Cambridge International Examinations
Cambridge International Advanced Subsidiary and Advanced Level

CANDIDATE NAME			
CENTRE NUMBER		CANDIDATE NUMBER	

9664884656

CHEMISTRY **9701/41**

Paper 4 A Level Structured Questions **October/November 2016**

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 **20** printed pages.

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[Turn over

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

1 Copper is a transition element and has atomic number 29.

(a) Complete the electronic configuration for the copper atom and the copper ion in the +2 oxidation state.

- copper atom [Ar] ....
- copper ion in the +2 oxidation state [Ar] ....

[2]

(b) The following equilibrium exists between two complex ions of copper in the +2 oxidation state.

$$[Cu(H_2O)_6]^{2+} + 4Cl^- \rightleftharpoons [CuCl_4]^{2-} + 6H_2O$$

(i) Name the *type of reaction* occurring here.

.... [1]

(ii) State the colours of these two complex ions.

$[Cu(H_2O)_6]^{2+}$ .... $[CuCl_4]^{2-}$ .... [1]

(iii) State the shape of the $[CuCl_4]^{2-}$ ion.

.... [1]

(iv) Write the expression for the stability constant, K_{stab}, for this equilibrium.

K_{stab} =

[1]

(c) Copper also forms the complex ions $[Cu(NH_3)_2(H_2O)_4]^{2+}$ and $[Cu(en)(H_2O)_4]^{2+}$ where *en* is the bidentate ligand ethane-1,2-diamine, $H_2NCH_2CH_2NH_2$.

$$[Cu(H_2O)_6]^{2+} + 2NH_3 \rightleftharpoons [Cu(NH_3)_2(H_2O)_4]^{2+} + 2H_2O \quad \text{equilibrium 1}$$

$$[Cu(H_2O)_6]^{2+} + en \rightleftharpoons [Cu(en)(H_2O)_4]^{2+} + 2H_2O \quad \text{equilibrium 2}$$

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

....

.... [2]

(ii) The table lists the values of stability constants for these two complexes.

	stability constant, K_{stab}
$[Cu(NH_3)_2(H_2O)_4]^{2+}$	7.94×10^7
$[Cu(en)(H_2O)_4]^{2+}$	3.98×10^{10}

What do these K_{stab} values tell us about the relative positions of equilibria 1 and 2?

....

.... [1]

(d) Nickel forms the complex ion $[Ni(en)_3]^{2+}$ in which it is surrounded octahedrally by six nitrogen atoms.

(i) Name the type of stereoisomerism displayed by $[Ni(en)_3]^{2+}$.

.... [1]

(ii) Draw three-dimensional diagrams to show the **two** stereoisomers of $[Ni(en)_3]^{2+}$.

[3]

(e) Ethane-1,2-diamine is a useful reagent in organic chemistry.

(i) Explain how the amino groups in ethane-1,2-diamine allow the molecule to act as a Brønsted-Lowry base.

....

.... [2]

(ii) Write an equation for the reaction of ethane-1,2-diamine with an excess of hydrochloric acid.

.... [1]

(f) **(i)** Under certain conditions, ethane-1,2-diamine reacts with ethanedioic acid, HO_2CCO_2H, to form the polymer **Z**.

Draw the structure of this polymer, **Z**, showing **two** repeat units.

[2]

(ii) Name the *type of reaction* occurring during this polymerisation.

.... [1]

(iii) Polymer **Z** is an example of a biodegradable polymer.

Name a polymer that is non-biodegradable.

.... [1]

[Total: 20]

2 **(a)** When copper(II) carbonate is heated strongly, it decomposes in a similar way to Group 2 carbonates.

Predict what would be observed when anhydrous copper(II) carbonate is heated.

....

.... [1]

(b) Describe and explain how the thermal stability of the Group 2 carbonates varies down the group.

....

....

....

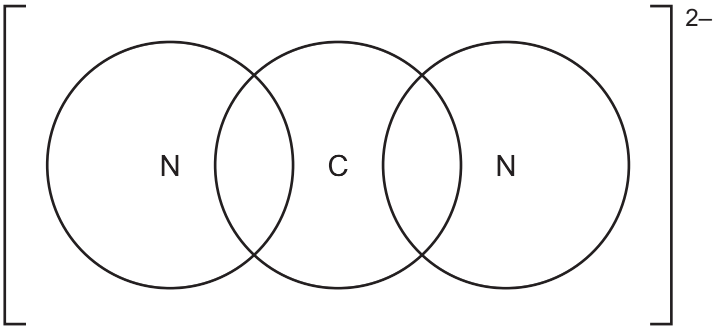
.... [3]

(c) Calcium cyanamide, $CaCN_2$, can be used as a fertiliser.

(i) Complete the 'dot-and-cross' diagram for the cyanamide ion, CN_2^{2-}.

Use the following key for the electrons.

● electrons from carbon
× electrons from nitrogen
☐ added electron(s) responsible for the overall negative charge



[2]

(ii) $CaCN_2$ decomposes readily on contact with water forming an insoluble white solid and ammonia only.

Suggest an equation for this reaction.

.... [2]

[Total: 8]

3 The spontaneity (feasibility) of a chemical reaction depends on the standard Gibbs free energy change, $\Delta G^{\ominus}$. This is related to the standard enthalpy and entropy changes by the equation shown.

$$\Delta G^{\ominus} = \Delta H^{\ominus} - \mathrm{T}\Delta S^{\ominus}$$

(a) State and explain whether the following processes will lead to an increase or decrease in entropy.

(i) the reaction of magnesium with hydrochloric acid

entropy change ....

explanation ....

[1]

(ii) solid potassium chloride dissolving in water

entropy change ....

explanation ....

[1]

(iii) steam condensing to water

entropy change ....

explanation ....

[1]

(b) Magnesium carbonate can be decomposed.

$$MgCO_3(s) \rightarrow MgO(s) + CO_2(g) \qquad \Delta H^{\ominus} = +117\,\mathrm{kJ\,mol^{-1}}$$

Standard entropies are shown in the table.

substance	$MgCO_3(s)$	$MgO(s)$	$CO_2(g)$
$S^{\ominus}$ / J mol^{-1} K^{-1}	+65.7	+26.9	+214

(i) Calculate $\Delta G^{\ominus}$ for this reaction at 298 K.
Include a relevant sign and give your answer to **three** significant figures.

$\Delta G^{\ominus}$ = ... kJ mol^{-1} [3]

(ii) Explain, with reference to $\Delta G^{\ominus}$, why this reaction becomes more feasible at higher temperatures.

....

.... [1]

(c) On heating, sodium hydrogencarbonate decomposes into sodium carbonate as shown.

$$2NaHCO_3(s) \rightarrow Na_2CO_3(s) + CO_2(g) + H_2O(g) \qquad \Delta H^{\ominus} = +130\,kJ\,mol^{-1}$$
$$\Delta S^{\ominus} = +316\,J\,mol^{-1}\,K^{-1}$$

Calculate the **minimum** temperature at which this reaction becomes spontaneous (feasible). Show your working.

temperature = ... K [2]

(d) The solubility of Group 2 sulfates decreases down the Group.

Explain this trend.

....

....

....

.... [2]

[Total: 11]

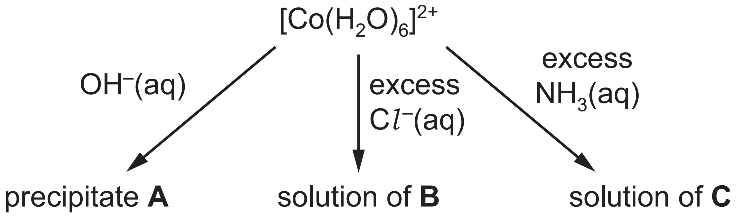
4 **(a)** Cobalt is a transition element that forms complex ions with oxidation states +2 and +3.

Explain what is meant by the term *transition element*.

....

.... [1]

(b) The following scheme shows some reactions of $[Co(H_2O)_6]^{2+}$.



(i) State the formula of each of the following.

A ....

B ....

C ....

[2]

(ii) State the colour of the following solutions.

$[Co(H_2O)_6]^{2+}$ ....

solution of **B** ....

solution of **C** ....

[2]

(c) Define the term *standard electrode potential*.

....

....

.... [2]

(d) An electrochemical cell was set up to measure the standard electrode potential, $E^{\ominus}_{\text{cell}}$, of a cell made of a Co^{2+}/Co half-cell and a Fe^{3+}/Fe^{2+} half-cell.

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

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

[1]

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

.... [1]

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

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

(e) The electrochemical cell in **(d)** was set up again but this time the concentration of $Co^{2+}(aq)$ was $0.050\,\text{mol}\,\text{dm}^{-3}$.

The Nernst equation can be used to calculate the value of an electrode potential at different concentrations.

$$E = E^{\ominus} + (0.059/z)\log[Co^{2+}(aq)] \qquad \text{Nernst equation}$$

(i) Use the *Data Booklet* and the Nernst equation to calculate the value of E for the Co^{2+}/Co half-cell in this experiment.

E for Co^{2+}/Co = ... V [1]

(ii) Suggest how this change will affect the overall cell potential, E_{cell}, compared to $E^{\ominus}_{\text{cell}}$ in **(d)(iii)**.
Circle your answer.

less positive   no change   more positive

[1]

(f) Iron(III) ions can oxidise vanadium metal.

Construct an equation for the reaction of an excess of iron(III) ions with vanadium metal.
Use of the *Data Booklet* will be helpful.

.... [2]

[Total: 14]

5 Compound **F** contains the elements carbon, hydrogen and oxygen only. All carbon-carbon bonds in **F** are single bonds. The structure of **F** was analysed by mass spectrometry and infra-red and NMR spectroscopy.

(a) The mass spectrum shows that the *m*/*e* value for the M peak is 90.

The ratio of the heights of the M and M+1 peaks is 22.1 : 0.7.

(i) Use the ratio of the heights of the M and M+1 peaks to calculate the number of carbon atoms in a molecule of **F**.

number of carbon atoms = ... [2]

(ii) Suggest the molecular formula of **F**.

molecular formula = C H O [1]

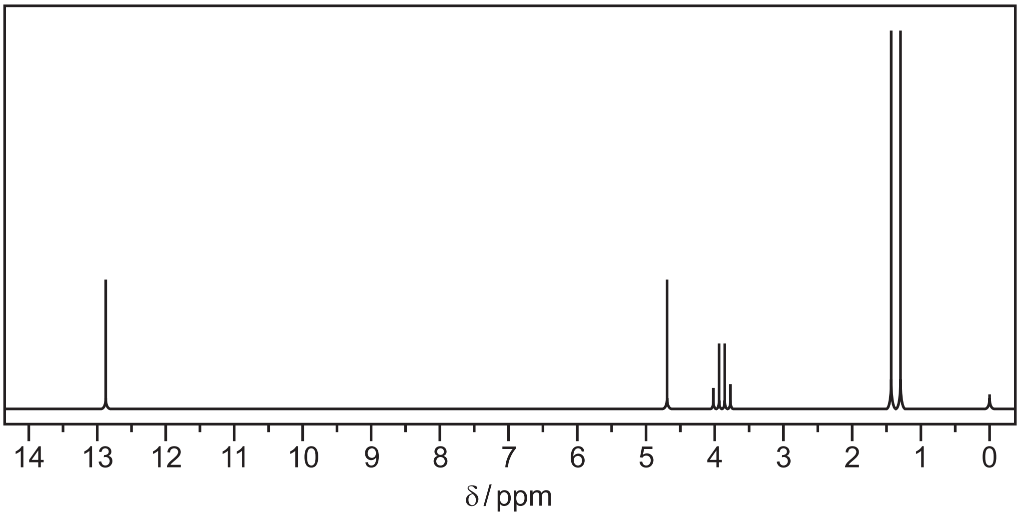
(b) The infra-red spectrum of **F** was obtained.

Use the *Data Booklet* and your knowledge of infra-red spectroscopy to identify the type of bond and the functional group responsible for these **three** absorptions.

absorption / cm^{-1}	appearance of the peak	type of bond	functional group
3350	broad and strong		
2680	very broad and strong		
1725	strong		

[2]

(c) **F** was dissolved in deuterated trichloromethane, $CDCl_3$, and the proton NMR spectrum of this solution obtained.



(i) Use the *Data Booklet* and your answer to **(a)(ii)** to complete Table 1 for the proton NMR spectrum of **F**.
The actual chemical shifts for the four absorptions in **F** have been added for you.

Table 1

δ / ppm	type of proton	relative peak area
1.4		
3.9		
4.7		
12.9		

[4]

(ii) Describe and explain the splitting pattern for the absorption at δ = 1.4.

....

.... [1]

(iii) **F** was dissolved in D_2O and the proton NMR spectrum of this new solution obtained.
Two of the absorptions in Table 1 were not present in this spectrum.

Which absorptions were **not** present?

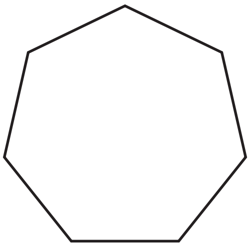
.... and .... [1]

(iv) Suggest the structure of **F**.

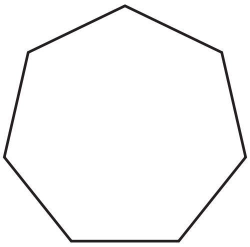
[1]

(d) Molecules of cycloheptadiene, C_7H_{10}, consist of a seven-membered ring with two carbon-carbon double bonds.

(i) Complete the skeletal formulae of two isomers of cycloheptadiene.



P



Q

[1]

The isomers **P** and **Q** were analysed using carbon-13 NMR spectroscopy.

(ii) Predict the number of peaks that will be seen in the carbon-13 NMR spectra of **P** and **Q**.

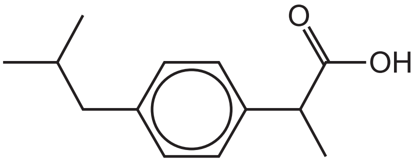
isomer	number of peaks
P	
Q	

[2]

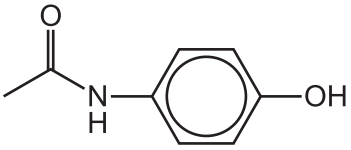
[Total: 15]

Question 6 starts on the next page.

6 Ibuprofen and paracetamol are pain-relief drugs.



ibuprofen



paracetamol

(a) Ibuprofen and paracetamol both contain the aryl (benzene) functional group.

Name the **other** functional groups present in each molecule.

ibuprofen ....

paracetamol .... [2]

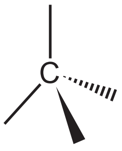
(b) Ibuprofen contains a chiral centre and shows stereoisomerism.

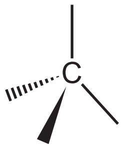
(i) State what is meant by the term *chiral centre*.

....

.... [1]

(ii) Draw the two stereoisomers of ibuprofen.





[2]

(c) Draw the structures of the organic products when ibuprofen and paracetamol react separately with $LiAlH_4$.

product with ibuprofen

product with paracetamol

[2]

(d) A student carried out some reactions with solutions of ibuprofen and paracetamol using reagents **D** and **E** and the following results were obtained.
(✓ means a reaction took place.)

reagent	ibuprofen	paracetamol
D	✓	✗
E	✗	✓

(i) Suggest a possible identity for each reagent **D** and **E**.

D ....

E ....

[2]

(ii) Give the structure of the organic product formed when reagent **D** reacted with ibuprofen.

product with ibuprofen

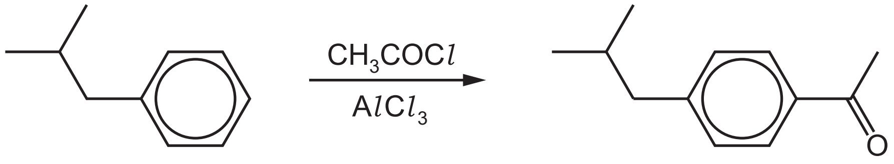
[1]

(iii) Give the structure of the organic product formed when reagent **E** reacted with paracetamol.

product with paracetamol

[1]

(e) One of the steps in the manufacture of ibuprofen is shown.

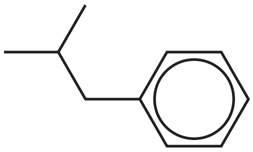


X **Y**

(i) Write an equation for the reaction between CH_3COCl and $AlCl_3$.

.... [1]

(ii) Complete the mechanism for the conversion of **X** into **Y**. Include all necessary curly arrows, any relevant dipoles and charges.



X

[3]

(iii) Name the mechanism in **(ii)**.

.... [1]

[Total: 16]

Question 7 starts on the next page.

7 **(a)** Sodium chlorate(I), $NaClO$, is the active ingredient in commercial bleach. The concentration of chlorate(I) ions was determined by titration.

- 10.0 cm^3 of a bleach solution was diluted to 250 cm^3 in a volumetric flask using distilled water.
- Dilute sulfuric acid and an excess of potassium iodide solution were added to a 25.0 cm^3 portion of this solution to liberate iodine.
- The resulting solution required 20.80 cm^3 of 0.100 mol dm^{-3} aqueous sodium thiosulfate solution to react with the iodine produced.

The titration reactions are shown.

$$ClO^- + 2I^- + 2H^+ \rightarrow I_2 + Cl^- + H_2O$$

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

Calculate the concentration, in mol dm^{-3}, of ClO^- ions in the bleach solution.

concentration of ClO^- = ... mol dm^{-3} [3]

(b) An indicator was used in the thiosulfate-iodine titration.

(i) Name a suitable indicator for this titration.

.... [1]

(ii) State the expected colour change you would observe at the end-point in this titration.

from .... to .... [1]

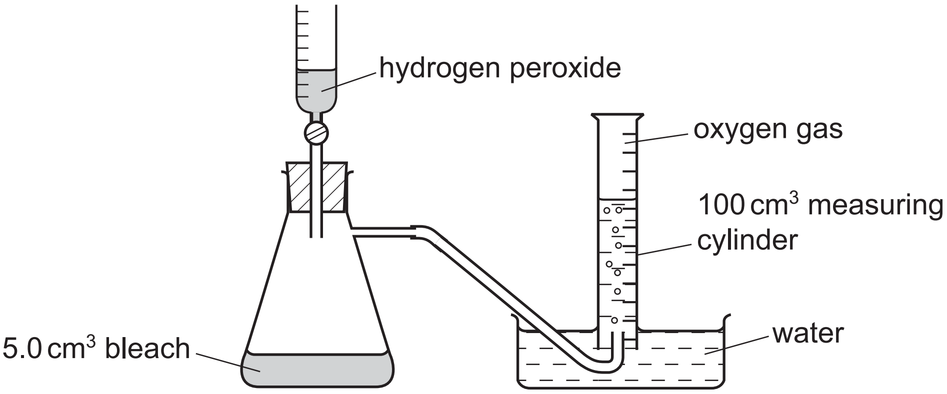
(iii) State when in the procedure you would add the indicator.

....

.... [1]

(c) The concentration of chlorate(I) ions can also be determined by adding an excess of hydrogen peroxide to the sample of bleach and measuring the volume of oxygen gas produced.

$$H_2O_2 + NaClO \rightarrow NaCl + O_2 + H_2O$$



When an excess of aqueous hydrogen peroxide was added to 5.0 cm^3 of a different bleach solution, 82 cm^3 of oxygen was produced at room temperature and pressure.

Calculate the concentration of ClO^- ions in this bleach solution.

concentration of ClO^- = ... mol dm^{-3} [2]

(d) Trichlorocyanuric acid, $C_3Cl_3N_3O_3$, acts as a chlorine buffer and disinfectant for swimming pools. It reacts with water to give chloric(I) acid, HC*l*O.

$$C_3Cl_3N_3O_3 + 3H_2O \rightleftharpoons C_3H_3N_3O_3 + 3HClO$$

(i) Write the expression for K_c for this equilibrium.

K_c =

[1]

(ii) In outdoor swimming pools, the HC*l*O is decomposed by sunlight. The decomposition of HC*l*O is a redox reaction which forms a gas that relights a glowing splint.

Describe and explain the effect of the decomposition of HC*l*O on the equilibrium in **(d)**. State the effect on K_c.

....

....

effect on K_c ....

[2]

(iii) The decomposition of HC*l*O is a redox reaction.

Suggest an equation for this reaction.

.... [1]

(e) The buffer solution in blood is a mixture of carbonic acid, H_2CO_3, and hydrogencarbonate ions, HCO_3^-. Healthy blood has a pH of 7.40.

$$H_2CO_3 + H_2O \rightleftharpoons HCO_3^- + H_3O^+ \qquad K_a = 7.94 \times 10^{-7}\,\text{mol dm}^{-3}$$

(i) Explain how this buffer system acts to control the blood pH. Include equations in your answer.

....

....

....

.... [2]

(ii) A patient's blood has a $[HCO_3^-] : [H_2CO_3]$ ratio of 9.5 : 1.

Calculate the pH of the patient's blood.

pH = ... [2]

[Total: 16]