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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*.

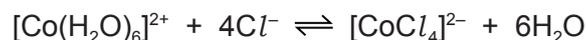
.....
 [1]

(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.

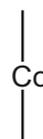
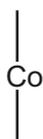
.....

 [2]

(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 $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$.

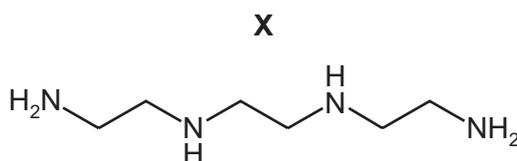
Suggest the type of stereoisomerism.



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]

- 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_{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]

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.

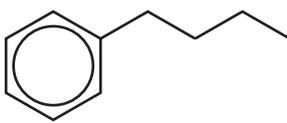
structure 1	structure 2	structure 3	structure 4
$CH_3CH_2CH_2CH_2^+$			

[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]

- (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

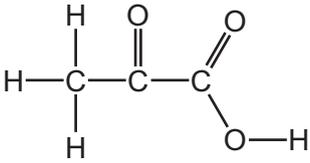
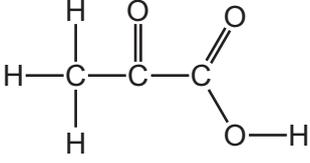
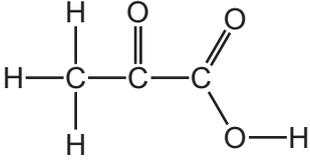
test	reagent(s) and conditions	HCO_2H	$\text{CH}_3\text{COCO}_2\text{H}$	$\text{HO}_2\text{CCO}_2\text{H}$	observed change
1	✓	x	x	
2	x	✓	x	
3	✓	x	✓	

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.

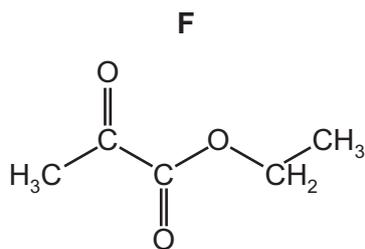
Complete the table by:

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

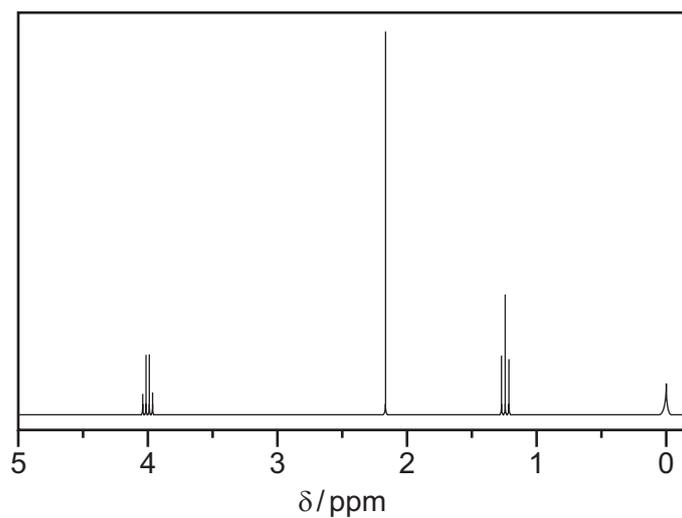
chemical shift (δ)	carbon atom responsible for chemical shift	hybridisation of the circled carbon atom
27	 <p>The structural formula of pyruvic acid is shown. The methyl carbon atom (the leftmost carbon) is circled in black.</p>	
163	 <p>The structural formula of pyruvic acid is shown. The carbonyl carbon 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]

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



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

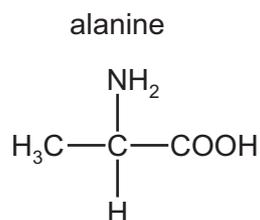


Use the proton NMR spectrum of **F** to complete the table.

chemical shift (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.



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.

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.

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

units =

[2]

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

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

- (iii) Solid Ag_2CO_3 is stirred at 25°C with $0.050 \text{ mol dm}^{-3} \text{ AgNO}_3$ until no more Ag_2CO_3 dissolves.

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

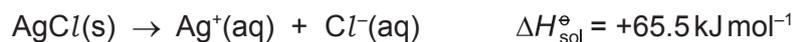
$$[\text{CO}_3^{2-}] = \dots\dots\dots \text{mol dm}^{-3} \quad [1]$$

- (iv) An electrochemical cell is set up to measure the electrode potential, E , for the Ag^+/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 Ag^+/Ag half-cell.

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

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



Standard entropies are shown in the table.

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

- (i) Calculate the standard entropy change of solution, ΔS^{\ominus} .

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

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

$$K_a =$$

[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]

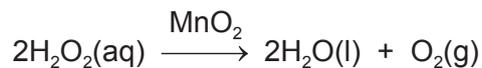
(iii) The numerical value of K_a for $\text{NH}_4^+(\text{aq})$ is 5.6×10^{-10} at 298 K.
 A buffer solution was prepared by adding 0.80 dm^3 of 0.25 mol dm^{-3} ammonia, an excess, to 0.20 dm^3 of 0.20 mol dm^{-3} hydrochloric acid.

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.



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.

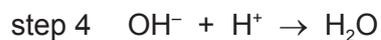
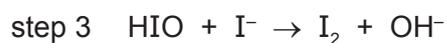
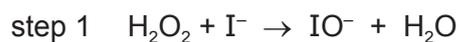


Under certain conditions this reaction is found to be first order with respect to hydrogen peroxide, with a rate constant, k , of $2.0 \times 10^{-6} \text{ s}^{-1}$ at 298 K.

Calculate the initial rate of decomposition of a 0.75 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.

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