



## Cambridge International AS & A Level

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**CHEMISTRY**

**9701/41**

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.



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

1 (a) An aqueous solution of cobalt(II) contains the  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  complex ion.

(i) Define the term *complex ion*.

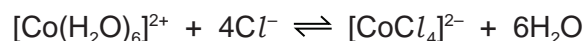
.....  
 ..... [1]

(ii) Samples of  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  are reacted separately with aqueous sodium hydroxide and with an excess of aqueous ammonia.

Give the following information about these reactions.

- the reaction of  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  with aqueous sodium hydroxide  
 colour and state of the cobalt-containing species .....  
 ionic equation .....  
 type of reaction .....
- the reaction of  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  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  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ , a blue solution of  $[\text{CoCl}_4]^{2-}$  is formed and the following equilibrium is established.



Use Le Chatelier's principle to suggest the expected observations when silver nitrate solution is added dropwise to the blue solution of  $[\text{CoCl}_4]^{2-}$ . Explain your answer.

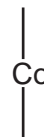
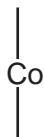
.....  
 .....  
 ..... [2]

3

(c) The  $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$  complex shows stereoisomerism.

Complete the three-dimensional diagrams to show the two isomers of  $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$ .

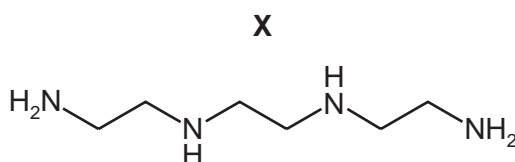
Suggest the type of stereoisomerism.



type of stereoisomerism .....

[2]

(d) Compound **X**,  $\text{C}_6\text{H}_{18}\text{N}_4$ , is a tetradentate ligand.



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

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

(ii)  $\text{C}_6\text{H}_{18}\text{N}_4$  reacts with aqueous cobalt(II) ions,  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ , 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  $\text{Mg}(\text{OH})_2$  and  $\text{Sr}(\text{OH})_2$  will decompose at a **lower** temperature.

Explain your answer.

.....

.....

.....

..... [2]

[Total: 6]

## 5

- 3 The overall reaction for photosynthesis is shown.



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



- (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  $\text{O}_2(\text{g})$  in half-equation 1 under standard conditions. Include all necessary chemicals.

[4]

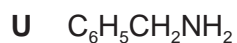
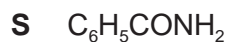
- (iii) For the cell drawn in (a)(ii), use the *Data Booklet* to calculate the  $E^\ominus_{\text{cell}}$  and deduce which electrode is positive.

$$E^\ominus_{\text{cell}} = \dots\dots\dots \text{V}$$

identity of the positive electrode =  $\dots\dots\dots$   
[1]

[Total: 7]

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



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

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

most basic  least basic

.....

.....

.....

.....

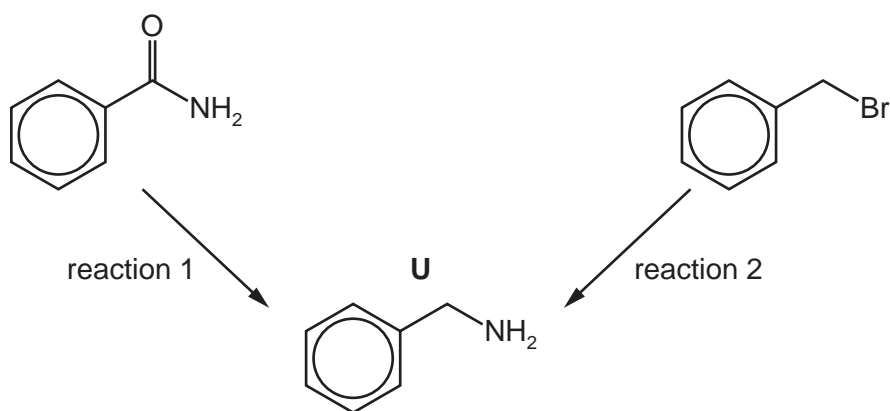
.....

.....

.....

[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]

8

- (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.

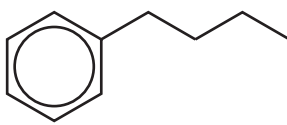
| structure 1          | structure 2 | structure 3 | structure 4 |
|----------------------|-------------|-------------|-------------|
| $CH_3CH_2CH_2CH_2^+$ |             |             |             |

[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 .....

.....

.....

.....

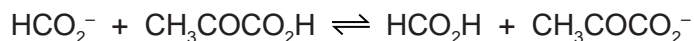
.....

[3]

- (b) (i) The numerical values of  $K_a$  for methanoic acid,  $\text{HCO}_2\text{H}$ , and pyruvic acid,  $\text{CH}_3\text{COCO}_2\text{H}$ , are given.

| acid                               | $K_a$                 |
|------------------------------------|-----------------------|
| $\text{HCO}_2\text{H}$             | $1.78 \times 10^{-4}$ |
| $\text{CH}_3\text{COCO}_2\text{H}$ | $4.07 \times 10^{-3}$ |

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



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

$$K_{\text{eq}} = \dots\dots\dots [1]$$

- (ii) Use your value of  $K_{\text{eq}}$  to predict the position of this equilibrium. Indicate this by placing a tick ( $\checkmark$ ) 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,  $\text{HO}_2\text{CCO}_2\text{H}$ , has two dissociation constants,  $K_{a1}$  and  $K_{a2}$ , whose  $\text{p}K_a$  values are 1.23 and 4.19.

Suggest equations to show the two dissociations that give rise to these  $\text{p}K_a$  values.

$\text{p}K_{a1}$  1.23 .....

$\text{p}K_{a2}$  4.19 .....

[2]

- (iv) State the mathematical relationship between  $\text{p}K_a$  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

x = no observed reaction

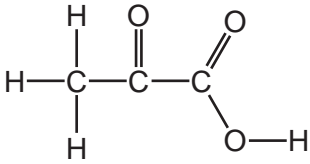
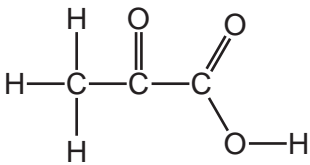
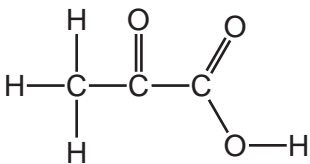
| test | reagent(s)<br>and conditions | $\text{HCO}_2\text{H}$ | $\text{CH}_3\text{COCO}_2\text{H}$ | $\text{HO}_2\text{CCO}_2\text{H}$ | observed change |
|------|------------------------------|------------------------|------------------------------------|-----------------------------------|-----------------|
| 1    | .....<br>.....<br>.....      | ✓                      | x                                  | x                                 |                 |
| 2    | .....<br>.....<br>.....      | x                      | ✓                                  | x                                 |                 |
| 3    | .....<br>.....<br>.....      | ✓                      | x                                  | ✓                                 |                 |

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,  $\text{CH}_3\text{COCO}_2\text{H}$ , is analysed by carbon-13 NMR spectroscopy. Three peaks are observed.

Complete the table by:

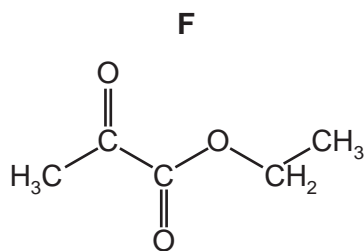
- circling the carbon atom responsible for the chemical shift
- stating the hybridisation of the circled carbon atom.

| chemical shift ( $\delta$ ) | carbon atom responsible for chemical shift                                                                                                                                                                      | hybridisation of the circled carbon atom |
|-----------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------|
| 27                          |  <p>The structural formula of pyruvic acid is shown. The methyl carbon atom (the leftmost carbon) is circled in black.</p>     |                                          |
| 163                         |  <p>The structural formula of pyruvic acid is shown. The carbonyl carbon atom (the middle carbon) is circled in black.</p>     |                                          |
| 192                         |  <p>The structural formula of pyruvic acid is shown. The carboxyl carbon atom (the rightmost carbon) is circled in black.</p> |                                          |

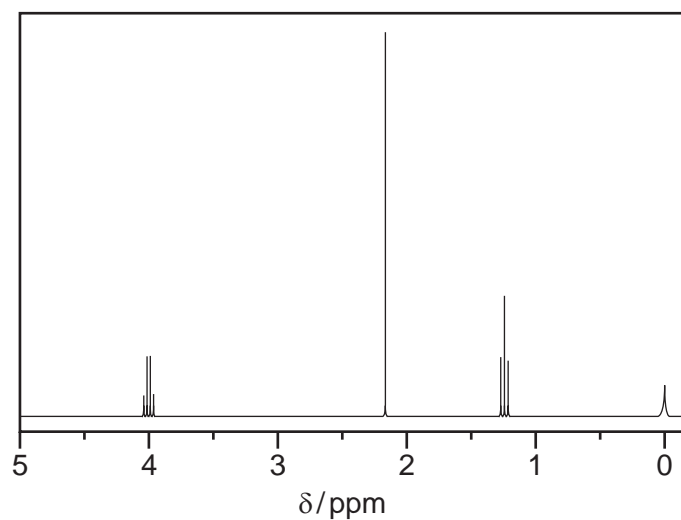
[2]

12

(e) An ester of pyruvic acid, **F**, is dissolved in  $\text{CDCl}_3$  and analysed by proton NMR spectroscopy.



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



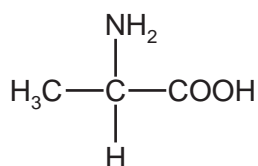
Use the proton NMR spectrum of **F** to complete the table.

| chemical shift ( $\delta$ ) | group responsible for the peak | splitting pattern | number of $^1\text{H}$ 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



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  $1.35 \times 10^{-15} \text{ mol}^2 \text{ dm}^{-6}$  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.

$$\text{pH} = \dots\dots\dots [2]$$

[Total: 23]

7 (a) Silver carbonate,  $\text{Ag}_2\text{CO}_3$ , is sparingly soluble in water. The numerical value of the solubility product,  $K_{\text{sp}}$ , for silver carbonate is  $6.3 \times 10^{-12}$  at  $25^\circ\text{C}$ .

(i) Write an expression for the solubility product,  $K_{\text{sp}}$ , of  $\text{Ag}_2\text{CO}_3$ , and state its units.

$$K_{\text{sp}} =$$

units = .....

[2]

(ii) Calculate the equilibrium concentration of  $\text{Ag}^+$  in a saturated solution of  $\text{Ag}_2\text{CO}_3$  at  $25^\circ\text{C}$ .

$$[\text{Ag}^+] = \dots\dots\dots \text{mol dm}^{-3} \quad [1]$$

(iii) Solid  $\text{Ag}_2\text{CO}_3$  is stirred at  $25^\circ\text{C}$  with  $0.050 \text{ mol dm}^{-3} \text{ AgNO}_3$  until no more  $\text{Ag}_2\text{CO}_3$  dissolves.

Calculate the concentration of carbonate ions,  $[\text{CO}_3^{2-}]$ , in this solution.

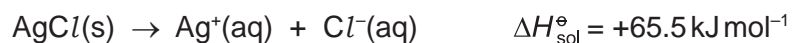
$$[\text{CO}_3^{2-}] = \dots\dots\dots \text{mol dm}^{-3} \quad [1]$$

(iv) An electrochemical cell is set up to measure the electrode potential,  $E$ , for the  $\text{Ag}^+/\text{Ag}$  half-cell using the saturated  $\text{Ag}_2\text{CO}_3(\text{aq})$  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  $\text{Ag}^+/\text{Ag}$  half-cell.

$$E \text{ for } \text{Ag}^+/\text{Ag} \text{ half-cell} = \dots\dots\dots \text{ V} \quad [2]$$

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



Standard entropies are shown in the table.

| species                                      | $\text{AgCl(s)}$ | $\text{Ag}^{\text{+}}(\text{aq})$ | $\text{Cl}^{-}(\text{aq})$ |
|----------------------------------------------|------------------|-----------------------------------|----------------------------|
| $S^{\circ} / \text{JK}^{-1} \text{mol}^{-1}$ | +96.2            | +72.7                             | +56.5                      |

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

$$\Delta S^{\circ} = \dots\dots\dots \text{JK}^{-1} \text{mol}^{-1} \quad [1]$$

- (ii) Explain, with the aid of a calculation, why  $\text{AgCl}$  is insoluble in water at  $25^{\circ}\text{C}$ .

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,  $\text{NH}_4^+(\text{aq})$ .

$$K_a =$$

[1]

(ii) Write **two** equations to describe how a solution containing ammonium ions,  $\text{NH}_4^+(\text{aq})$ , and ammonia,  $\text{NH}_3(\text{aq})$ , can act as a buffer.

.....  
..... [2]

(iii) The numerical value of  $K_a$  for  $\text{NH}_4^+(\text{aq})$  is  $5.6 \times 10^{-10}$  at 298 K.  
A buffer solution was prepared by adding  $0.80 \text{ dm}^3$  of  $0.25 \text{ mol dm}^{-3}$  ammonia, an excess, to  $0.20 \text{ dm}^3$  of  $0.20 \text{ mol dm}^{-3}$  hydrochloric acid.

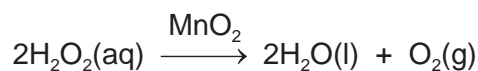
Calculate the pH of the buffer solution formed at 298 K.

pH = ..... [3]

[Total: 8]



- 9 (a) Manganese(IV) oxide,  $\text{MnO}_2$ , catalyses the decomposition of hydrogen peroxide,  $\text{H}_2\text{O}_2$ , as shown.



The mechanism involves the formation of the intermediate species,  $\text{Mn}^{2+}$ , 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  $\text{MnO}_2$  can catalyse this reaction.

.....

.....

.....

.....

.....

equation 1 .....

equation 2 .....

[3]

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

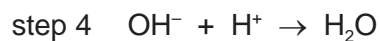
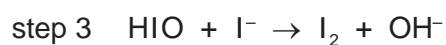
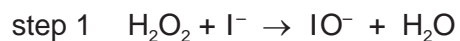


Under certain conditions this reaction is found to be first order with respect to hydrogen peroxide, with a rate constant,  $k$ , of  $2.0 \times 10^{-6} \text{ s}^{-1}$  at 298 K.

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

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

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



Step 1 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.

$\text{H}_2\text{O}_2 = \dots\dots\dots$        $\text{I}^- = \dots\dots\dots$        $\text{H}^+ = \dots\dots\dots$       [1]

[Total: 7]

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

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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