Cambridge International Examinations
Cambridge International Advanced Subsidiary and Advanced Level

CANDIDATE NAME			
CENTRE NUMBER		CANDIDATE NUMBER	

9990102503

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.

IB17 06_9701_41/6RP

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	$\Delta H_f^{\ominus}$ / kJ mol^{-1}
Ba^{2+}(aq)	–538
OH^-(aq)	–230
CO_2(g)	–394
$BaCO_3$(s)	–1216
H_2O(l)	–286

(b) **(i)** Reaction 1 occurs when CO_2(g) is bubbled through an aqueous solution of $Ba(OH)_2$.

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

$$Ba(OH)_2(aq) + CO_2(g) \rightarrow BaCO_3(s) + H_2O(l) \qquad \text{reaction 1}$$

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

If $CO_2(g)$ is bubbled through an aqueous solution of $Ba(OH)_2$ for a long time, the precipitated $BaCO_3(s)$ dissolves, as shown in reaction 2.

$$BaCO_3(s) + CO_2(g) + H_2O(l) \rightarrow Ba(HCO_3)_2(aq) \qquad \text{reaction 2}$$

The standard enthalpy change for reaction 2, $\Delta H^{\ominus}_{r2}$, = $-26\,kJ\,mol^{-1}$.

(ii) Use this information and the data in the table to calculate the standard enthalpy change of formation of the $HCO_3^-(aq)$ ion.

$\Delta H^{\ominus}_f$ $HCO_3^-(aq)$ = ... $kJ\,mol^{-1}$ [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, $\Delta H^{\ominus}_{r3}$.

$$Ba(OH)_2(aq) + 2CO_2(g) \rightarrow Ba(HCO_3)_2(aq) \qquad \text{reaction 3}$$

$\Delta H^{\ominus}_{r3}$ = ... $kJ\,mol^{-1}$ [1]

(iv) How would the value of $\Delta H^{\ominus}_{r3}$ compare with the value of $\Delta H^{\ominus}_{r4}$ for the similar reaction with $Ca(OH)_2(aq)$ as shown in reaction 4?
Explain your answer.

$$Ca(OH)_2(aq) + 2CO_2(g) \rightarrow Ca(HCO_3)_2(aq) \qquad \text{reaction 4}$$

....

....

.... [2]

(c) The standard entropy change for reaction 1 is $\Delta S^{\ominus}_{r1}$.

Suggest, with a reason, how the standard entropy change for reaction 3 might compare with $\Delta S^{\ominus}_{r1}$.

....

....

.... [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.

HOCN, cyanic acid

HNCO, isocyanic acid

[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.

$$HNCO \rightleftharpoons H^+ + NCO^- \qquad K_a = 1.2 \times 10^{-4}\,mol\,dm^{-3}$$

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, $(NH_2)_2CO$, 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, $Ba(OH)_2$, is completely ionised in aqueous solutions.
During the addition of 30.0 cm^3 of 0.100 mol dm^{-3} $Ba(OH)_2$ to 20.0 cm^3 of 0.100 mol dm^{-3} isocyanic acid, the pH was measured.

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

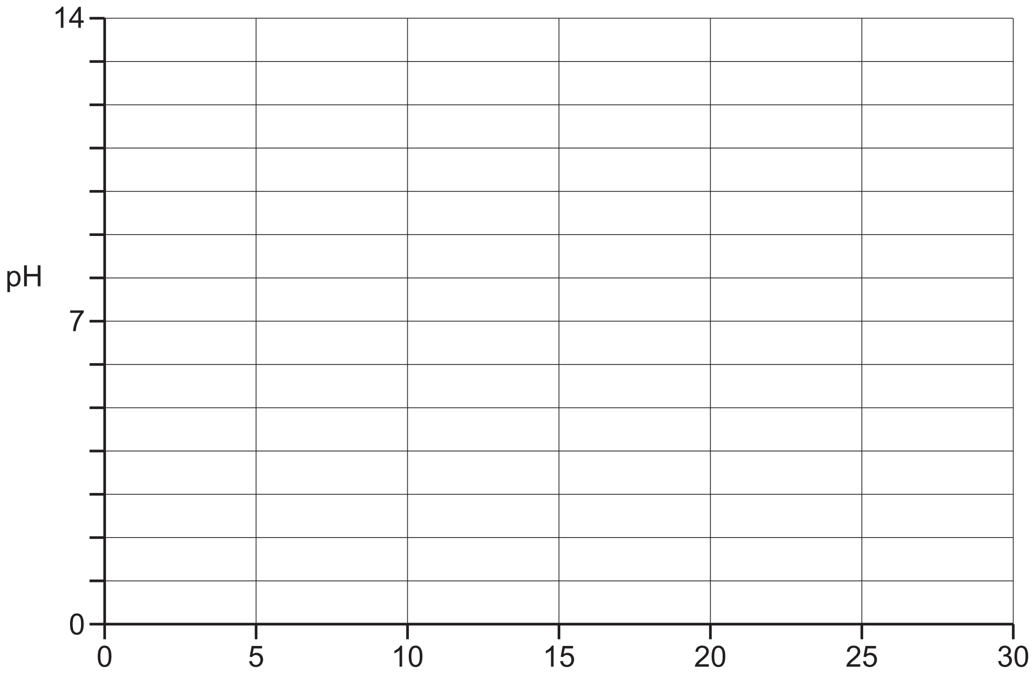
$[OH^-]$ = ... mol dm^{-3} [2]

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

final $[H^+]$ = ... mol dm^{-3}

final pH = ...
[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} $Ba(OH)_2$ 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.

$$RNCO + H_2O + HCl \rightarrow RNH_3Cl + CO_2$$

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.

$$Ba(OH)_2(aq) + CO_2(g) \rightarrow BaCO_3(s) + H_2O(l)$$

(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 $\mathrm{RNH_3C}l$ 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 $\mathrm{RNH_2}$, which forms the amine salt, $\mathrm{RNH_3C}l$.

[1]

[Total: 23]

[Turn over

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

(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 $[Co(NH_3)_4Cl_2]^+$ shows isomerism.

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

isomer 1

isomer 2

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+}	$H_2NCH_2CH_2NH_2$	6		
E	Pt^{2+}	Cl^-			2–
F	Fe^{3+}	$^-O_2C–CO_2^-$		$[Fe(O_2CCO_2)_3]$	

[6]

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

$$Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons [FeSCN]^{2+}(aq) \qquad \text{equilibrium 1}$$

$$Fe^{3+}(aq) + 4Cl^-(aq) \rightleftharpoons [FeCl_4]^-(aq) \qquad \text{equilibrium 2}$$

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

K_{stab1} =

units = ...

K_{stab2} =

units = ...
[3]

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

$$[FeCl_4]^-(aq) + SCN^-(aq) \rightleftharpoons [FeSCN]^{2+}(aq) + 4Cl^-(aq) \qquad \text{equilibrium 3}$$

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

K_{eq3} = ... [1]

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

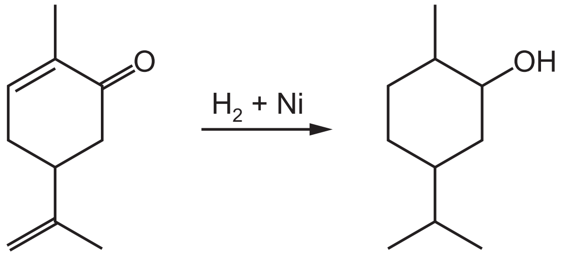
$$K_{stab1} = 1.4 \times 10^2 \qquad K_{stab2} = 8.0 \times 10^{-2}$$

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

K_{eq3} = ... units = ...
[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**.



carvone **X**

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

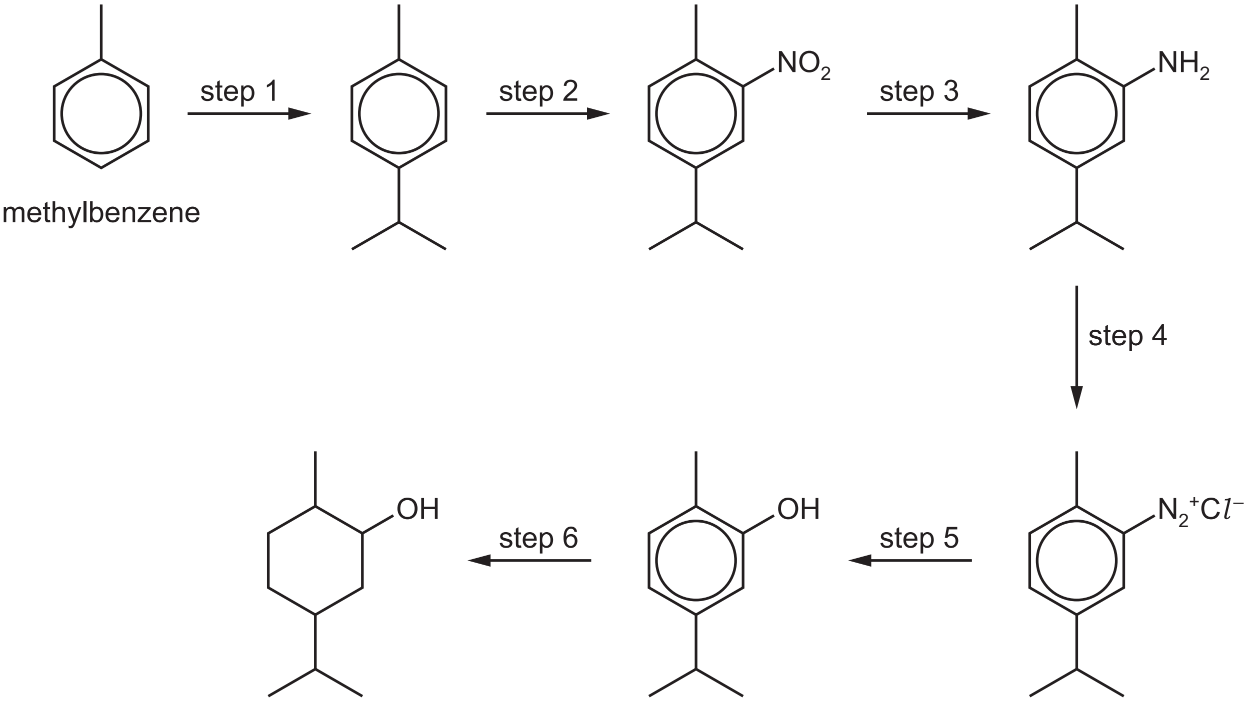
....

.... [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.



X

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

.... [1]

(ii) What type of reaction is occuring 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]

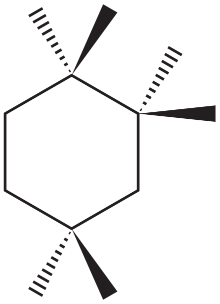
(c) During step 6, hydrogen is added to the benzene ring to produce the cyclohexane ring in **X**. The six hydrogen atoms are all added to the **same side** of the benzene ring.

(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 HC*l*(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**.

P (C_6H_7N)

Q ($C_3H_5O_2Na$)

[2]

(c) Isomers **J**, **K**, **L** and **M** all have the molecular formula $C_9H_{11}NO$.

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**.

J

K

L

M

[5]

(d) Compound **N** is another isomer which has the same molecular formula $C_9H_{11}NO$ 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**.

W

[1]

[Total: 14]

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

$$\underset{\text{1-chloro-1-phenylethane}}{C_6H_5CHClCH_3} + OH^- \rightarrow \underset{\text{1-phenylethanol}}{C_6H_5CH(OH)CH_3} + Cl^-$$

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	$[C_6H_5CHClCH_3]$ / 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 $[C_6H_5CHClCH_3]$ and $[OH^-]$. Explain your reasoning.

order with respect to $[C_6H_5CHClCH_3]$ ....

....

order with respect to $[OH^-]$ ....

....

[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]

(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, $C_6H_5CH(OH)CH_3$.
Use of the *Data Booklet* might be helpful.

δ / ppm	number of ^{1}H 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]