Cambridge Assessment International Education

Cambridge International AS & A Level

CANDIDATE NAME									
CENTRE NUMBER						CANDIDATE NUMBER				

3952457672

CHEMISTRY **9701/42**

Paper 4 A Level Structured Questions **October/November 2021**

2 hours

You must answer on the question paper.

You will need: Data booklet

INSTRUCTIONS

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

INFORMATION

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

This document has **20** pages. Any blank pages are indicated.

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

1 Radium is a Group 2 element.

The predicted lattice energy, $\Delta H^{\ominus}_{latt}$, of radium sulfide, RaS, is –2612 kJ mol^{-1}.

(a) Define $\Delta H^{\ominus}_{latt}$.

.....

..... [2]

Some data relating to radium and sulfur are listed. Select relevant data from this list for use in your answers to parts **(b)** to **(e)**.

process	value / kJ mol^{-1}
enthalpy change for $Ra(s) \rightarrow Ra^{2+}(g) + 2e^-$	+1619
first ionisation energy of sulfur	+1000
second ionisation energy of sulfur	+2260
first electron affinity of sulfur	–200
second electron affinity of sulfur	+532
enthalpy change for $\frac{1}{8}S_8(s) + 2e^- \rightarrow S^{2-}(g)$	+555
lattice energy of RaS(s)	–2612

(b) Write an equation for the process corresponding to the **second** electron affinity of sulfur. Include state symbols.

..... [1]

(c) Sulfur exists as S_8 molecules in the solid state.

Use the data in this question to calculate the enthalpy change for the reaction $S_8(s) \rightarrow 8S(g)$.

enthalpy change = ... kJ mol^{-1} [3]

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(d) Calculate the standard enthalpy change of formation, $\Delta H_f^{\ominus}$, of radium sulfide.

standard enthalpy change, $\Delta H_f^{\ominus}$ = ... $kJ\,mol^{-1}$ [2]

(e) (i) State the **two** major factors that affect the numerical magnitude of a lattice energy.

.....

..... [2]

(ii) For **each** factor you have identified in **(e)(i)**, state whether it tends to make the lattice energy of radium sulfide more or less exothermic than that of sodium chloride.

Explain your answer.

.....

.....

.....

..... [2]

(iii) The lattice energies of sodium chloride, NaC*l*, and radium sulfide, RaS, are $-771\,kJ\,mol^{-1}$ and $-2612\,kJ\,mol^{-1}$, respectively.

Identify the **dominant** factor in determining the relative numerical magnitudes of the lattice energies of radium sulfide and sodium chloride.

Explain your answer.

.....

..... [1]

[Total: 13]

2 Ethoxyethane, $C_2H_5OC_2H_5$, can dissolve both in water and in octan-1-ol. The expression and numerical value for the partition coefficient of ethoxyethane between water and octan-1-ol are given. Water and octan-1-ol are immiscible.

$$K_{pc} = \frac{\text{concentration of } C_2H_5OC_2H_5 \text{ in octan-1-ol}}{\text{concentration of } C_2H_5OC_2H_5 \text{ in water}} = 6.760 \text{ at } 20\,°C$$

(a) In an experiment, octan-1-ol at 20 °C is added to a solution of ethoxyethane in water at 20 °C. The mixture is analysed immediately and a value of K_{pc} is calculated.

The calculation is performed correctly; the value calculated is 5.625.

Explain why the value calculated is **less** than 6.760.

.....

..... [2]

(b) A second experiment is performed and the value of K_{pc} is found to be 6.760. The concentration of ethoxyethane in the octan-1-ol layer is 7.62 g dm^{-3}.

(i) Calculate the concentration, in g dm^{-3}, of ethoxyethane in the aqueous layer.

..... g dm^{-3} [1]

(ii) 100 cm^3 of the octan-1-ol layer is taken and shaken with 100 cm^3 of water.

Calculate the maximum amount, in mol, of ethoxyethane that can be extracted into the water.

..... mol [3]

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(c) An aqueous solution of lead(II) nitrate is mixed with an aqueous solution of sodium iodide. A yellow precipitate of lead(II) iodide is formed and is filtered out, leaving solution **X**.

The concentration of Pb^{2+} in solution **X** is 5.68×10^{-3} mol dm^{-3}.

The concentration of I^- in solution **X** is 4.20×10^{-4} mol dm^{-3}.

(i) Use these data to calculate a value for the solubility product, K_{sp}, of lead(II) iodide.

State the units of K_{sp}.

K_{sp} = ...

units = ...
[2]

(ii) Potassium iodide is very soluble in water.

Describe and explain what is seen if a few drops of saturated potassium iodide solution are added to a portion of solution **X**.

.....

.....

..... [2]

[Total: 10]

3 Pure water is a very poor conductor of electricity. However, when hydrogen chloride gas is dissolved in water, ions are formed and a current flows during electrolysis.

$$HCl(g) + aq \rightarrow H^+(aq) + Cl^-(aq)$$

The overall change after electrolysis is that hydrogen chloride gas is converted into hydrogen and chlorine.

$$2HCl(g) \rightarrow H_2(g) + Cl_2(g)$$

When a current of 3.10A is passed through the solution for *Y* minutes, 351 cm^3 of chlorine are produced at the anode, measured under room conditions.

(a) Calculate the number of chlorine molecules produced during the electrolysis.

number of chlorine molecules = ... [2]

(b) Calculate the total number of electrons transferred to produce this number of chlorine molecules.

total number of electrons = ... [1]

(c) Calculate the quantity of charge, in coulombs, of the total number of electrons calculated in **(b)**.

quantity of charge = ... C [1]

(d) Calculate the time, *Y*, in minutes, for which the current flows.

Y = ... minutes [1]

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(e) The standard entropies, $S^{\ominus}$, of three species are given in the table.

species	$S^{\ominus}$ / J K^{-1} mol^{-1}
HCl(g)	+187
H_2(g)	+131
Cl_2(g)	+223

(i) Calculate $\Delta S^{\ominus}$ for the reaction $2HCl(g) \rightarrow H_2(g) + Cl_2(g)$.

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

(ii) $\Delta H^{\ominus}$ for the reaction $2HCl(g) \rightarrow H_2(g) + Cl_2(g)$ is +185 kJ mol^{-1}.

Calculate $\Delta G^{\ominus}$ for this reaction at 298 K.

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

(iii) Predict the effect of increasing temperature on the spontaneity of this reaction. Explain your answer.

.....

..... [1]

[Total: 9]

4 Separate samples of 0.01 mol of magnesium nitrate and 0.01 mol of strontium nitrate are heated until completely decomposed to the metal oxide, nitrogen dioxide and oxygen.

(a) State which of these two Group 2 nitrates requires the **higher** temperature before it begins to decompose. Explain your answer.

.....

.....

.....

..... [2]

(b) After decomposition is complete the 0.01 mol sample of magnesium oxide is taken and increasing amounts of water are added to it, with stirring, until no solid remains.

This procedure is repeated with the 0.01 mol sample of strontium oxide.

Identify the sample to which most water must be added to cause all the solid to dissolve. Explain your answer by reference to the solubilities of the products formed when water is added to the oxides. You should refer to relevant energy terms in your answer.

.....

.....

.....

.....

..... [3]

(c) The nitrogen dioxide given off by the decomposition of 0.0100 mol of strontium nitrate is dissolved in water. The oxidising agent $H_2O_2(aq)$ is then added to give 150.0 cm^3 of a solution in which nitric acid, HNO_3, is the only nitrogen-containing product.

(i) Calculate the concentration, in mol dm^{-3}, of HNO_3 in the 150.0 cm^3 of solution.

concentration = ... mol dm^{-3} [1]

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(ii) The HNO_3 present in 25.0 cm^3 of this solution is neutralised using 0.125 mol dm^{-3} NaOH(aq).

Calculate the minimum volume, in cm^3, of NaOH(aq) needed. Give your answer to three significant figures.

volume = ... cm^3 [1]

[Total: 7]

5 Transition elements form complexes.

(a) Molybdenum, Mo, forms an octahedral complex consisting of one Mo atom surrounded by carbon monoxide, CO, molecules. CO is a monodentate ligand. Iron forms an octahedral complex consisting of one Fe^{3+} and a number of cyanide, CN^-, ions. CN^- is a monodentate ligand.

(i) Define the term *monodentate ligand*.

.....

..... [1]

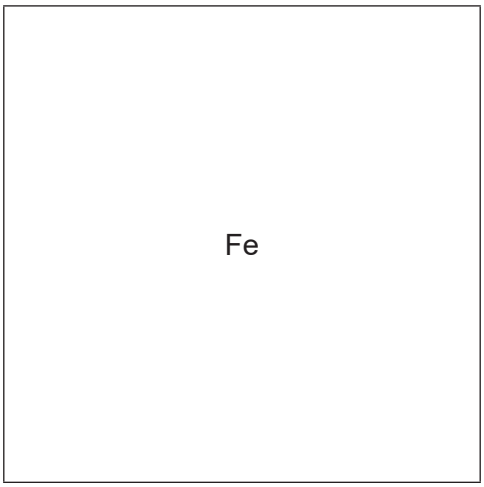
(ii) Complete the table by stating the formulae and charges of the complexes described.

	formula	charge
molybdenum complex		
iron(III) complex		

[2]

(iii) Draw a three-dimensional diagram to show the shape of this iron(III) complex.

Label one 180° bond angle on your diagram.



[1]

(b) An excess of aqueous ammonia is added to dilute copper(II) sulfate solution. A dark blue complex, $[Cu(NH_3)_4(H_2O)_2]^{2+}$, is formed.

(i) Write an ionic equation for this reaction.

..... [1]

(ii) Explain the origin of colour in copper(II) complexes.

.....

.....

.....

.....

.....

..... [4]

(c) An excess of concentrated hydrochloric acid is added to the dark blue solution of $[Cu(NH_3)_4(H_2O)_2]^{2+}$. A new complex, **Z**, is formed. The colour of the solution changes.

(i) Write an equation for the formation of **Z** from the solution of $[Cu(NH_3)_4(H_2O)_2]^{2+}$. Include the formula and charge of **Z**.

..... [2]

(ii) Name the type of reaction when **Z** forms from $[Cu(NH_3)_4(H_2O)_2]^{2+}$.

..... [1]

(iii) State the geometry of **Z**.

..... [1]

(iv) State the colour of a solution of **Z**.

..... [1]

(v) Explain why the colour of a solution of $[Cu(NH_3)_4(H_2O)_2]^{2+}$ is different from the colour of a solution of **Z**. You should refer to the energies of the orbitals involved in your answer.

.....

..... [1]

[Total: 15]

6 An excess of aqueous ammonia is added to a solution containing the complex ion $[Co(H_2O)_6]^{2+}$.

$$[Co(H_2O)_6]^{2+} + 6NH_3 \rightleftharpoons [Co(NH_3)_6]^{2+} + 6H_2O$$

(a) Complete the sentence to describe the colour change that will be seen during this reaction.

The colour changes from ..... to ..... . [1]

(b) Write an expression for the stability constant, K_{stab}, of $[Co(NH_3)_6]^{2+}$.

K_{stab} =

[1]

(c) The numerical value of K_{stab} of $[Co(NH_3)_6]^{2+}$ is 7.7×10^4.

What deduction about the properties of $[Co(NH_3)_6]^{2+}$ and $[Co(H_2O)_6]^{2+}$ can be made from this K_{stab} value?

..... [1]

(d) Oxygen can oxidise $[Co(NH_3)_6]^{2+}$ to $[Co(NH_3)_6]^{3+}$ under standard conditions in alkaline solutions.

$$[Co(NH_3)_6]^{3+} + e^- \rightleftharpoons [Co(NH_3)_6]^{2+} \qquad E^\ominus = +0.10\,V$$

(i) Use this information and the *Data Booklet* to calculate the $E^\ominus_{cell}$ value for this oxidation of $[Co(NH_3)_6]^{2+}$.

.....

.....

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

(ii) Write an ionic equation for this oxidation of $[Co(NH_3)_6]^{2+}$.

..... [1]

(iii) Predict, by selecting suitable data from the *Data Booklet*, whether oxygen can oxidise $Co^{2+}(aq)$ in **acidic** solution, in the absence of ammonia. Explain your answer.

.....

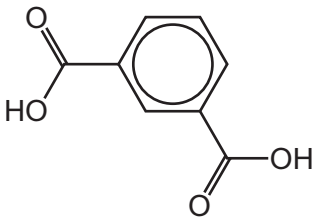
..... [2]

[Total: 7]

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7 The structure of benzene-1,3-dicarboxylic acid is shown.

benzene-1,3-dicarboxylic acid



(a) State the empirical formula of benzene-1,3-dicarboxylic acid.

..... [1]

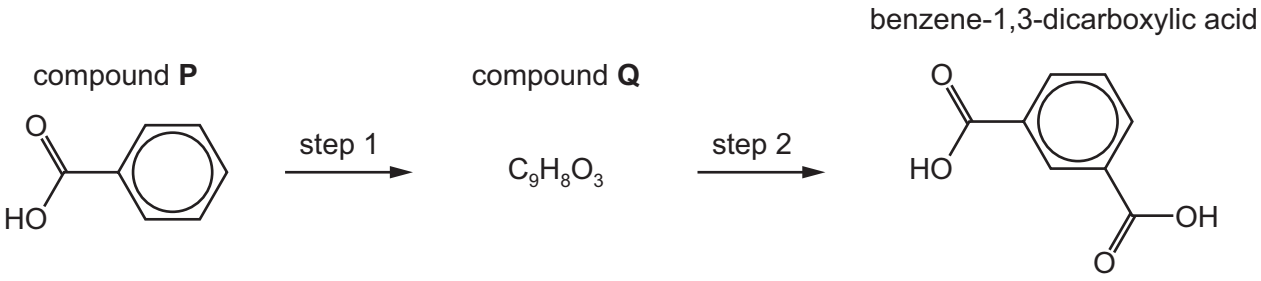
(b) Benzene-1,3-dicarboxylic acid is an isomer of benzene-1,4-dicarboxylic acid. These two isomers can be distinguished by carbon-13 (^{13}C) NMR spectroscopy.

State the number of peaks in the carbon-13 (^{13}C) NMR spectrum of each compound.

benzene-1,3-dicarboxylic acid	
benzene-1,4-dicarboxylic acid	

[2]

(c) Benzene-1,3-dicarboxylic acid can be made by the two-step synthesis shown below.



(i) Name compound **P**.

..... [1]

(ii) Explain why the major product of this two-step synthesis is benzene-1,3-dicarboxylic acid and **not** benzene-1,4-dicarboxylic acid.

.....

..... [1]

(iii) The reagents used for step 1 are CH_3COCl and $AlCl_3$. These reagents give rise to $CH_3\overset{+}{C}{=}O$ ions which react with compound **P**.

Name the mechanism of this reaction.

..... [1]

(iv) Draw the mechanism of the reaction of $CH_3\overset{+}{C}{=}O$ ions with compound **P**. Include all relevant curly arrows and charges, the structure of the intermediate and the structure of compound **Q**.

intermediate compound **Q**

$CH_3\overset{+}{C}{=}O$



[3]

(v) Suggest a reagent and conditions to convert compound **Q** into benzene-1,3-dicarboxylic acid, in step 2.

..... [1]

[Total: 10]

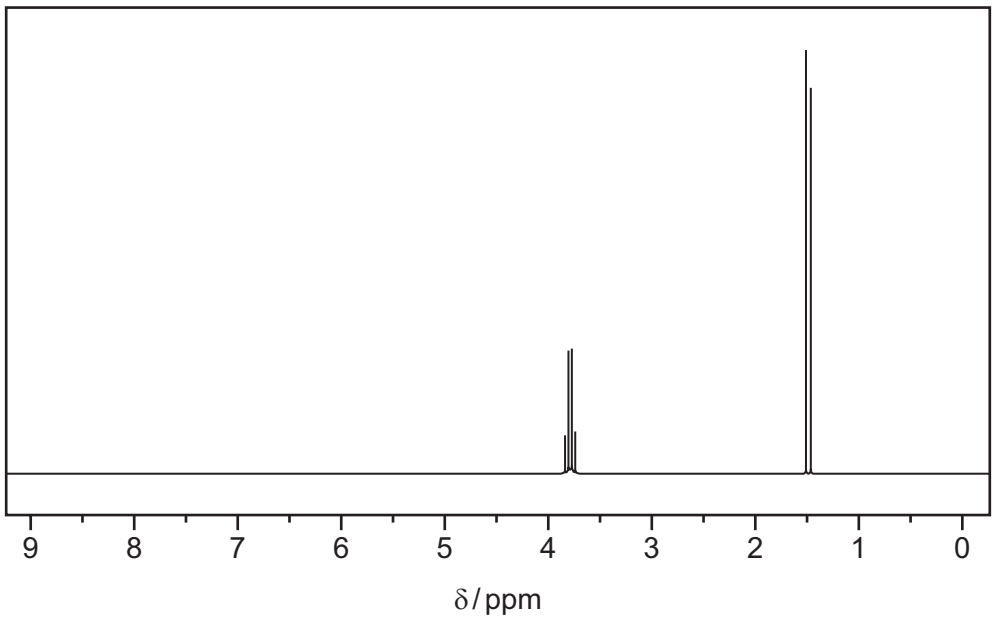
8 Alanine, $H_2NCH(CH_3)CO_2H$, and glutamic acid, $H_2NCH(CH_2CH_2CO_2H)CO_2H$, are two naturally occurring amino acids.

(a) $H_2NCH(CH_3)CO_2H$ exists as two optical isomers.

Draw three-dimensional structures of these two optical isomers.

[2]

(b) The proton (^1H) NMR spectrum of **either** alanine in D_2O or glutamic acid in D_2O is shown.



State whether this is the spectrum of alanine in D_2O or the spectrum of glutamic acid in D_2O. Explain your answer by reference to the number of peaks and splitting patterns.

.....

.....

.....

..... [3]

(c) The mass spectrum of glutamic acid, $H_2NCH(CH_2CH_2CO_2H)CO_2H$, is obtained.

(i) State the *m*/*e* value of the molecular ion peak in this spectrum.

..... [1]

(ii) The spectrum has peaks with *m*/*e* values of 88 and 131.

Draw the structures of the ions responsible for these peaks.

m/*e*	structure of ion
88	
131	

[2]

(d) At pH 11 alanine exists as $H_2NCH(CH_3)CO_2^-$ ions and glutamic acid exists as $H_2NCH(CH_2CH_2CO_2^-)CO_2^-$ ions. A mixture of alanine and glutamic acid at pH 11 is subjected to electrophoresis.

(i) State how the mixture can be maintained at pH 11 during electrophoresis.

..... [1]

(ii) Draw a fully labelled diagram for the apparatus that would be used to carry out this electrophoresis. Your diagram should include the position of the mixture of alanine and glutamic acid at the start of the electrophoresis experiment.

[2]

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(iii) Identify the electrode that each amino acid travels towards during electrophoresis at pH 11.

alanine .....

glutamic acid .....
[1]

(iv) In a particular electrophoresis experiment at pH 11, the glutamic acid travels 3.4 cm. Alanine travels a shorter distance.

Explain the factors that account for the difference in the distances travelled.

.....

.....

.....

..... [2]

[Total: 14]

9 Butylamine, $CH_3CH_2CH_2CH_2NH_2$, can be synthesised from different organic compounds by using suitable reagents. Each reaction involves one step.

(a) Complete the table to describe three different syntheses.

- One of the three syntheses should involve a nucleophilic substitution reaction.
- The starting organic compound for each synthesis should contain a different functional group.
- A different reagent should be used for each synthesis.

starting organic compound	reagent and conditions

[6]

(b) Compare and explain the relative basicities of ammonia, butylamine and phenylamine.

..... > ..... > .....
most basic least basic

.....

.....

.....

.....

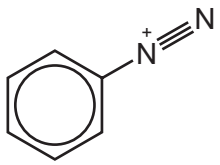
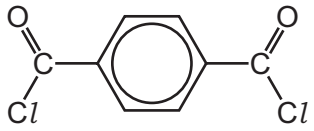
.....

..... [4]

[Total: 10]

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10 (a) Complete the table to show the structure of the organic product from each reaction of phenol, C_6H_5OH.

reaction	reaction mixture	structure of organic product
1	phenol + NaOH(aq)	
2	phenol + Na(s)	
3	phenol +  (aq) + NaOH, at 4 °C	
4	an excess of phenol + 	

[4]

(b) Identify **two** reactions from the table in which ethanol would behave in a similar way to phenol.

..... [1]

[Total: 5]

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