Cambridge International AS & A Level

**Cambridge International Examinations**
Cambridge International Advanced Subsidiary and Advanced Level

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*8205941016*

**CHEMISTRY** **9701/42**

Paper 4 A Level Structured Questions **February/March 2018**

**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 **19** printed pages and **1** blank page.


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

**1** **(a)** **(i)** State how the solubilities of the hydroxides of the Group 2 elements vary down the group.

..... [1]

**(ii)** Explain the factors that are responsible for this variation.

.....

.....

.....

.....

..... [3]

**(b)** The solubility of $Sr(OH)_2$ is $3.37 \times 10^{-2}$ mol dm$^{-3}$ at 0 °C.

**(i)** Write an expression for the solubility product of $Sr(OH)_2$.

$K_{sp}$ =

[1]

**(ii)** Calculate the value of $K_{sp}$ at 0 °C. Include units in your answer.

$K_{sp}$ = ..... units = .....

[2]

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**(c)** Metal peroxides contain the $^{-}O–O^{-}$ ion.
The peroxides of the Group 2 elements, $MO_2$, decompose on heating to produce a single gas and the solid oxide, MO, only.

**(i)** Write an equation for the thermal decomposition of strontium peroxide, $SrO_2$.

..... [1]

**(ii)** Suggest how the temperature at which thermal decomposition of $MO_2$ occurs varies down Group 2.
Explain your answer.

.....

.....

.....

.....

..... [3]

**(d) (i)** The ethanedioates of the Group 2 elements, $MC_2O_4$, decompose on heating to produce a mixture of two different gases and the solid oxide, MO, only.

Complete the equation for the thermal decomposition of barium ethanedioate.

$$BaC_2O_4 \rightarrow \text{.....} + \text{.....} + \text{.....}$$

[1]

**(ii)** Describe **two** observations you would make during the reaction when ethanedioic acid, $H_2C_2O_4$, is warmed with acidified manganate(VII) ions.

.....

.....

.....

..... [2]

[Total: 14]

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**[Turn over**

**2** **(a)** Describe the trend in the reactivity of the halogens $Cl_2$, $Br_2$ and $I_2$ as oxidising agents. Explain this trend using values of $E^{\ominus}$ ($X_2/X^-$) from the *Data Booklet*.

.....

.....

.....

.....

..... [2]

**(b)** **(i)** Write an equation for the reaction between chlorine and water.

..... [1]

**(ii)** Use standard electrode potential, $E^{\ominus}$, data from the *Data Booklet* to calculate the $E^{\ominus}_{cell}$ for the following reaction.

$$Cl_2 + 2OH^- \rightleftharpoons Cl^- + ClO^- + H_2O$$

$E^{\ominus}_{cell}$ = ..... V [2]

**(iii)** The $[OH^-]$ was increased and the $E_{cell}$ was measured.

Indicate how the value of the $E_{cell}$ measured would compare to the $E^{\ominus}_{cell}$ calculated in **(ii)** by placing **one** tick (✓) in the table.

| | |
|---|---|
| $E_{cell}$ becomes less positive than $E^{\ominus}_{cell}$. | |
| $E_{cell}$ stays the same as $E^{\ominus}_{cell}$. | |
| $E_{cell}$ becomes more positive than $E^{\ominus}_{cell}$. | |

Explain your answer.

.....

.....

.....

[2]

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**(c)** A half-equation involving bromate(V) ions, $BrO_3^-$, and bromide ions is shown.

$$BrO_3^-(aq) + 3H_2O(l) + 6e^- \rightleftharpoons Br^-(aq) + 6OH^-(aq) \qquad E^\ominus = +0.58\,V$$

**(i)** An alkaline solution of chlorate(I), $ClO^-$, can be used to oxidise bromide ions to bromate(V) ions.

Use the *Data Booklet* and the half-equation shown to write an equation for this reaction.

..... [1]

**(ii)** Calculate the $E^\ominus_{cell}$ for the reaction in **(i)**.

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

**(iii)** When a concentrated solution of bromic(V) acid, $HBrO_3$, is warmed, it decomposes to form bromine, oxygen and water only.

Write an equation for this reaction. The use of oxidation numbers may be helpful.

..... [1]

[Total: 10]

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**[Turn over**

**3** **(a)** Hydrogen cyanide, HCN, is a weak acid in aqueous solution.

$$HCN(aq) \rightleftharpoons H^+(aq) + CN^-(aq) \qquad K_a = 6.2 \times 10^{-10}\,mol\,dm^{-3}$$

**(i)** Calculate the pH of $0.10\,mol\,dm^{-3}$ HCN(aq).

pH = ..... [2]

**(ii)** Draw a 'dot-and-cross' diagram to represent the bonding in the hydrogen cyanide molecule. Show the outer shell electrons only.

[1]

**(iii)** State the hybridisation of the carbon and nitrogen atoms in hydrogen cyanide, and give the H–C–N bond angle.

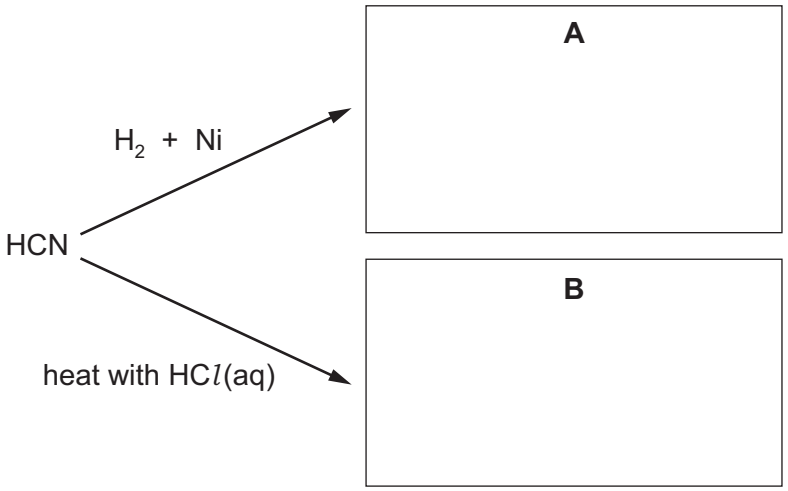
hybridisation of C .....

hybridisation of N .....

H–C–N bond angle .....

[2]

**(iv)** Suggest structures for the organic products **A** and **B** in the following reactions. Assume that HCN reacts in a similar way to RCN.




[2]

**(b)** Adding a measured quantity of KCN to a solution of $NiCl_2$ produces the complex $[Ni(CN)_2Cl_2]^x$.

**(i)** Deduce the overall charge, *x*, on this complex.

*x* = ..... [1]

The complex can exist as two separate isomers with the same geometry (shape) around the nickel ion.

**(ii)** State the type of isomerism shown by these isomers.

..... [1]

**(iii)** If bromide ions are present in the solution, the complex $[Ni(CN)_2ClBr]^x$ can form.

Assuming that $[Ni(CN)_2ClBr]^x$ has the same geometry as $[Ni(CN)_2Cl_2]^x$, state the number of isomers of $[Ni(CN)_2ClBr]^x$ that could exist, and draw their structures in the box.

- number of isomers of $[Ni(CN)_2ClBr]^x$ .....

| structures of the isomers of $[Ni(CN)_2ClBr]^x$ |
| --- |
| |

[3]

**(c)** An aqueous solution of KCN is gradually added to a solution of $NiSO_4$ until the KCN is in excess. The following series of reactions takes place.

$NiSO_4$ —KCN→ **C** (green precipitate) —more KCN→ **D** (yellow solution) —KCN in excess→ **E** (red solution)

- The oxidation state of nickel does **not** change during these reactions.
- None of **C**, **D** or **E** contains sulfur.
- **C** contains no potassium.
- The K : Ni ratio in **D** is 2 : 1.
- The K : Ni ratio in **E** is 3 : 1.

Use the information to suggest the formulae of **C**, **D** and **E**.

**C** .....

**D** .....

**E** .....

[3]

[Total: 15]

**4 (a) (i)** State what is meant by the term *partition coefficient*.

.....

.....

..... [1]

Ammonia is soluble in both water and organic solvents.
An aqueous solution of ammonia is shaken with the immiscible organic solvent trichloromethane.
The mixture is left to reach equilibrium.

Samples are taken from each layer and titrated with dilute hydrochloric acid.

- A 25.0 $cm^3$ sample from the trichloromethane layer requires 13.0 $cm^3$ of 0.100 mol $dm^{-3}$ HC$l$ to reach the end-point.
- A 10.0 $cm^3$ sample from the aqueous layer requires 12.5 $cm^3$ of 0.100 mol $dm^{-3}$ HC$l$ to reach the end-point.

**(ii)** Calculate the partition coefficient, $K_{partition}$, of ammonia between trichloromethane and water.

$K_{partition}$ = ..... [2]

**(iii)** Butylamine, $C_4H_9NH_2$, is also soluble in both water and organic solvents.

Suggest how the value of $K_{partition}$ of butylamine between trichloromethane and water would compare to the value of $K_{partition}$ calculated in **(ii)**. Explain your answer.

.....

.....

..... [2]

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**(b) (i)** Explain why butylamine is basic.

.....

..... [1]

**(ii)** Write an equation to show butylamine reacting as a base.

..... [1]

**(iii)** State how the basicity of butanamide, $C_3H_7CONH_2$, compares to that of butylamine.

..... [1]

**(iv)** State a reagent for the conversion of butanamide into butylamine.

..... [1]

[Total: 9]

**5** **(a)** **(i)** Complete the electronic configuration of a chromium atom.

$1s^2 2s^2 2p^6 3s^2$ ..... [1]

**(ii)** State the **two** highest oxidation states of chromium commonly seen in its compounds.

..... [1]

**(b)** Six different compounds or complexes, **H**, **J**, **K**, **L**, **M** and **N**, are formed when an excess of aqueous $NH_3$, aqueous NaOH and concentrated aqueous HC*l* are separately added to separate solutions containing $Cu^{2+}(aq)$ or $Co^{2+}(aq)$.

| solution | reagent | | |
|---|---|---|---|
| | an excess of $NH_3(aq)$ | an excess of NaOH(aq) | an excess of concentrated HC*l*(aq) |
| $Cu^{2+}(aq)$ | **H** | **J** | **K** |
| $Co^{2+}(aq)$ | **L** | **M** | **N** |

**(i)** State the colours of the following compounds or complexes.

**H** .....

**K** .....

**M** .....

[2]

**(ii)** Write the formulae of the following compounds or complexes.

**L** .....

**N** .....

[2]

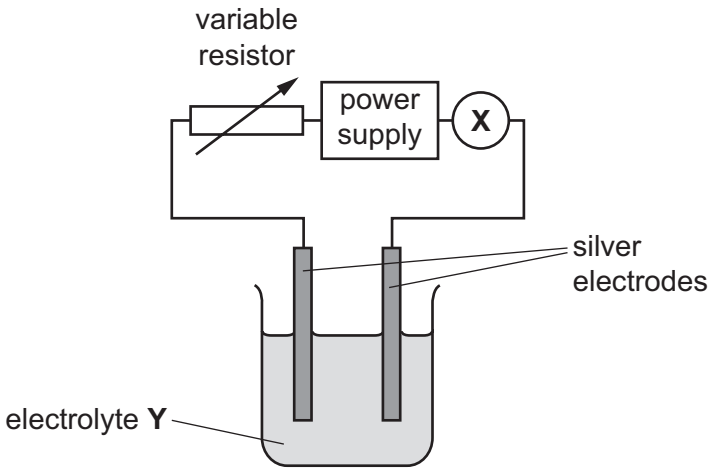
**(iii)** State the appearance of compound **J**.

..... [1]

[Total: 7]

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**6** The apparatus shows a cell which can be used to determine a value of the Avogadro constant, L.




**(a) (i)** Name component **X**.

..... [1]

**(ii)** Suggest a suitable electrolyte **Y**.

..... [1]

**(b)** In an experiment, a current of 0.200 A was passed through the cell for 40.0 minutes. The mass of the silver cathode increased by 0.500 g.

The charge on the electron is $-1.60 \times 10^{-19}$ C.

Calculate the:

- number of moles of silver deposited on the cathode

- number of coulombs of charge passed

- number of electrons passed

- number of electrons needed to deposit 1 mol of silver at the cathode.

[3]

[Total: 5]

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**[Turn over**

**7 (a) (i)** Complete the equations to show the **two** types of polymerisation. Draw **one** repeat unit for each polymer. Include any other products.

- addition polymerisation

$n\,CH_2{=}CHCH_3(g) \rightarrow$ [ ]

- condensation polymerisation

$n\,HO_2CCH_2CO_2H(s)$ + $n\,HOCH_2CH_2OH(l) \rightarrow$ [ ]

[3]

**(ii)** Suggest the sign of the entropy changes, $\Delta S^{\ominus}$, for each of the **two** types of polymerisation. Explain your answers.

- $\Delta S^{\ominus}$ for addition polymerisation

.....

.....

.....

- $\Delta S^{\ominus}$ for condensation polymerisation

.....

.....

.....

[2]

**(b)** An amide bond forms when a carboxylic acid reacts with an amine.

**(i)** Complete the equation by writing the products in the box.

$R–CO_2H + H_2N–R' \rightarrow$ [ ] + [ ]

[1]

**(ii)** Use your answer to **(i)** to work out the bonds that are broken and the bonds that are formed during the reaction between a carboxylic acid and an amine.

- bonds that are broken

.....

- bonds that are formed

.....

[2]

**(iii)** Use bond energy values from the *Data Booklet* to calculate the enthalpy change, $\Delta H^{\ominus}$, when **one** mole of amide bonds is formed in the reaction in **(i)**.

$\Delta H^{\ominus}$ = ..... kJ [2]

**(c)** Amide bonds can also be formed by reacting acyl chlorides with amines.

The enthalpy change for this process, $\Delta H^{\ominus}$, is $-6.00\,kJ\,mol^{-1}$.

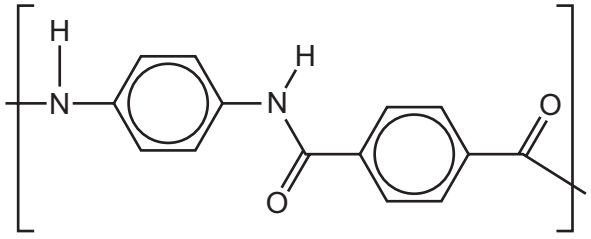
Calculate the minimum entropy change, $\Delta S^{\ominus}$, for this reaction to be spontaneous (feasible) at 298 K.

$\Delta S^{\ominus}$ = ..... $J\,K^{-1}\,mol^{-1}$ [2]

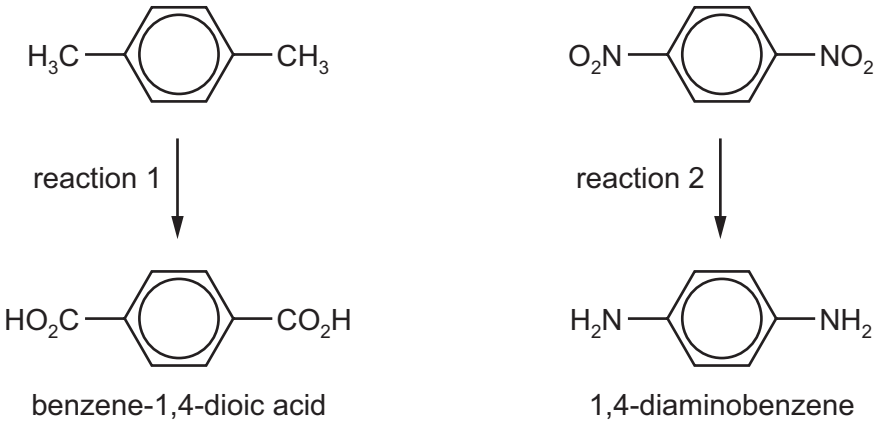
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**[Turn over**

The repeat unit of the polyamide *Kevlar* is shown.



**(d)** The monomers of *Kevlar*, benzene-1,4-dioic acid and 1,4-diaminobenzene, can be synthesised as follows.




benzene-1,4-dioic acid

1,4-diaminobenzene

State the reagents and conditions needed for:

**(i)** reaction 1

..... [1]

**(ii)** reaction 2

.....

..... [2]

**(e)** *Kevlar* is both strong and rigid.

Complete the table to identify **two** intermolecular forces and the groups involved which are responsible for these properties of *Kevlar*.

| intermolecular force | group(s) involved |
|---|---|
| | |
| | |

[2]

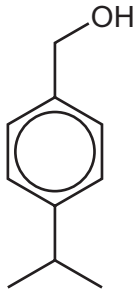
[Total: 17]

**Question 8 starts on the next page.**

**8** **(a)** Cumin is a spice used to flavour food. Two compounds responsible for its flavour are cuminaldehyde and cuminyl alcohol.




cuminaldehyde




cuminyl alcohol

**(i)** Deduce the number of peaks that would be present in the $^{13}C$ NMR spectrum of cuminyl alcohol.

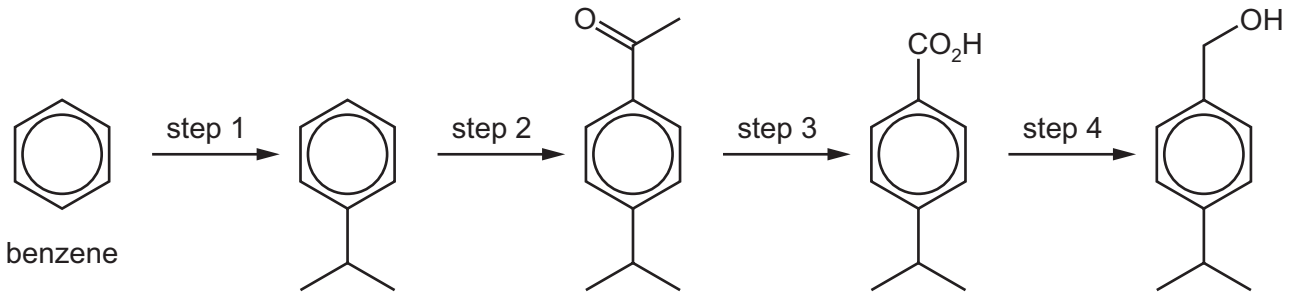
number of peaks ..... [1]

**(ii)** Identify **two** bonds that are responsible for the differences in the infra-red spectra of cuminaldehyde and cuminyl alcohol, and state their absorption ranges.

| | absorption range in the infra-red spectrum / $cm^{-1}$ | |
|---|---|---|
| bond responsible for the difference | cuminaldehyde | cuminyl alcohol |
| | | |
| | | |

[2]

**(b)** Cuminyl alcohol can be synthesised from benzene by the following route.




**(i)** Suggest reagents and conditions for steps 1–4.

step 1 .....

step 2 .....

step 3 .....

step 4 .....

[4]

**(ii)** Name the mechanism of step 2 and state the type of reaction in step 4.

mechanism of step 2 .....

type of reaction in step 4 .....

[2]

[Total: 9]

**9** **(a)** Two molecules of compound **F** react together under suitable conditions to form compound **G**. Some information about compounds **F** and **G** is given.

- The mass spectrum of **F** has a peak due to the molecular ion at m/e = 106, and a peak at m/e = 107 with an abundance 8% of the 106 peak.
- The mass spectrum of **G** has a peak due to the molecular ion at m/e = 212, and major peaks at m/e = 91 and m/e = 105.
- Both **F** and **G** contain oxygen and are neutral compounds which are insoluble in water.
- The $^1$H NMR spectrum of **F** includes a singlet peak at $\delta$ = 10.0 due to one proton.
- The $^1$H NMR spectrum of **G** includes a singlet peak at $\delta$ = 5.1 due to two protons.
- When **G** is heated with dilute sulfuric acid, benzoic acid, $C_6H_5CO_2H$, and phenylmethanol, $C_6H_5CH_2OH$, are produced.

Use this information to answer **(i)**–**(vi)**.

**(i)** Explain how the mass spectrum of **F** shows that a molecule of **F** contains seven carbon atoms. Show your working.

[1]

**(ii)** Suggest the molecular formula of the fragment of **G** at m/e = 91.

..... [1]

**(iii)** Suggest the molecular formulae of **F** and **G**.

**F** .....

**G** .....

[2]

**(iv)** Suggest structures for compounds **F** and **G**.

| **F** | **G** |
|---|---|
| | |

[2]

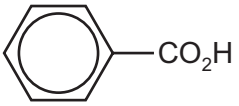
**(v)** On the structures you have drawn in **(iv)**, circle the protons responsible for the $^1$H NMR peaks at $\delta$ = 10.0 in **F** and $\delta$ = 5.1 in **G**. [1]

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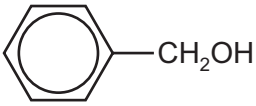
**(vi)** State the type of reaction that **G** undergoes when heated with dilute sulfuric acid.

..... [1]

**(b)** Describe and explain the relative acidities of benzoic acid, phenylmethanol and 4-methylphenol.




benzoic acid




phenylmethanol




4-methylphenol

.....

.....

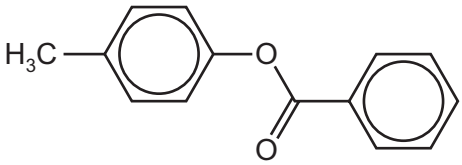
.....

.....

.....

..... [3]

**(c)** The ester 4-methylphenyl benzoate is used in the manufacture of perfumes.




4-methylphenyl benzoate

Suggest a **two**-step route for the synthesis of 4-methylphenyl benzoate from 4-methylphenol and benzoic acid.
Include reagents and conditions for each step, and the structure of the intermediate compound.

[3]

[Total: 14]

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