are formed.



A 1.00 g sample of a carboxylic acid RCO_2H was treated in this way, and the gases were absorbed in 60.0 cm^3 of $0.500 \text{ mol dm}^{-3}$ $\text{NaOH}(\text{aq})$, an excess.

- (i) Write equations for the reactions between

NaOH and HCl , ...

NaOH and SO_2 , ... [2]

The excess NaOH was titrated with $0.500 \text{ mol dm}^{-3}$ $\text{H}^+(\text{aq})$. It required 10.8 cm^3 of the $\text{H}^+(\text{aq})$ solution to reach the end-point.

- (ii) Calculate the total number of moles of NaOH that reacted with the SO_2 and HCl .

moles of NaOH = ... [2]

- (iii) Calculate the number of moles of RCO_2H that produced the SO_2 and HCl .

moles of RCO_2H = ... [1]

(iv) Hence calculate the M_r of the carboxylic acid, RCO_2H .

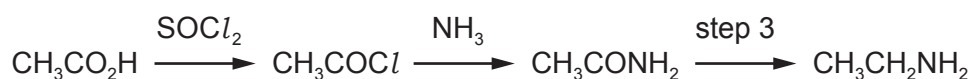
$M_r \text{RCO}_2\text{H} = \dots\dots\dots$ [1]

(v) The R group contains carbon and hydrogen only.

Suggest the molecular formula of RCO_2H .

$\dots\dots\dots$ [1]

(c) The following synthetic route shows how a carboxylic acid can be converted into an amine.



(i) Suggest a reagent for step 3.

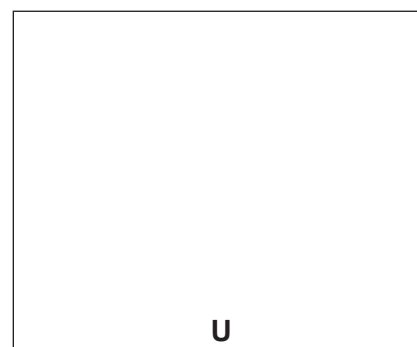
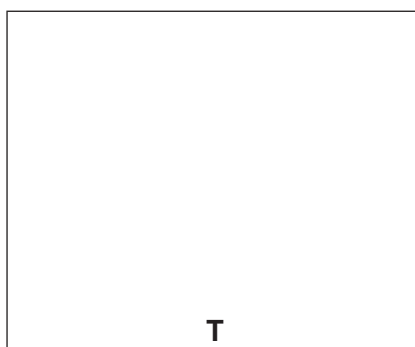
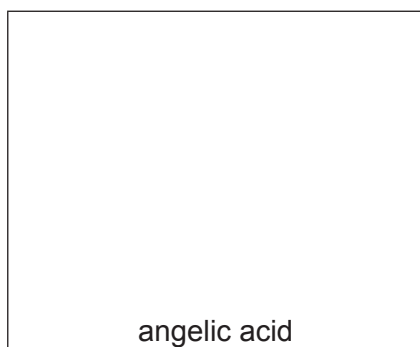
$\dots\dots\dots$ [1]

Angelic acid, $\text{C}_5\text{H}_8\text{O}_2$, is a natural product isolated from the roots of the angelica plant.

- Angelic acid reacts with $\text{H}_2 + \text{Ni}$ to form **T**, $\text{C}_5\text{H}_{10}\text{O}_2$.
- **T** undergoes the above synthetic route to form the amine **U**, $\text{C}_5\text{H}_{13}\text{N}$.
- **U** can also be made by reacting 1-bromo-2-methylbutane with ammonia.

Both angelic acid and **T** exist as stereoisomers.

(ii) Suggest structures for angelic acid, **T** and **U**.



[3]

(iii) State the type of stereoisomerism shown by angelic acid and **T**.

angelic acid $\dots\dots\dots$

compound **T** $\dots\dots\dots$

[1]

[Total: 14]

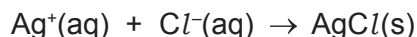
- 4 (a) A number of isomers with the formula $\text{Cr}(\text{H}_2\text{O})_6\text{Cl}_3$ exist. Their general formula is $[\text{Cr}(\text{H}_2\text{O})_{6-n}\text{Cl}_n]\text{Cl}_{3-n} \cdot n\text{H}_2\text{O}$.

Each isomer contains a six co-ordinated $\text{Cr}(\text{III})$ ion in an octahedral complex.

Water molecules not directly bonded with the Cr atom are held in the crystal lattice as water of crystallisation.

The $\text{Cr}-\text{Cl}$ bond is not easily broken and so chloride bonded with the $\text{Cr}(\text{III})$ ion in the complex does not react.

1.00 g samples of three of the isomers, **A**, **B** and **C**, were dissolved in separate samples of water. An excess of $\text{AgNO}_3(\text{aq})$ was added to each and the mass of $\text{AgCl}(\text{s})$ formed was measured.



The number of moles of $\text{AgCl}(\text{s})$ formed was calculated. The table shows the results.

isomer	moles of AgCl formed from 1.00 g of isomer
A	3.75×10^{-3}
B	7.50×10^{-3}
C	1.13×10^{-2}

- (i) Calculate the M_r of $\text{Cr}(\text{H}_2\text{O})_6\text{Cl}_3$.

$$M_r \text{Cr}(\text{H}_2\text{O})_6\text{Cl}_3 = \dots\dots\dots [1]$$

- (ii) Use the data in the table above to calculate the value of n for each of the isomers, **A**, **B** and **C**. Complete the table below with the values of n and the molecular formula of each isomer, in the style of the general formula given above.

Show your working for at least one calculation of n .

isomer	n	molecular formula
A		
B		
C		

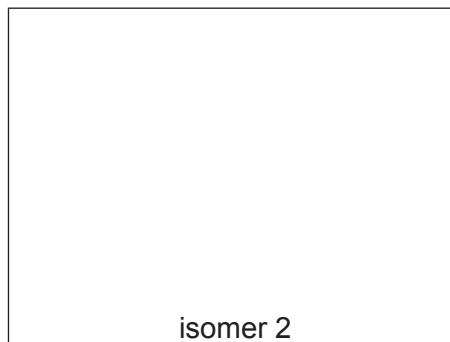
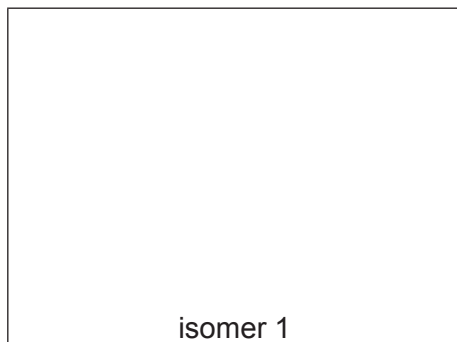
[2]

- (b) Two isomers have the same shape and their formula is $\text{Ni}(\text{R}_3\text{P})_2(\text{CN})_2$, where $\text{R} = \text{CH}_3$. Only one of these isomers has a dipole moment.

(i) Name the *type of isomerism* shown by $\text{Ni}(\text{R}_3\text{P})_2(\text{CN})_2$.

..... [1]

(ii) Draw structures of these two isomers.



[1]

(iii) State which isomer has a dipole moment. Explain your answer.

.....

..... [1]

[Total: 6]

5 (a) 1,2-diaminoethane, *en*, $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$, is a bidentate ligand.

(i) What is meant by the terms *bidentate* and *ligand*?

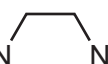
bidentate

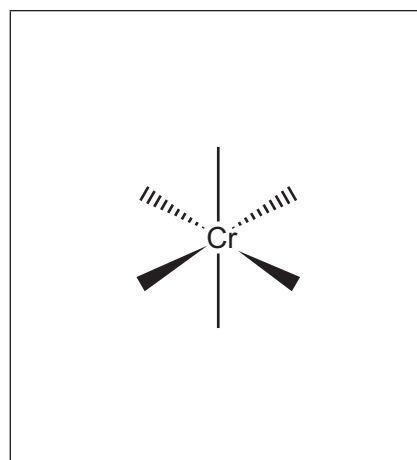
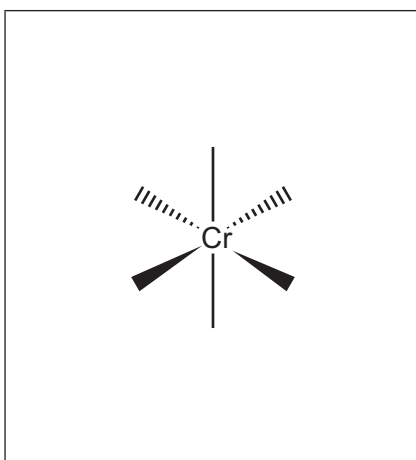
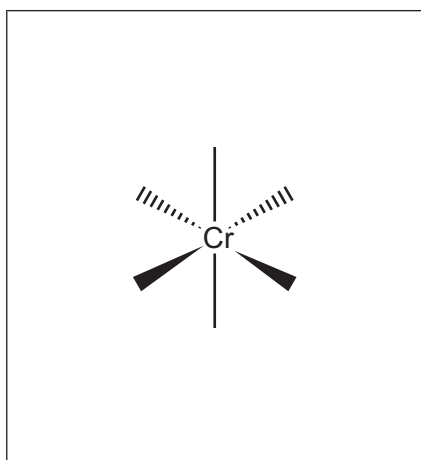
ligand

[2]

(ii) There are three isomeric complex ions with the formula $[\text{Cr}(\text{en})_2\text{Cl}_2]^+$.

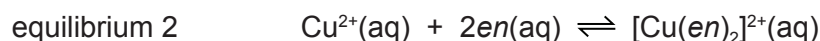
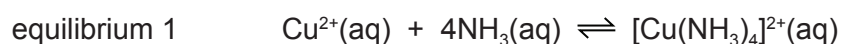
Complete the three-dimensional diagrams of the isomers in the boxes.

You may use  to represent *en*.



[3]

(b) Copper forms complexes with NH_3 and *en* according to equilibria 1 and 2.



(i) Write the expressions for the stability constants, K_{stab1} and K_{stab2} , for equilibria 1 and 2. Include units in your answers.

$K_{\text{stab1}} =$

units = ...

$K_{\text{stab2}} =$

units = ...

[3]

- (ii) An equilibrium is set up when both *en* and NH_3 ligands are added to a solution containing $\text{Cu}^{2+}(\text{aq})$ as shown in equilibrium 3.



Write an expression for the equilibrium constant, K_{eq3} , in terms of K_{stab1} and K_{stab2} .

$K_{\text{eq3}} = \dots\dots\dots$ [1]

- (iii) The numerical values for these stability constants are shown.

$$K_{\text{stab1}} = 1.2 \times 10^{13} \quad K_{\text{stab2}} = 5.3 \times 10^{19}$$

Calculate the value of K_{eq3} stating its units.

$K_{\text{eq3}} = \dots\dots\dots$ unit = $\dots\dots\dots$ [2]

- (c) ΔS° values for equilibria 1 and 2 differ greatly, as can be seen in the table. All values are at a temperature of 298 K.

equilibrium	$\Delta H^\circ/\text{kJ mol}^{-1}$	$\Delta S^\circ/\text{JK}^{-1} \text{mol}^{-1}$	$\Delta G^\circ/\text{kJ mol}^{-1}$
1	-92	-60	-74
2	-100	+40	

- (i) Explain why $\Delta S_{\text{eq2}}^\circ$ is so different from $\Delta S_{\text{eq1}}^\circ$.

$\dots\dots\dots$
 $\dots\dots\dots$ [1]

- (ii) Calculate $\Delta G_{\text{eq2}}^\circ$ at 298 K.

$\Delta G_{\text{eq2}}^\circ = \dots\dots\dots \text{kJ mol}^{-1}$
 [2]

- (iii) What conclusion can be made about the relative feasibility of equilibria 1 and 2?

Explain your answer.

$\dots\dots\dots$ [1]

- (iv) Using data from the table, suggest a value of ΔH° for equilibrium 3.

$\dots\dots\dots$ [1]

- (v) State the *type of reaction* that is occurring in equilibrium 2.

$\dots\dots\dots$ [1]

[Total: 17]

- 6 The table lists some organic acids and their pK_a values.

acid	formula	pK_a
ethanoic acid	$\text{CH}_3\text{CO}_2\text{H}$	4.76
chloroethanoic acid	$\text{ClCH}_2\text{CO}_2\text{H}$	2.86
aminoethanoic acid (glycine)	$\text{H}_2\text{NCH}_2\text{CO}_2\text{H}$	9.87

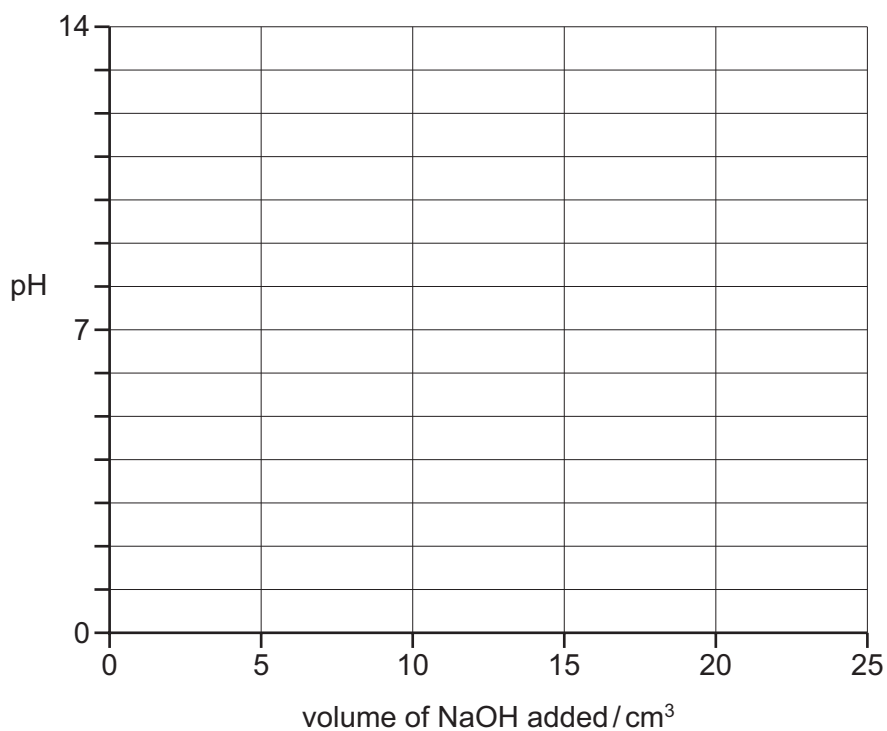
- (a) (i) State the relationship between pK_a and the strength of an acid.
 [1]
- (ii) State the mathematical relationship between pK_a and the acidity constant K_a .
 [1]
- (iii) Give reasons for why the pK_a value for chloroethanoic acid is **smaller** than that for ethanoic acid.

 [2]
- (b) (i) Use the zwitterionic structure for aminoethanoic acid (glycine) in aqueous solution to write an equation for its dissociation giving $\text{H}^+(\text{aq})$ ions.
 [1]
- (ii) Calculate the pH of a $0.100 \text{ mol dm}^{-3}$ solution of aminoethanoic acid.

pH = ... [2]

A 10.0 cm^3 sample of 0.100 mol dm^{-3} aminoethanoic acid (glycine) was titrated with 0.100 mol dm^{-3} NaOH. After 20.0 cm^3 of NaOH, an excess, had been added, the pH was found to be 12.5.

(iii) Using the following axes, sketch a graph showing how the pH changes during this titration.



[3]

[Total: 10]

- 7 Compounds **W**, **X**, **Y** and **Z** are isomers of each other with the molecular formula C_8H_7ClO . All four isomers contain a benzene ring. Only **one** of the isomers contains a chiral centre. The results of six tests carried out on **W**, **X**, **Y** and **Z** are shown in the table.

test		observations with each isomer			
		W	X	Y	Z
1	add cold $AgNO_3(aq)$	white ppt. forms immediately	none	white ppt. forms very slowly	none
2	heat with $NaOH(aq)$, then add dilute $HNO_3 + AgNO_3(aq)$	white ppt.	none	white ppt.	none
3	add $NaOH(aq) + I_2(aq)$	none	pale yellow ppt.	none	none
4	warm with Fehling's solution	none	none	red ppt.	none
5	add cold, dilute, acidified $KMnO_4(aq)$	no change	no change	no change	decolourises
6	add $Br_2(aq)$	no change	no change	no change	decolourises and forms white ppt.

- (a) Use the experimental results in the table above to determine the group(s), in addition to the benzene ring, present in the four isomers **W**, **X**, **Y** and **Z**.

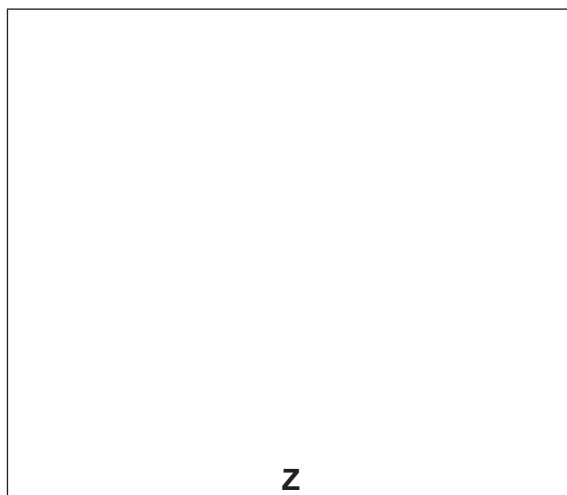
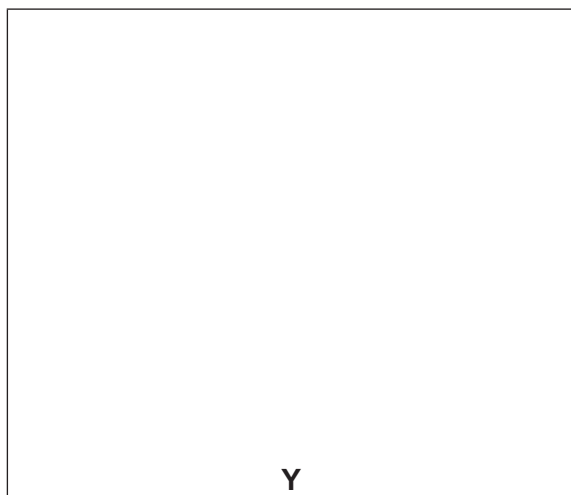
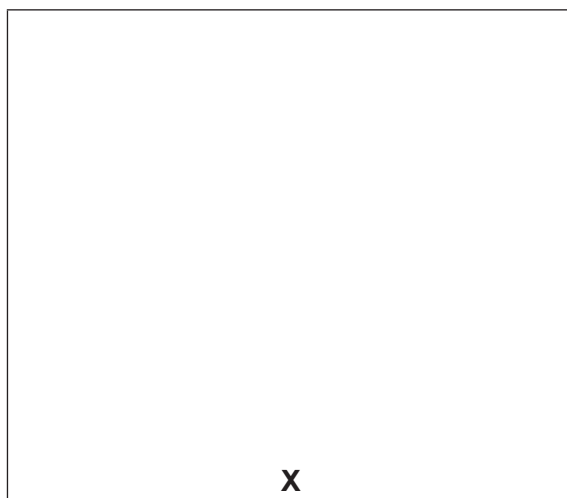
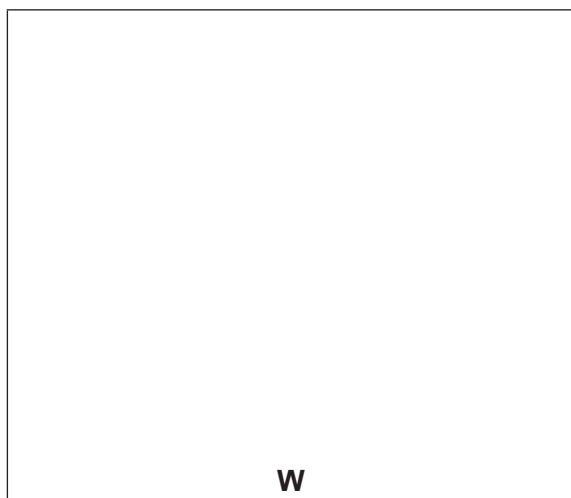
Complete the table below, identifying the group(s) present in each isomer.

group(s) in compound			
W	X	Y	Z
.....			
.....			
.....			

[5]

(b) Isomers **W**, **X**, **Y** and **Z** all have the molecular formula $\text{C}_8\text{H}_7\text{ClO}$.

(i) Use the information in (a) to suggest a structure for each of these isomers and draw these in the boxes.



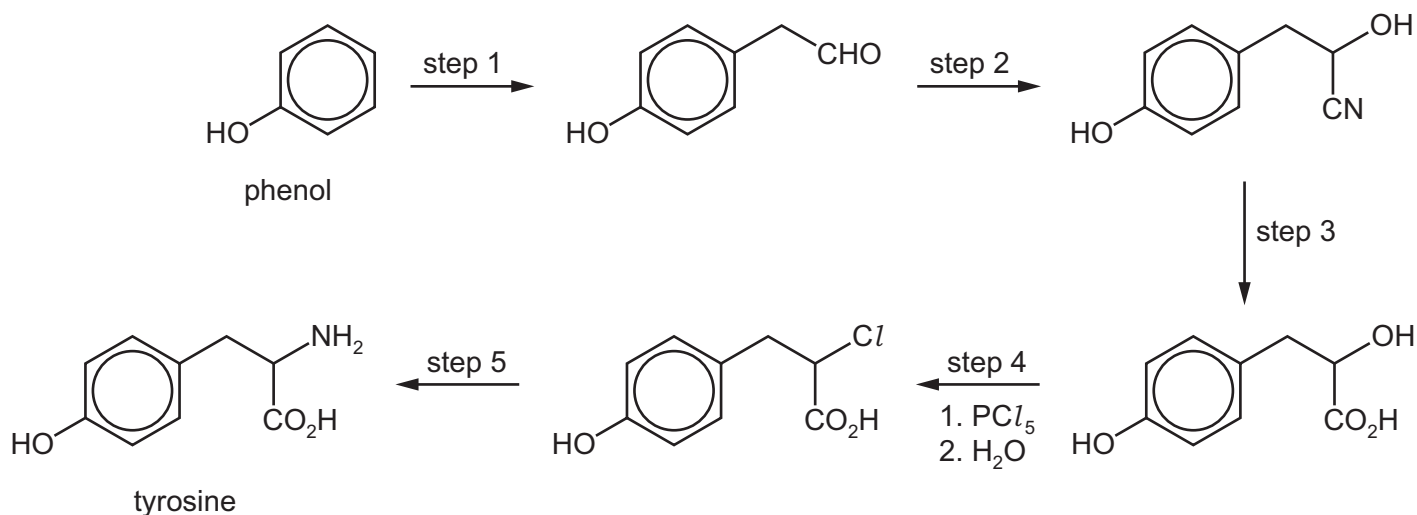
[4]

(ii) Draw a **circle** around the chiral centre in **one** of the above structures.

[1]

[Total: 10]

- 8 (a) The amino acid tyrosine can be synthesised from phenol by the route shown.



- (i) Name the mechanism occurring in the following steps.

step 1

step 2 [2]

- (ii) What *type of reaction* is occurring in step 3?

..... [1]

- (iii) Suggest reagents and conditions for each of the following steps.

step 1

step 2

step 3

step 5 [5]

- (iv) Draw the structures of the products of the reactions of tyrosine with an **excess** of each of the following reagents.

with NaOH(aq)

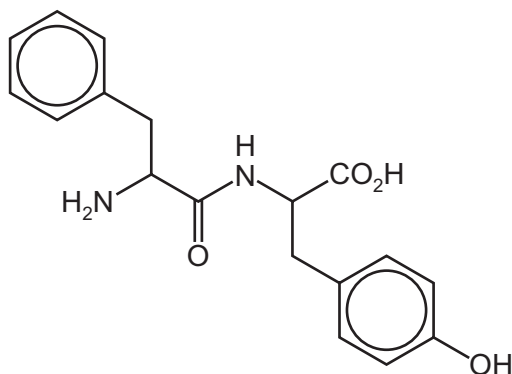
with HCl(aq)

with Br₂(aq)

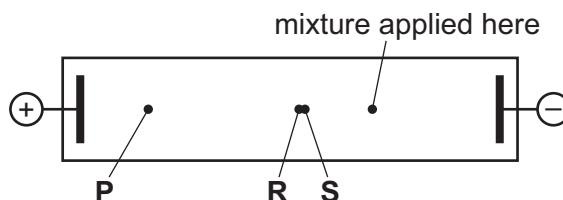
[4]

Question 8 continues on the next page.

(b) The dipeptide phe-tyr has the following structure.



A mixture of this dipeptide (phe-tyr) and its two constituent amino acids (phe and tyr) was subjected to electrophoresis in a buffer at pH 12. At the end of the experiment the following results were seen. Spots **R** and **S** remained very close together.



The three spots are due to the three species phe, tyr and phe-tyr.

(i) Which species is responsible for spot **P**? Explain your answer.

.....
 [2]

(ii) Suggest why the other two species give spots **R** and **S** that are so close together.

.....
 [1]

[Total: 15]

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CHEMISTRY

9701/43

Paper 4 A Level Structured Questions

May/June 2017

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your Centre number, candidate number and name on all the work you hand in.

Write in dark blue or black pen.

You may use an HB pencil for any diagrams or graphs.

Do not use staples, paper clips, glue or correction fluid.

DO **NOT** WRITE IN ANY BARCODES.

Answer **all** questions.

Electronic calculators may be used.

You may lose marks if you do not show your working or if you do not use appropriate units.

A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.

The number of marks is given in brackets [] at the end of each question or part question.

This document consists of **16** printed pages.



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

- 1 (a) Describe and explain the variation in the solubilities of the hydroxides of the Group 2 elements.

.....

.....

.....

.....

.....

..... [4]

The table lists the standard enthalpy changes of formation, $\Delta H_f^\ominus$, for some compounds and aqueous ions.

species	$\Delta H_f^\ominus / \text{kJ mol}^{-1}$
$\text{Ba}^{2+}(\text{aq})$	–538
$\text{OH}^-(\text{aq})$	–230
$\text{CO}_2(\text{g})$	–394
$\text{BaCO}_3(\text{s})$	–1216
$\text{H}_2\text{O}(\text{l})$	–286

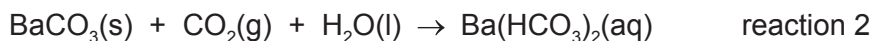
- (b) (i) Reaction 1 occurs when $\text{CO}_2(\text{g})$ is bubbled through an aqueous solution of $\text{Ba}(\text{OH})_2$.

Use the data in the table to calculate the standard enthalpy change for reaction 1, $\Delta H_{r1}^\ominus$.



$$\Delta H_{r1}^\ominus = \dots\dots\dots \text{kJ mol}^{-1} \quad [2]$$

If $\text{CO}_2(\text{g})$ is bubbled through an aqueous solution of $\text{Ba}(\text{OH})_2$ for a long time, the precipitated $\text{BaCO}_3(\text{s})$ dissolves, as shown in reaction 2.



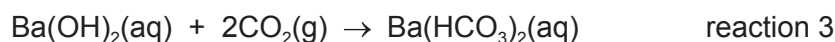
The standard enthalpy change for reaction 2, $\Delta H_{\text{r}2}^\ominus = -26 \text{ kJ mol}^{-1}$.

- (ii) Use this information and the data in the table to calculate the standard enthalpy change of formation of the $\text{HCO}_3^-(\text{aq})$ ion.

$$\Delta H_{\text{f}}^\ominus \text{HCO}_3^-(\text{aq}) = \dots\dots\dots \text{ kJ mol}^{-1} \quad [2]$$

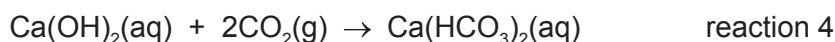
- (iii) The overall process is shown by reaction 3.

Use your answer to (ii), and the data given in the table, to calculate the standard enthalpy change for reaction 3, $\Delta H_{\text{r}3}^\ominus$.



$$\Delta H_{\text{r}3}^\ominus = \dots\dots\dots \text{ kJ mol}^{-1} \quad [1]$$

- (iv) How would the value of $\Delta H_{\text{r}3}^\ominus$ compare with the value of $\Delta H_{\text{r}4}^\ominus$ for the similar reaction with $\text{Ca}(\text{OH})_2(\text{aq})$ as shown in reaction 4?
Explain your answer.



.....

 [2]

- (c) The standard entropy change for reaction 1 is $\Delta S_{\text{r}1}^\ominus$.

Suggest, with a reason, how the standard entropy change for reaction 3 might compare with $\Delta S_{\text{r}1}^\ominus$.

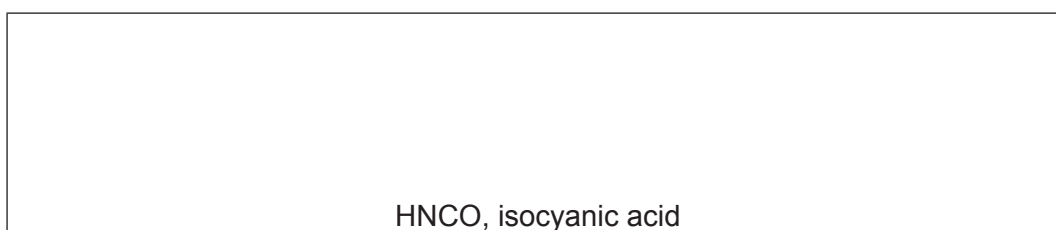
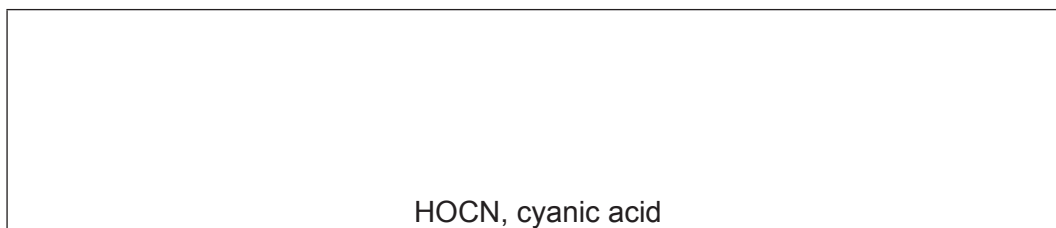
.....

 [2]

[Total: 13]

- 2 (a) One atom of each of the four elements H, C, N and O can bond together in different ways. Two examples are molecules of cyanic acid, HOCN, and isocyanic acid, HNCO. The atoms are bonded in the order they are written.

(i) Draw 'dot-and-cross' diagrams of these two acids, showing outer shell electrons only.



[3]

(ii) Suggest the values of the bond angles HNC and NCO in **isocyanic acid**.

HNC NCO

[1]

(iii) Suggest which acid, cyanic or isocyanic, will have the **shorter** C–N bond length. Explain your answer.

.....
 [1]

(b) (i) Isocyanic acid is a weak acid.



Calculate the pH of a 0.10 mol dm^{-3} solution of isocyanic acid.

pH = ... [2]

(ii) Sodium cyanate, NaNCO, is used in the production of isocyanic acid. Sodium cyanate is prepared commercially by reacting urea, $(\text{NH}_2)_2\text{CO}$, with sodium carbonate. Other products in this reaction are carbon dioxide, ammonia and steam.

Write an equation for the production of NaNCO by this method.

..... [1]

- (c) Barium hydroxide, $\text{Ba}(\text{OH})_2$, is completely ionised in aqueous solutions. During the addition of 30.0 cm^3 of 0.100 mol dm^{-3} $\text{Ba}(\text{OH})_2$ to 20.0 cm^3 of 0.100 mol dm^{-3} isocyanic acid, the pH was measured.

(i) Calculate the $[\text{OH}^-]$ at the end of the addition.

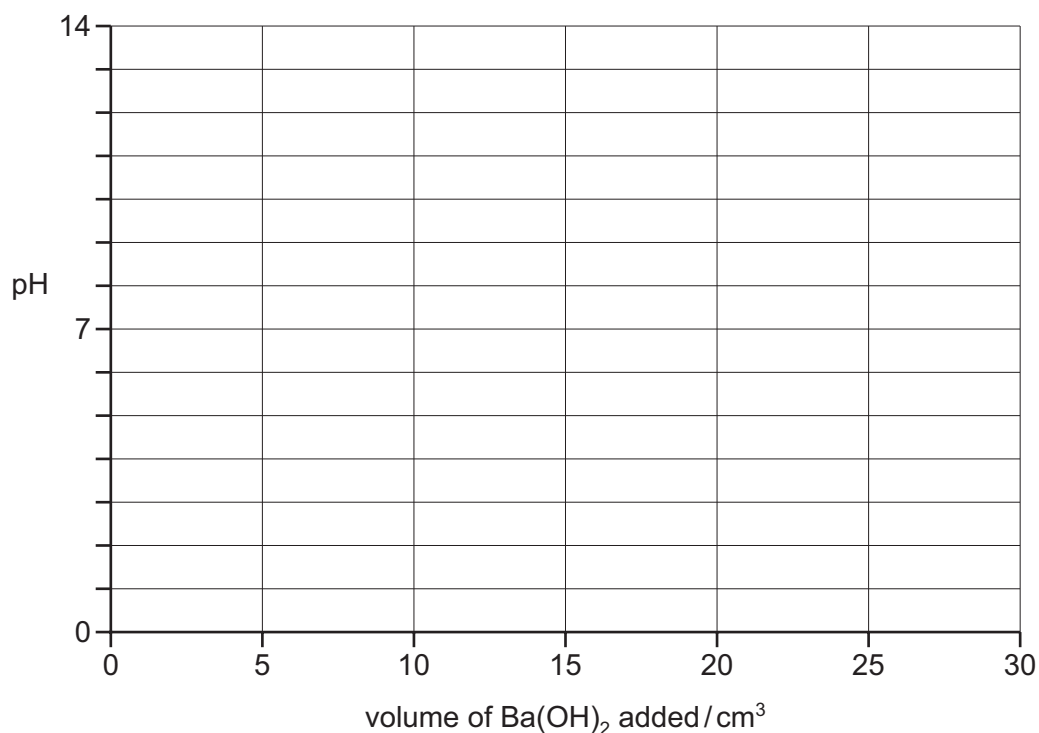
$[\text{OH}^-] = \dots\dots\dots \text{ mol dm}^{-3}$ [2]

(ii) Use your value in (i) to calculate $[\text{H}^+]$ and the pH of the solution at the end of the addition.

final $[\text{H}^+] = \dots\dots\dots \text{ mol dm}^{-3}$

final pH = $\dots\dots\dots$
[2]

(iii) On the following axes, sketch how the pH changes during the addition of a total of 30.0 cm^3 of 0.100 mol dm^{-3} $\text{Ba}(\text{OH})_2$ to 20.0 cm^3 of 0.100 mol dm^{-3} isocyanic acid.



[3]

(d) The cyanate ion, NCO^- , can act as a *monodentate ligand*.

(i) State what is meant by the terms

monodentate, ...

.....

ligand.

.....

[2]

Silver ions, Ag^+ , react with cyanate ions to form a linear complex.

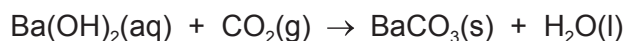
(ii) Suggest the formula of this complex, including its charge.

..... [2]

(e) When heated with HCl(aq) , organic isocyanates, RNCO , are hydrolysed to the amine salt, RNH_3Cl , and CO_2 .



A 1.00 g sample of an organic isocyanate, RNCO , was treated in this way, and the CO_2 produced was absorbed in an excess of aqueous Ba(OH)_2 according to the equation shown. The solid BaCO_3 precipitated weighed 1.66 g.



(i) Calculate the number of moles of BaCO_3 produced.

moles of BaCO_3 = ... [1]

(ii) Hence calculate the M_r of the organic isocyanate RNCO .

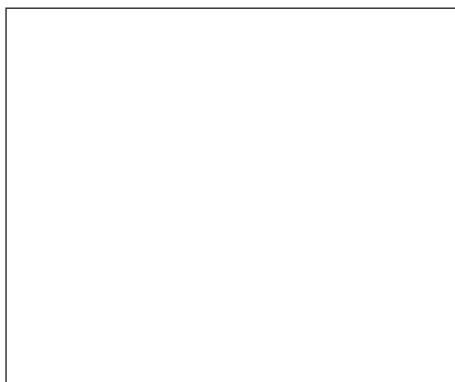
M_r of RNCO = ... [1]

The R group in RNCO and RNH_3Cl contains carbon and hydrogen only.

- (iii) Use your M_r value calculated in (ii) to suggest the molecular formula of the organic isocyanate RNCO .

molecular formula of RNCO [1]

- (iv) Suggest a possible structure of the amine RNH_2 , which forms the amine salt, RNH_3Cl .



[1]

[Total: 23]

- 3 Bubbling air through different aqueous mixtures of CoCl_2 , NH_4Cl and NH_3 produces various complex ions with the general formula $[\text{Co}(\text{NH}_3)_{6-n}\text{Cl}_n]^{3-n}$.

(a) (i) Determine the oxidation state of the cobalt in these complex ions.

..... [1]

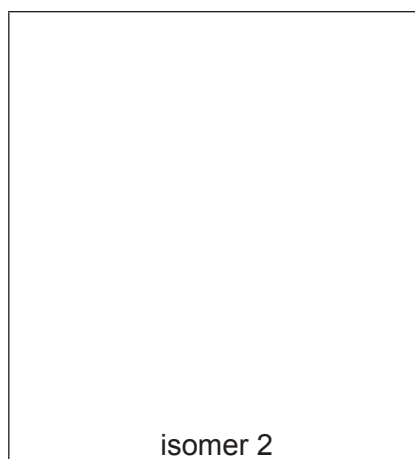
(ii) Name the **two** types of reaction undergone by the cobalt ions during the formation of these complex ions.

.....

..... [2]

(iii) The complex $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ shows isomerism.

Draw three-dimensional structures of the two isomers, and suggest the type of isomerism shown here.



type of isomerism [3]

(b) (i) What is meant by the term *co-ordination number*?

.....

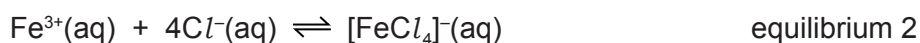
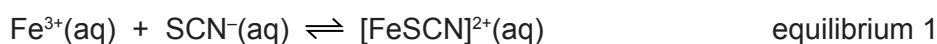
..... [1]

- (ii) Complete the table by predicting appropriate co-ordination numbers, formulae and charges for the complexes **C**, **D**, **E** and **F**.

complex	metal ion	ligand	co-ordination number	formula of complex	charge on complex
C	Cr^{3+}	CN^-			3–
D	Ni^{2+}	$\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$	6		
E	Pt^{2+}	Cl^-			2–
F	Fe^{3+}	$^-\text{O}_2\text{C}-\text{CO}_2^-$		$[\text{Fe}(\text{O}_2\text{CCO}_2)_3]$	

[6]

- (c) Iron(III) forms complexes in separate reactions with both SCN^- ions and Cl^- ions.



- (i) Write the expressions for the stability constants, K_{stab} , for these two equilibria. Include units in your answers.

$$K_{\text{stab1}} =$$

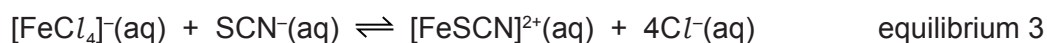
units = ...

$$K_{\text{stab2}} =$$

units = ...

[3]

- (ii) An equilibrium can be set up between these two complexes as shown in equilibrium 3.



Write an expression for K_{eq3} in terms of K_{stab1} and K_{stab2} .

$$K_{\text{eq3}} = \dots\dots\dots [1]$$

- (iii) The numerical values for these stability constants are shown.

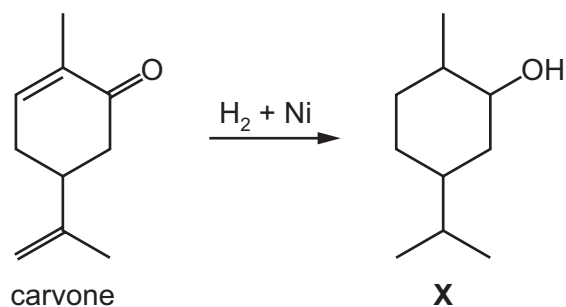
$$K_{\text{stab1}} = 1.4 \times 10^2 \quad K_{\text{stab2}} = 8.0 \times 10^{-2}$$

Calculate the value of K_{eq3} stating its units.

$$K_{\text{eq3}} = \dots\dots\dots \text{units} = \dots\dots\dots [2]$$

[Total: 19]

- 4 Carvone occurs in spearmint and a stereoisomer of carvone occurs in caraway seeds. Treating either isomer with hydrogen over a nickel catalyst produces a mixture of isomers with the structural formula **X**.



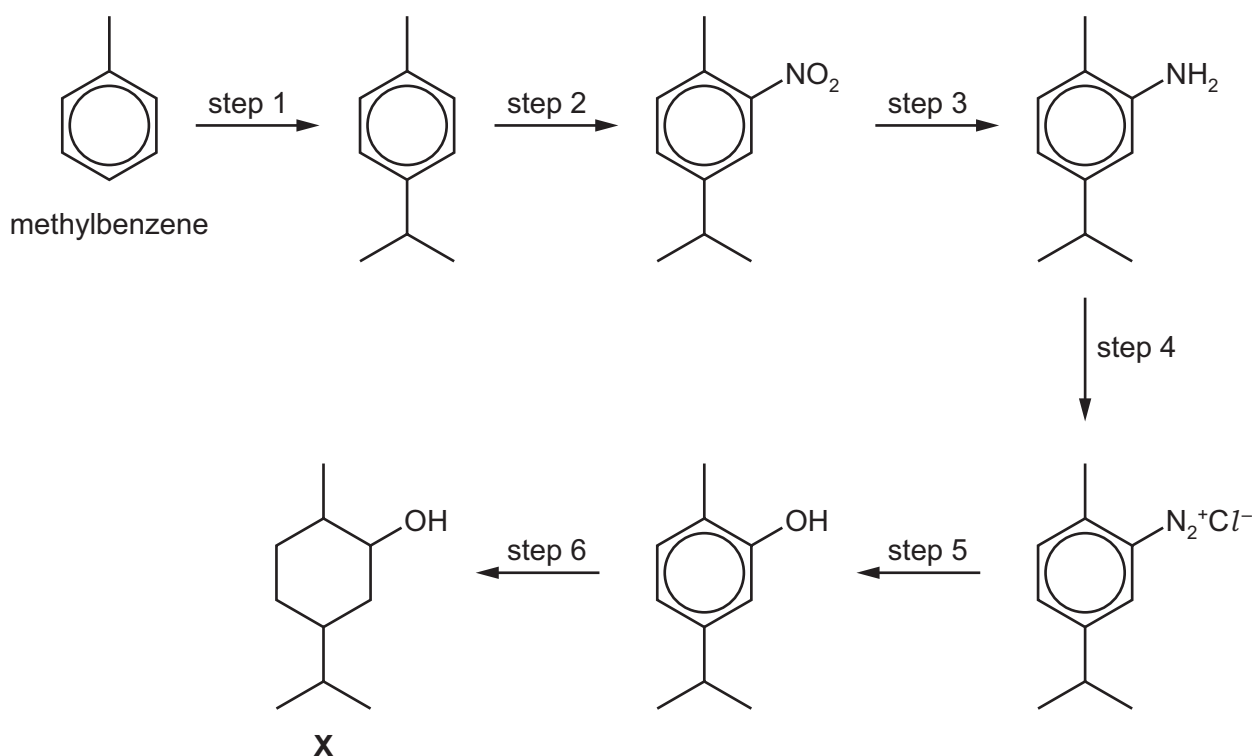
- (a) (i) State the type of stereoisomerism carvone can show. Explain your answer.

..... [1]

- (ii) Write an equation, using molecular formulae, for this conversion of carvone to **X**.

..... [2]

X can be synthesised from methylbenzene by the following route.



(b) (i) Name the mechanism in step 1.

..... [1]

(ii) What type of reaction is occurring in the following steps?

step 3

step 5 [2]

(iii) Suggest reagents and conditions for each of the following steps.

step 1

step 2

step 3

step 4 [6]

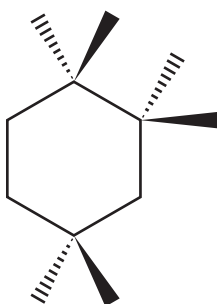
(c) During step 6, hydrogen is added to the benzene ring to produce the cyclohexane ring in **X**. The six hydrogen atoms are all added to the **same side** of the benzene ring.

(i) State the reagents and conditions needed for this reaction.

..... [1]

(ii) Complete the part structure to show the structure of the isomer of **X** that would most likely be obtained during this reaction.

X



[2]

[Total: 15]

- 5** Compounds **J**, **K**, **L** and **M** are isomers of each other with the molecular formula $C_9H_{11}NO$. All four isomers contain a benzene ring.
Two of the isomers contain a chiral centre.
 The results of six tests carried out on **J**, **K**, **L** and **M** are shown in the table.

test		observations with each isomer			
		J	K	L	M
1	add cold $HCl(aq)$	soluble	soluble	soluble	insoluble
2	add 2,4-DNPH reagent	orange ppt.	orange ppt.	orange ppt.	no reaction
3	add $NaOH(aq) + I_2(aq)$	pale yellow ppt.	no reaction	pale yellow ppt.	no reaction
4	warm with Fehling's solution	no reaction	red ppt.	no reaction	no reaction
5	heat with $NaOH(aq)$	no reaction	no reaction	no reaction	P (C_6H_7N) and Q ($C_3H_5O_2Na$) produced
6	diazotization and addition of alkaline phenol	no dye produced	orange dye produced	no dye produced	no dye produced

- (a) Use the experimental results in the table above to determine the group(s), in addition to the benzene ring, present in each of the four isomers **J**, **K**, **L** and **M**.

Complete the table below, identifying the group(s) present in each isomer.

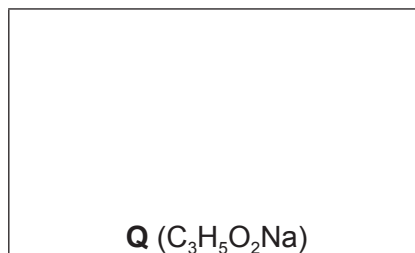
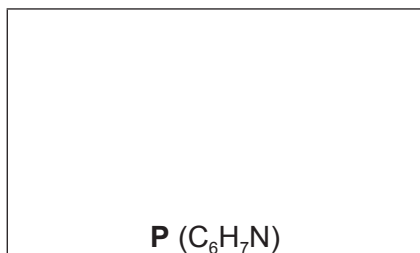
group(s) in compound			
J	K	L	M
.....			
.....			
.....			

[5]

- (b) (i) Name the *type of reaction* occurring in test 5 that converts **M** into **P** + **Q**.

..... [1]

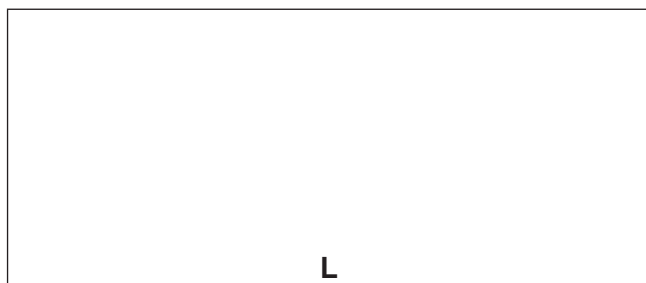
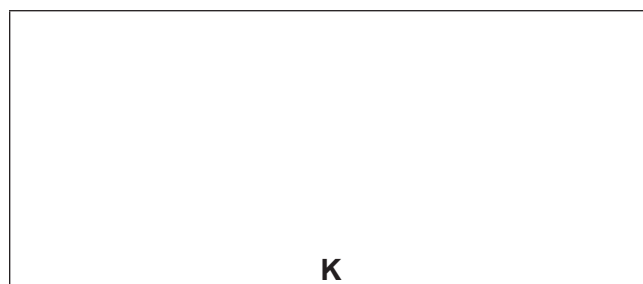
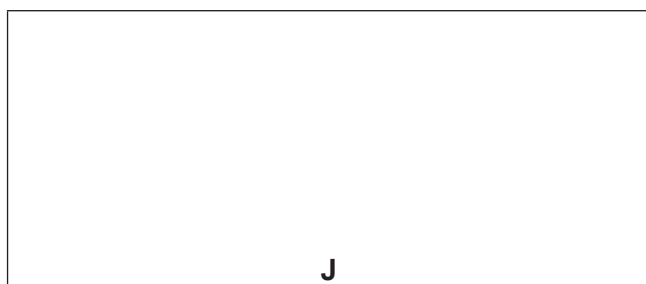
- (ii) Suggest structures for compounds **P** and **Q**.



[2]

- (c) Isomers **J**, **K**, **L** and **M** all have the molecular formula $\text{C}_9\text{H}_{11}\text{NO}$.

Use the information in (a) to suggest a structure for each of these isomers and draw these in the boxes. Draw **circles** around all chiral centres in **K** and **L**.



[5]

- (d) Compound **N** is another isomer which has the same molecular formula $\text{C}_9\text{H}_{11}\text{NO}$ and also contains a benzene ring.

N contains the same functional group as **M**.

When heated with NaOH(aq) , **N** produces ethylamine and a sodium salt **W**.

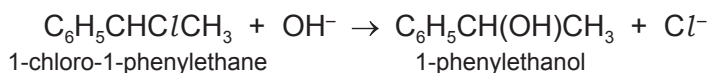
Suggest the structure of **W**.



[1]

[Total: 14]

- 6 The reaction between 1-chloro-1-phenylethane and hydroxide ions to produce 1-phenylethanol is:



The rate of this reaction can be studied by measuring the amount of hydroxide ions that remain in solution at a given time. The reaction can effectively be stopped if the solution is diluted with an ice-cold solvent.

- (a) Describe a suitable method for studying the rate of this reaction at a temperature of 40 °C, given the following.

- a solution of 0.10 mol dm⁻³ 1-chloro-1-phenylethane, labelled **A**
- a solution of 0.10 mol dm⁻³ sodium hydroxide, labelled **B**
- 0.10 mol dm⁻³ HCl
- volumetric glassware
- ice-cold solvent
- stopclock
- access to standard laboratory equipment and chemicals

.....

.....

.....

.....

.....

.....

.....

.....

..... [4]

- (b) The rate of this reaction was measured at different initial concentrations of the two reagents. The table shows the results obtained.

experiment	[C ₆ H ₅ CHClCH ₃] /mol dm ⁻³	[OH ⁻] /mol dm ⁻³	relative rate
1	0.05	0.10	0.5
2	0.10	0.20	1.0
3	0.15	0.10	1.5
4	0.20	0.15	to be calculated

- (i) Deduce the order of reaction with respect to each of [C₆H₅CHClCH₃] and [OH⁻]. Explain your reasoning.

order with respect to [C₆H₅CHClCH₃]

.....

order with respect to [OH⁻]

.....

[2]

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

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

units of k = ... [1]

- (iii) Calculate the relative rate for experiment 4.

relative rate for experiment 4 = ... [1]

- (c) (i) Use your answers in (b)(i) to help you to draw the mechanism for the reaction of 1-chloro-1-phenylethane with hydroxide ions, including the following.

- all relevant lone pairs and dipoles
- curly arrows to show the movement of electron pairs
- the structures of any transition state or intermediate

[3]

- (ii) This reaction was carried out using a single optical isomer of 1-chloro-1-phenylethane.

Use your mechanism in (i) to predict whether the product will be a single optical isomer or a mixture of two optical isomers. Explain your answer.

.....
 [1]

- (d) The proton NMR spectrum of a sample of 1-phenylethanol shows four peaks: a multiplet for the C_6H_5 protons and three other peaks as shown in the table. When the sample is shaken with D_2O and the proton NMR spectrum recorded, **fewer** peaks are seen.

Complete the table for the proton NMR spectrum of 1-phenylethanol, $\text{C}_6\text{H}_5\text{CH}(\text{OH})\text{CH}_3$.
Use of the *Data Booklet* might be helpful.

δ/ppm	number of ^1H atoms responsible for the peak	group responsible for the peak	splitting pattern	result on shaking with D_2O
1.4				
2.7				
4.0				
7.2-7.4	5	C_6H_5	multiplet	peak remains

[4]

[Total: 16]

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