Cambridge Assessment
International Education

Cambridge International AS & A Level

CANDIDATE NAME			
CENTRE NUMBER		CANDIDATE NUMBER	

8982359904

CHEMISTRY **9701/43**

Paper 4 A Level Structured Questions **May/June 2020**

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. Blank pages are indicated.

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

1 **(a)** An aqueous solution of cobalt(II) contains the $[Co(H_2O)_6]^{2+}$ complex ion.

(i) Define the term *complex ion*.

....

.... [1]

(ii) Samples of $[Co(H_2O)_6]^{2+}$ are reacted separately with aqueous sodium hydroxide and with an excess of aqueous ammonia.

Give the following information about these reactions.

- the reaction of $[Co(H_2O)_6]^{2+}$ with aqueous sodium hydroxide

  colour and state of the cobalt-containing species ....

  ionic equation ....

  type of reaction ....

- the reaction of $[Co(H_2O)_6]^{2+}$ with an excess of aqueous ammonia

  colour and state of the cobalt-containing species ....

  ionic equation ....

  type of reaction ....

[6]

(b) When concentrated hydrochloric acid is added to a solution containing $[Co(H_2O)_6]^{2+}$, a blue solution of $[CoCl_4]^{2-}$ is formed and the following equilibrium is established.

$$[Co(H_2O)_6]^{2+} + 4Cl^- \rightleftharpoons [CoCl_4]^{2-} + 6H_2O$$

Use Le Chatelier's principle to suggest the expected observations when silver nitrate solution is added dropwise to the blue solution of $[CoCl_4]^{2-}$. Explain your answer.

....

....

.... [2]

(c) The $[Co(NH_3)_3Cl_3]$ complex shows stereoisomerism.

Complete the three-dimensional diagrams to show the two isomers of $[Co(NH_3)_3Cl_3]$.

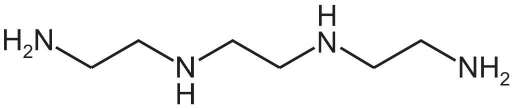
Suggest the type of stereoisomerism.

type of stereoisomerism ....

[2]

(d) Compound **X**, $C_6H_{18}N_4$, is a tetradentate ligand.

X



(i) Suggest why one molecule of **X** can form four dative bonds.

....

....

.... [1]

(ii) $C_6H_{18}N_4$ reacts with aqueous cobalt(II) ions, $[Co(H_2O)_6]^{2+}$, in a 1 : 1 ratio to form a new complex ion.

Construct an equation for this reaction.

.... [1]

[Total: 13]

2 **(a)** **(i)** Describe and explain the trend in the solubility of the Group 2 hydroxides down the group.

....

....

....

....

....

.... [4]

Group 2 hydroxides decompose on heating to give the corresponding metal oxide and water vapour.

(ii) Suggest which of $Mg(OH)_2$ and $Sr(OH)_2$ will decompose at a **lower** temperature.

Explain your answer.

....

....

....

.... [2]

[Total: 6]

3 The overall reaction for photosynthesis is shown.

$$6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2$$

Water is oxidised in this process according to the following half-equation.

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \qquad \text{half-equation 1}$$

(a) (i) Use these equations to deduce the half-equation for the reduction of carbon dioxide in this process.

[2]

(ii) Draw a fully labelled diagram of the apparatus that should be used to measure the standard electrode potential, $E^\ominus$, of O_2(g) in half-equation 1 under standard conditions. Include all necessary chemicals.

[4]

(iii) For the cell drawn in **(a)(ii)**, use the *Data Booklet* to calculate the $E^\ominus_{cell}$ and deduce which electrode is positive.

$E^\ominus_{cell}$ = ... V

identity of the positive electrode = ...

[1]

[Total: 7]

4 **(a)** The molecular formulae of three nitrogen-containing compounds are given.

S $C_6H_5CONH_2$

T $C_6H_5NH_2$

U $C_6H_5CH_2NH_2$

Describe and explain the relative basicities of **S**, **T** and **U**.

.... > .... > ....

most basic least basic

....

....

....

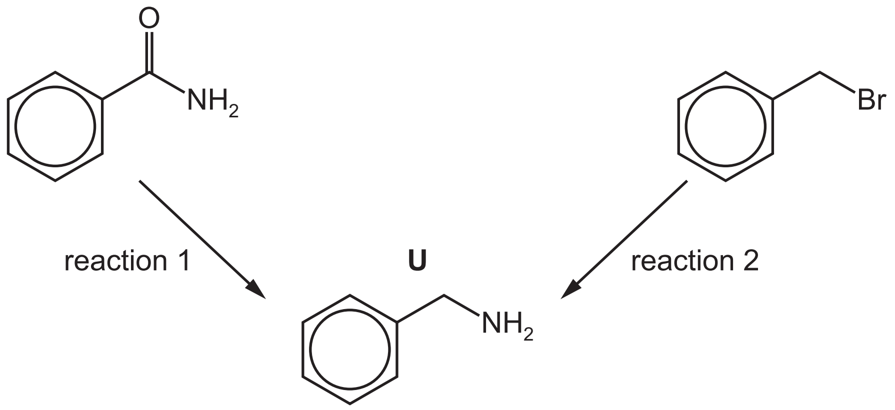
....

....

....

[3]

(b) Compound **U** can be prepared by two different methods as shown.



(i) Suggest reagents and conditions for reaction 1 and for reaction 2.

reaction 1 ....

reaction 2 ....

[2]

(ii) State the type of reaction in reaction 1 and name the mechanism in reaction 2.

type of reaction in reaction 1 ....

mechanism of reaction 2 ....

[2]

[Total: 7]

5 **(a)** Benzene reacts with bromine in the presence of an aluminium bromide catalyst, $AlBr_3$, to form bromobenzene. This is a substitution reaction. No addition reaction takes place.

(i) Explain why no addition reaction takes place.

....

.... [1]

$AlBr_3$ reacts with bromine to generate an electrophile, Br^+.

(ii) Draw the mechanism of the reaction between benzene and Br^+ ions. Include all relevant arrows and charges.

[3]

(iii) Write an equation to show how the $AlBr_3$ catalyst is reformed.

.... [1]

(b) Suggest why bromination of phenol occurs more readily than bromination of benzene.

....

....

....

....

.... [2]

(c) **(i)** There are four different carbocations with the same formula, $C_4H_9^+$. One structure is given in the table.

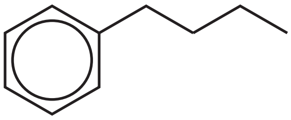
Suggest the structural formulae of the three other carbocations.

structure 1	structure 2	structure 3	structure 4
$CH_3CH_2CH_2CH_2^+$			

[3]

(ii) Benzene reacts with each of these carbocations in separate Friedel-Crafts alkylation reactions.
In each reaction an organic compound with formula $C_{10}H_{14}$ is formed. The number of peaks observed in the carbon-13 NMR spectrum of each compound is given.

Suggest the structures for the three other compounds.

 number of peaks in carbon-13 NMR = 8	number of peaks in carbon-13 NMR = 6
number of peaks in carbon-13 NMR = 7	number of peaks in carbon-13 NMR = 8

[4]

[Total: 14]

6 **(a)** Compare and explain the relative acidities of 2-chloropropanoic acid, 3-chloropropanoic acid, and propanoic acid. Explain your answer.

.... > .... > ....

most acidic   least acidic

explanation ....

....

....

....

....

.... [3]

(b) **(i)** The numerical values of K_a for methanoic acid, HCO_2H, and pyruvic acid, CH_3COCO_2H, are given.

acid	K_a
HCO_2H	1.78×10^{-4}
CH_3COCO_2H	4.07×10^{-3}

An equilibrium mixture containing the two acid-base pairs is formed.

$$HCO_2^- + CH_3COCO_2H \rightleftharpoons HCO_2H + CH_3COCO_2^-$$

Use the K_a values to calculate the equilibrium constant, K_{eq}, for this equilibrium.

K_{eq} = ... [1]

(ii) Use your value of K_{eq} to predict the position of this equilibrium. Indicate this by placing a tick (✓) in the appropriate box in the table. Explain your answer.

equilibrium lies to the left	equilibrium lies in the middle	equilibrium lies to the right

....

.... [1]

(iii) Ethanedioic acid, HO_2CCO_2H, has two dissociation constants, K_{a1} and K_{a2}, whose pK_a values are 1.23 and 4.19.

Suggest equations to show the two dissociations that give rise to these pK_a values.

pK_{a1} 1.23 ....

pK_{a2} 4.19 ....

[2]

(iv) State the mathematical relationship between pK_a and the acid dissociation constant K_a.

.... [1]

(c) Three tests were carried out on separate samples of the organic acids shown in the table.
The following results were obtained.
✓ = observed change
✗ = no observed reaction

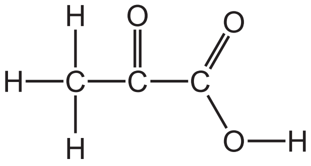
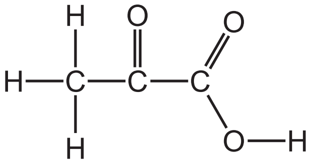
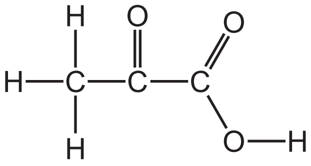
test	reagent(s) and conditions	HCO_2H	CH_3COCO_2H	HO_2CCO_2H	observed change
1	....	✓	✗	✗	
2	....	✗	✓	✗	
3	....	✓	✗	✓	

Complete the table with the reagent(s) and conditions and the observed change for each test.
Assume these organic acids all have a similar acid strength. [5]

(d) A sample of pyruvic acid, CH_3COCO_2H, is analysed by carbon-13 NMR spectroscopy. Three peaks are observed.

Complete the table by:

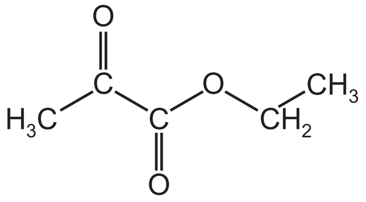
- circling the carbon atom responsible for the chemical shift
- stating the hybridisation of the circled carbon atom.

chemical shift (δ)	carbon atom responsible for chemical shift	hybridisation of the circled carbon atom
27		
163		
192		

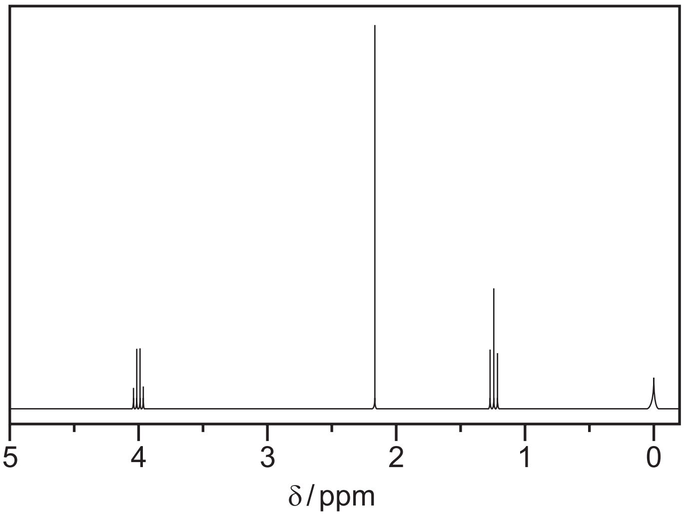
[2]

(e) An ester of pyruvic acid, **F**, is dissolved in $CDCl_3$ and analysed by proton NMR spectroscopy.

F



The proton NMR spectrum of **F** is shown.



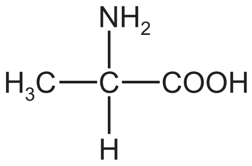
Use the proton NMR spectrum of **F** to complete the table.

chemical shift (δ)	group responsible for the peak	splitting pattern	number of ^1H atoms responsible for the peak
1.3			
2.2			
4.0			

[3]

(f) Deuterium oxide, D_2O, where D is ^2H, can be used as a solvent in proton NMR spectroscopy. The proton NMR spectrum of alanine in $CDCl_3$ has 4 peaks.
The proton NMR spectrum of alanine in D_2O has 2 peaks.

alanine



$$H_3C-\overset{\displaystyle NH_2}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}-COOH$$

On the diagram of alanine, circle the protons that show peaks in **both** NMR spectra.
Explain your answer.

....

....

.... [2]

(g) The ionic product, K_w, for D_2O has a value of $1.35 \times 10^{-15}\,mol^2\,dm^{-6}$ at 298 K.

(i) Write the expression for the K_w of D_2O.

$K_w =$

[1]

(ii) Calculate the pH of pure, neutral D_2O at 298 K.
Assume $[D^+]$ is equivalent to $[H^+]$ for pH calculations.

pH = ... [2]

[Total: 23]

7 **(a)** Silver carbonate, Ag_2CO_3, is sparingly soluble in water. The numerical value of the solubility product, K_{sp}, for silver carbonate is 6.3×10^{-12} at 25 °C.

(i) Write an expression for the solubility product, K_{sp}, of Ag_2CO_3, and state its units.

K_{sp} =

units = ... [2]

(ii) Calculate the equilibrium concentration of Ag^+ in a saturated solution of Ag_2CO_3 at 25 °C.

$[Ag^+]$ = ... $mol\,dm^{-3}$ [1]

(iii) Solid Ag_2CO_3 is stirred at 25 °C with 0.050 $mol\,dm^{-3}$ $AgNO_3$ until no more Ag_2CO_3 dissolves.

Calculate the concentration of carbonate ions, $[CO_3^{2-}]$, in this solution.

$[CO_3^{2-}]$ = ... $mol\,dm^{-3}$ [1]

(iv) An electrochemical cell is set up to measure the electrode potential, *E*, for the Ag^+/Ag half-cell using the saturated $Ag_2CO_3(aq)$ with a standard hydrogen electrode.

Use the *Data Booklet*, your answer to **(a)(ii)**, and the Nernst equation to calculate the electrode potential, *E*, for this Ag^+/Ag half-cell.

E for Ag^+/Ag half-cell = ... V [2]

(b) Silver chloride, $AgCl$, is sparingly soluble in water. The equation for the enthalpy change of solution is shown.

$$AgCl(s) \rightarrow Ag^+(aq) + Cl^-(aq) \qquad \Delta H^{\ominus}_{sol} = +65.5\,kJ\,mol^{-1}$$

Standard entropies are shown in the table.

species	$AgCl(s)$	$Ag^+(aq)$	$Cl^-(aq)$
$S^{\ominus}$ / $J\,K^{-1}\,mol^{-1}$	+96.2	+72.7	+56.5

(i) Calculate the standard entropy change of solution, $\Delta S^{\ominus}$.

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

(ii) Explain, with the aid of a calculation, why $AgCl$ is insoluble in water at 25 °C.

You should use data from this question and your answer to **(b)(i)**.

....

.... [3]

[Total: 10]

8 **(a)** Explain what is meant by the term *buffer solution*.

....

....

.... [2]

(b) **(i)** Write an expression for the acid dissociation constant, K_a, for ammonium ions, $NH_4^+(aq)$.

$K_a =$

[1]

(ii) Write **two** equations to describe how a solution containing ammonium ions, $NH_4^+(aq)$, and ammonia, $NH_3(aq)$, can act as a buffer.

....

.... [2]

(iii) The numerical value of K_a for $NH_4^+(aq)$ is 5.6×10^{-10} at 298 K.
A buffer solution was prepared by adding 0.80 dm^3 of 0.25 mol dm^{-3} ammonia, an excess, to 0.20 dm^3 of 0.20 mol dm^{-3} hydrochloric acid.

Calculate the pH of the buffer solution formed at 298 K.

pH = ... [3]

[Total: 8]

9 **(a)** Manganese(IV) oxide, MnO_2, catalyses the decomposition of hydrogen peroxide, H_2O_2, as shown.

$$2H_2O_2(aq) \xrightarrow{MnO_2} 2H_2O(l) + O_2(g)$$

The mechanism involves the formation of the intermediate species, Mn^{2+}, in the first step which is subsequently used up in the second step.

State and use relevant electrode potentials, $E^{\ominus}$, to construct **two** equations to show how MnO_2 can catalyse this reaction.

....

....

....

....

....

equation 1 ....

equation 2 ....
[3]

(b) The equation for the decomposition of hydrogen peroxide without a catalyst is shown.

$$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$$

Under certain conditions this reaction is found to be first order with respect to hydrogen peroxide, with a rate constant, k, of $2.0 \times 10^{-6}\,s^{-1}$ at 298 K.

Calculate the initial rate of decomposition of a $0.75\,mol\,dm^{-3}$ hydrogen peroxide solution at 298 K.

initial rate = ... $mol\,dm^{-3}\,s^{-1}$ [1]

(c) A four-step mechanism is suggested for the reaction between hydrogen peroxide and iodide ions in an acidic solution.

step 1 $H_2O_2 + I^- \rightarrow IO^- + H_2O$

step 2 $H^+ + IO^- \rightarrow HIO$

step 3 $HIO + I^- \rightarrow I_2 + OH^-$

step 4 $OH^- + H^+ \rightarrow H_2O$

Step 1 is the rate-determining step.

(i) State what is meant by the term *rate-determining step*.

....

.... [1]

(ii) Use this mechanism to construct a balanced equation for this reaction.

.... [1]

(iii) Deduce the order of reaction with respect to each of the following.

H_2O_2 = ... I^- = ... H^+ = ... [1]

[Total: 7]

10 **(a)** The electronic configuration of transition element **Q** is [Ar] $3d^2\ 4s^2$.

Predict the likely oxidation states of element **Q** in compounds.

.... [1]

(b) Suggest why transition elements often show variable oxidation states in their compounds, but typical s-block elements such as calcium do not.

....

.... [1]

(c) Many enzymes contain transition element complexes.

Describe, with the aid of a suitably labelled diagram, how an enzyme catalyses the breakdown of a substrate molecule.

....

....

....

.... [3]

[Total: 5]

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