



CANDIDATE
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9701/41

May/June 2020

2 hours

You must answer on the question paper.

You will need: Data booklet

- 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.

- 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*.

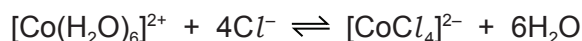
.....
 [1]

(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.

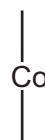
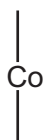
.....

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

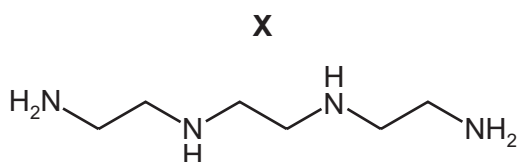
Suggest the type of stereoisomerism.



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.

.....

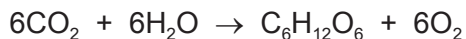
.....

.....

..... [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 $E^\ominus_{\text{cell}}$ and deduce which electrode is positive.

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

identity of the positive electrode = ...
[1]

[Total: 7]

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

S $\text{C}_6\text{H}_5\text{CONH}_2$

T $\text{C}_6\text{H}_5\text{NH}_2$

U $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$

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

..... > >
 most basic least basic

.....

.....

.....

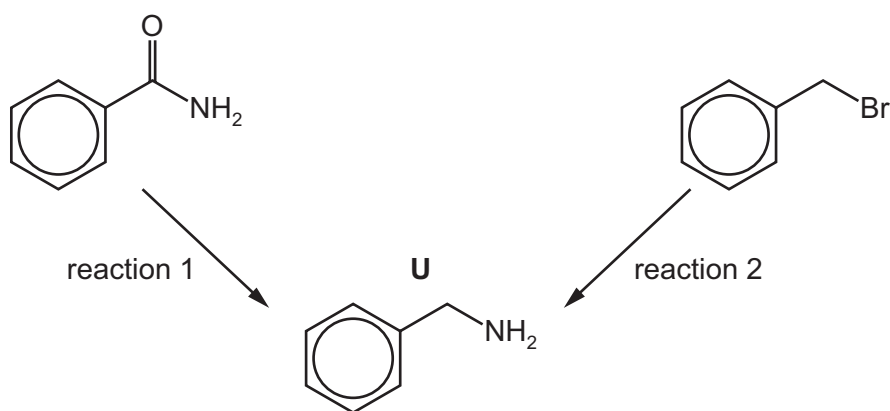
.....

.....

.....

[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.

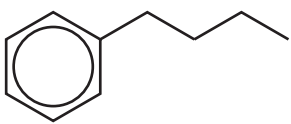
structure 1	structure 2	structure 3	structure 4
$CH_3CH_2CH_2CH_2^+$			

[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

.....

.....

.....

.....

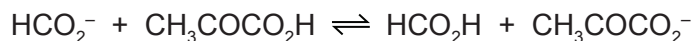
.....

[3]

- (b) (i) The numerical values of K_a for methanoic acid, HCO_2H , and pyruvic acid, $\text{CH}_3\text{COCO}_2\text{H}$, are given.

acid	K_a
HCO_2H	1.78×10^{-4}
$\text{CH}_3\text{COCO}_2\text{H}$	4.07×10^{-3}

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



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

$K_{\text{eq}} = \dots\dots\dots$ [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, $\text{HO}_2\text{CCO}_2\text{H}$, 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

✗ = no observed reaction

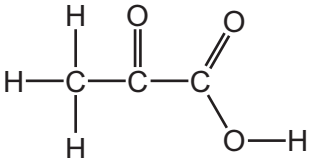
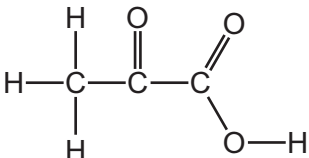
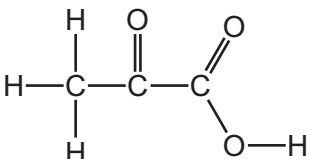
test	reagent(s) and conditions	HCO_2H	$\text{CH}_3\text{COCO}_2\text{H}$	$\text{HO}_2\text{CCO}_2\text{H}$	observed change
1		✓	✗	✗	
2		✗	✓	✗	
3		✓	✗	✓	

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

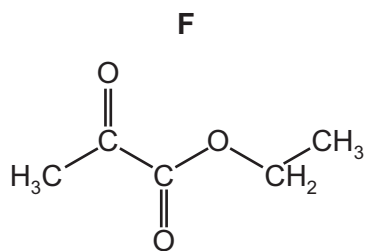
Complete the table by:

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

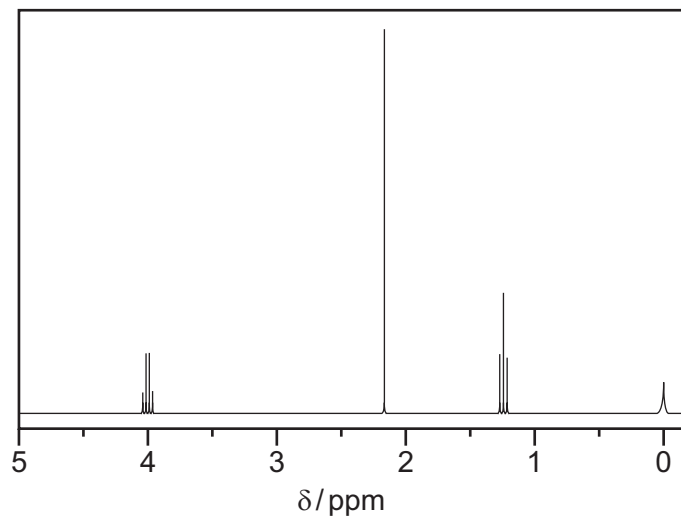
chemical shift (δ)	carbon atom responsible for chemical shift	hybridisation of the circled carbon atom
27		
163		
192		

[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.



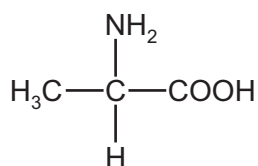
Use the proton NMR spectrum of **F** to complete the table.

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.

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.

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.

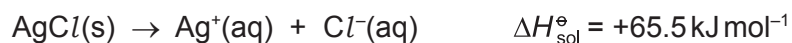
$$[\text{CO}_3^{2-}] = \dots\dots\dots \text{mol dm}^{-3} \quad [1]$$

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

- (i) Calculate the standard entropy change of solution, ΔS° .

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

- (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]

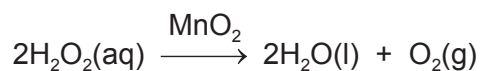
- (iii) The numerical value of K_a for $\text{NH}_4^+(\text{aq})$ is 5.6×10^{-10} at 298 K.
 A buffer solution was prepared by adding 0.80 dm^3 of 0.25 mol dm^{-3} ammonia, an excess, to 0.20 dm^3 of 0.20 mol dm^{-3} hydrochloric acid.

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.

.....

.....

.....

.....

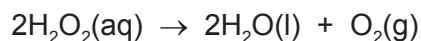
.....

equation 1

equation 2

[3]

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

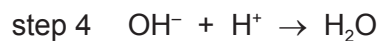
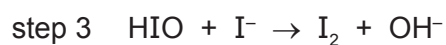
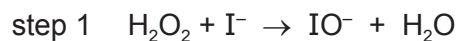


Under certain conditions this reaction is found to be first order with respect to hydrogen peroxide, with a rate constant, k , of $2.0 \times 10^{-6} \text{ s}^{-1}$ at 298 K.

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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9701/42

May/June 2020

2 hours

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

1 EDTA⁴⁻ is a polydentate ligand.

(a) (i) Explain what is meant by the term *polydentate ligand*.

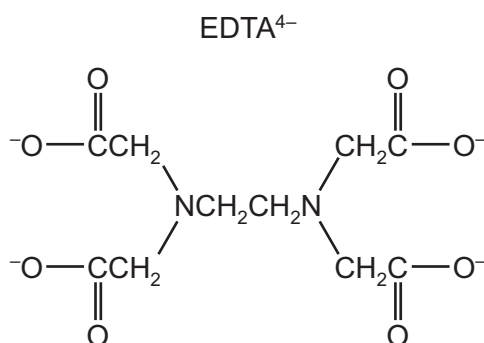
.....

 [2]

(ii) When a solution containing EDTA⁴⁻ is added to a solution containing [Cd(H₂O)₆]²⁺ a new complex is formed, [CdEDTA]²⁻.



Circle, on the structure of EDTA⁴⁻, the **six** atoms that form bonds with the metal ion.



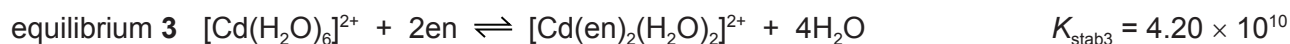
[1]

(iii) Write an expression for the stability constant, K_{stab1} , for equilibrium 1, and state its units.

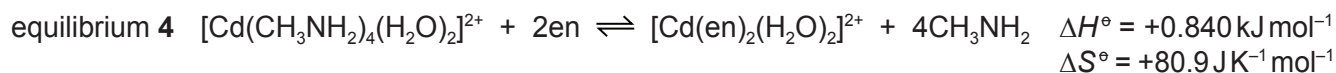
$$K_{\text{stab1}} =$$

units = ...
 [2]

- (b) Cadmium ions form complexes with methylamine, CH_3NH_2 , and with 1,2-diaminoethane, $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$, as shown in equilibria **2** and **3**. 1,2-diaminoethane is shown as en.



An equilibrium is set up between these two complexes as shown in equilibrium **4**.



- (i) K_{eq4} is the equilibrium constant for equilibrium **4**.

Write an expression for K_{eq4} in terms of K_{stab2} and K_{stab3} .

$$K_{\text{eq4}} =$$

[1]

- (ii) Calculate the value of the standard Gibbs free energy change, ΔG° , for equilibrium **4** at 298 K.

$$\Delta G^\circ = \dots\dots\dots \text{ kJ mol}^{-1} \quad [2]$$

- (iii) State how the value of ΔG° changes as the temperature increases. Explain your answer.

.....

 [1]

[Total: 9]

- 2 (a) Describe and explain how the solubility of the Group 2 sulfates varies down the group.

.....

.....

.....

.....

.....

..... [4]

- (b) The trend in the decomposition temperatures of Group 2 peroxides, MO_2 , is similar to that of Group 2 carbonates.

Suggest which of barium peroxide, BaO_2 , and calcium peroxide, CaO_2 , will decompose at the **lower** temperature. Explain your answer.

.....

.....

..... [2]

- (c) Magnesium iodate(V), $\text{Mg}(\text{IO}_3)_2$, decomposes when heated to form magnesium oxide, oxygen and iodine.

Construct an equation for this reaction.

..... [1]

- (d) Calcium iodate(V), $\text{Ca}(\text{IO}_3)_2$, is sparingly soluble in water.
The concentration of its saturated solution is $5.6 \times 10^{-3} \text{ mol dm}^{-3}$ at 298 K.

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

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

units = ... [2]

- (ii) Calculate the numerical value for K_{sp} $\text{Ca}(\text{IO}_3)_2$ at 298 K.

$$K_{\text{sp}} = \text{.....} [1]$$

- (iii) When a few cm³ of concentrated Ca(NO₃)₂(aq) is added to a saturated solution of Ca(IO₃)₂ a white precipitate forms.

Identify the white precipitate and give an explanation for this observation.

.....

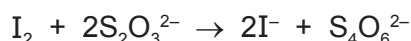
 [2]

- (e) Iodised salt is sodium chloride mixed with a small amount of sodium iodate(V), NaIO₃.

- 50.00 g of iodised salt is dissolved in distilled water and the solution made up to 250 cm³ in a volumetric flask with distilled water.
- 50.0 cm³ of this solution is pipetted into an excess of aqueous acidified potassium iodide.



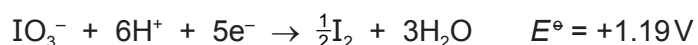
- The iodine produced requires 12.40 cm³ of 0.00200 mol dm⁻³ aqueous sodium thiosulfate solution for complete reaction.



Calculate the mass of sodium iodate(V) present in 50.00 g of iodised salt.

mass of NaIO₃ = ... g [3]

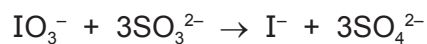
- (f) The half-equation for the reduction of iodate(V) ions is shown.



Use data from the *Data Booklet* to predict whether a reaction is feasible when aqueous solutions of acidified iodate(V) ions and bromide ions are mixed. Explain your answer.

.....
 [1]

(g) Iodate(V) ions react with sulfite ions in acidic solution at pH 5.00 as shown.



The initial rate of reaction was found to be first order with respect to IO_3^- , first order with respect to SO_3^{2-} and first order with respect to H^+ .

(i) Write the rate equation for this reaction, stating the units of the rate constant, k .

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

units of k = ... [2]

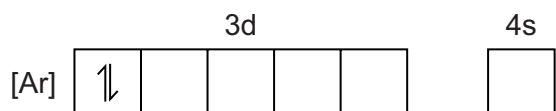
(ii) The rate of reaction depends on the pH of the solution. Assume all other concentrations remain the same.

Use the expression $x = \frac{\text{rate at pH 5.00}}{\text{rate at pH 4.00}}$ to calculate the value of x .

x = ... [1]

[Total: 19]

- 3 (a)** Complete the electronic configuration of an isolated gaseous nickel(II) ion, Ni^{2+} .

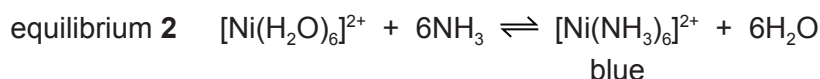
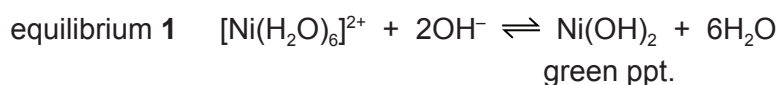


[1]

- (b)** Explain the origin of colour in transition element complexes.

[4]

- (c) Hexaaquanickel(II) ions are green. They form a green precipitate with hydroxide ions, OH^- , in equilibrium **1** and a blue complex with ammonia, NH_3 , in equilibrium **2**.



Use Le Chatelier's principle to suggest explanations for the following observations.

- (i) Explain why when aqueous NH_3 is added dropwise to $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ a green precipitate is formed.

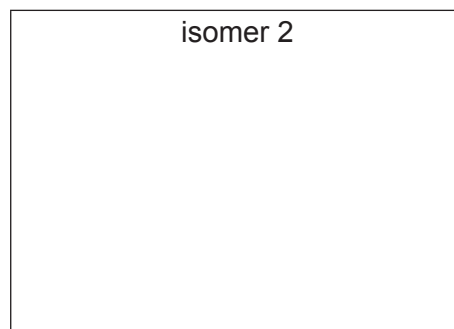
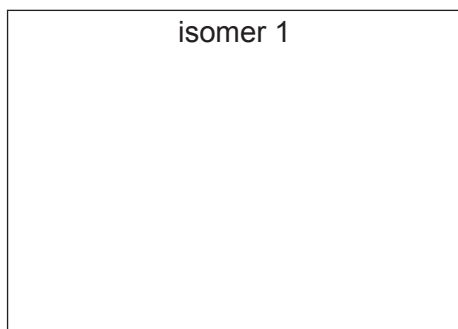
..... [1]

- (ii) Explain why when a large excess of aqueous NH_3 is added to $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$, the green precipitate dissolves and a blue solution is formed.

..... [1]

(d) The complex ion $[\text{NiBr}_2(\text{CN})_2]^{2-}$ shows stereoisomerism.

Draw diagrams to show the two isomers of $[\text{NiBr}_2(\text{CN})_2]^{2-}$. Name the type of stereoisomerism.



type of stereoisomerism

[2]

[Total: 9]

- 4 (a) (i) When benzene undergoes nitration a nitro group substitutes at a carbon atom.

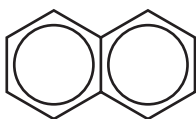
State the shape (geometry) around the substituted carbon atom

- in the benzene molecule, ...
- in the intermediate complex, ...
- in the nitrobenzene product.

[2]

- (ii) Naphthalene, $C_{10}H_8$, is an arene hydrocarbon.

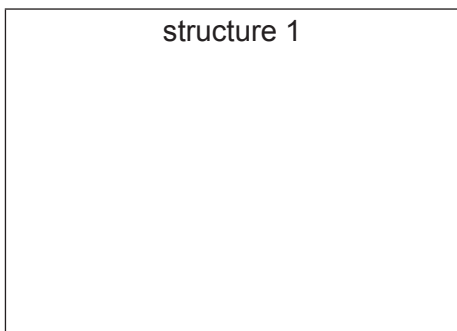
naphthalene



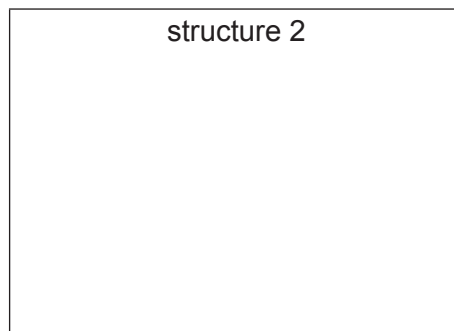
When naphthalene undergoes nitration, a mixture of two organic compounds is formed. Each compound contains **one** nitro group.

Suggest the structures of these compounds.

structure 1



structure 2



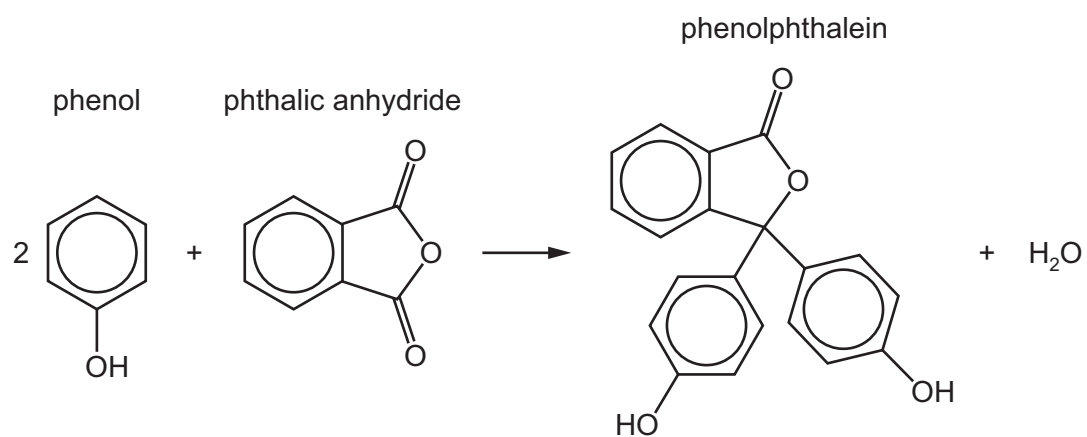
[1]

- (b) Naphthalene can be oxidised under certain conditions to phthalic anhydride, $C_8H_4O_3$, carbon dioxide and water.

Construct an equation for this reaction. Use [O] to represent an atom of oxygen from the oxidising agent.

..... [1]

- (c) The indicator, phenolphthalein, can be synthesised from phthalic anhydride and phenol under certain conditions.



Deduce the *type of reaction* shown by this equation.

..... [1]

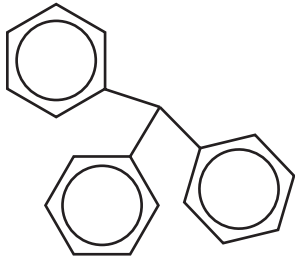
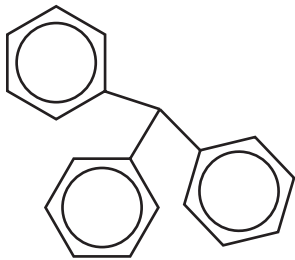
- (d) (i) Name the functional groups, in addition to the benzene ring, present in a phenolphthalein molecule.

..... [1]

- (ii) Phenolphthalein reacts separately with the two reagents shown in the table.

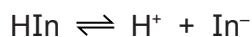
Complete the table by:

- drawing the structures of the organic products formed (part of the structure has been given for you)
- stating the types of reaction.

reagent	organic product structure	type of reaction
an excess of hot NaOH(aq)		
an excess of Br ₂ (aq)		

[4]

- (e) Phenolphthalein is an indicator and is represented by the formula HIn. Phenolphthalein, HIn, is a weak acid.



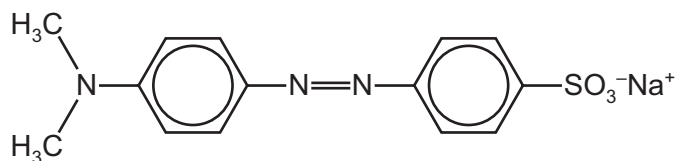
The K_a value for phenolphthalein is $5.0 \times 10^{-10} \text{ mol dm}^{-3}$ at 298 K. This indicator changes colour at a pH of approximately 8.8.

Calculate the ratio $\frac{[\text{In}^-]}{[\text{HIn}]}$ at pH 8.8.

$$\text{ratio } \frac{[\text{In}^-]}{[\text{HIn}]} = \dots\dots\dots [2]$$

- (f) Methyl orange is another acid-base indicator. Its structure in aqueous solution at pH 4.4 is shown.

methyl orange



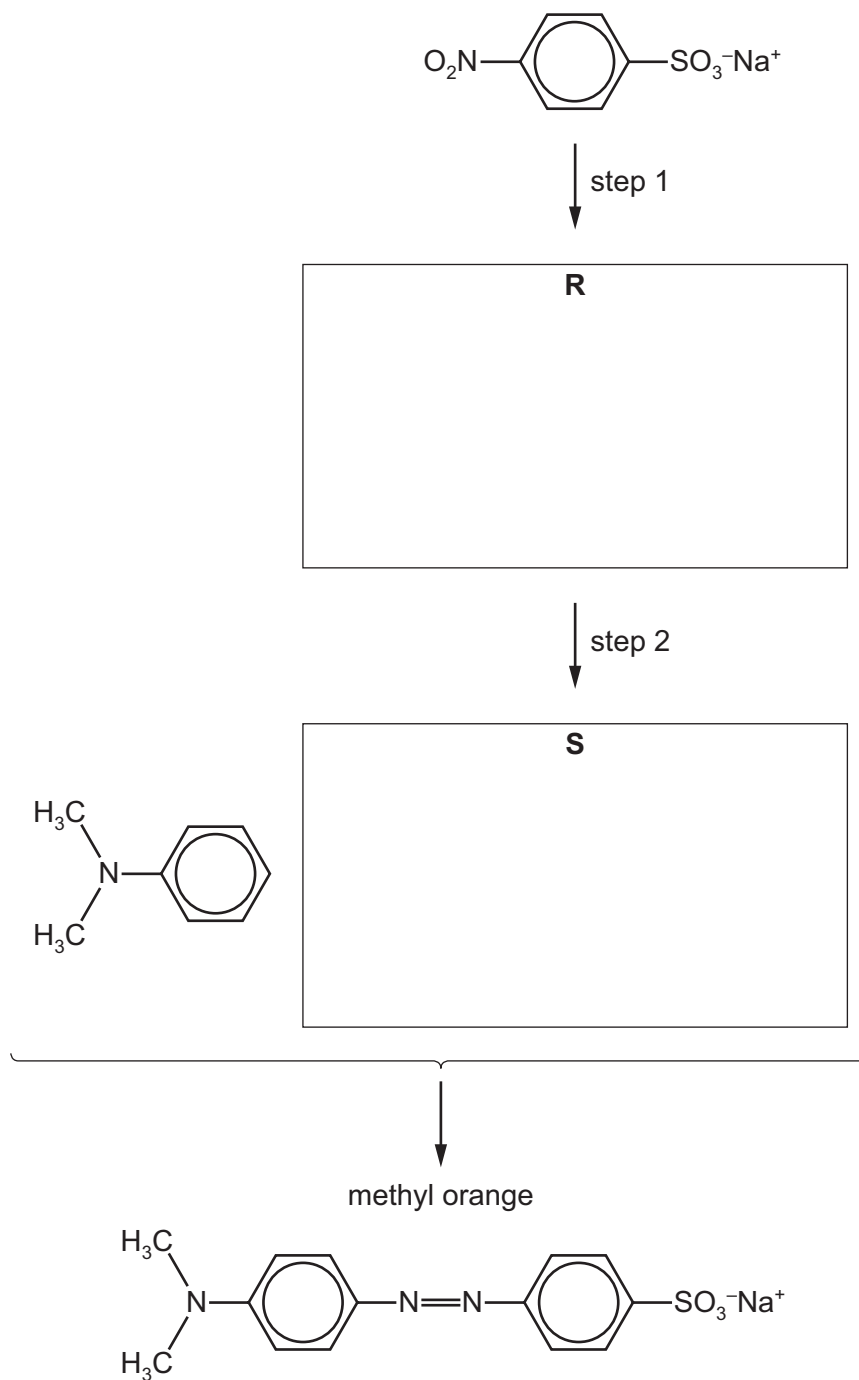
- (i) On the structure of methyl orange, **circle** the bond or bonds that make this compound a dye. [1]

The colour of this indicator changes between pH 3.2 and pH 4.4.

- (ii) Suggest the structure of methyl orange at pH 3.0. Assume the $-\text{SO}_3^- \text{Na}^+$ group is unreactive.

[1]

(g) Methyl orange can be synthesised as shown.



- (i) Deduce the identities of compounds **R** and **S** and draw their structures in the boxes. [2]
- (ii) Suggest reagents and conditions for step 1 and step 2.

step 1

step 2

[3]

[Total: 19]

- 5 (a) Define the term *partition coefficient*, K_{pc} .

.....

 [2]

- (b) K_{pc} of benzoic acid between octan-1-ol and water is 79.4.

- (i) A solution of 0.400 g of benzoic acid in 25.0 cm³ octan-1-ol is shaken with 125 cm³ of water.

Calculate the mass of benzoic acid extracted into the water layer.

mass of benzoic acid extracted = ... g [2]

- (ii) K_{pc} of benzophenone, C₆H₅COC₆H₅, between octan-1-ol and water is different from the value of K_{pc} of benzoic acid given in (b)(i).

Explain why.

.....

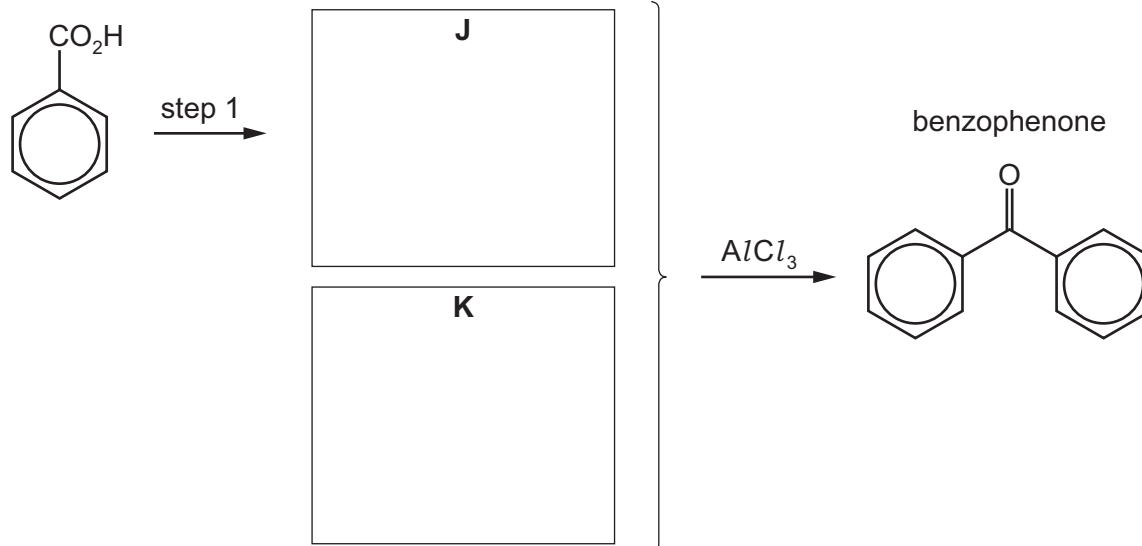
 [1]

(c) Benzophenone can be synthesised from benzoic acid in two steps as shown.

In step 1 compound **J**, a reactive reaction intermediate, is formed.

Compound **J** then reacts with an organic compound, **K**, to form benzophenone.

benzoic acid

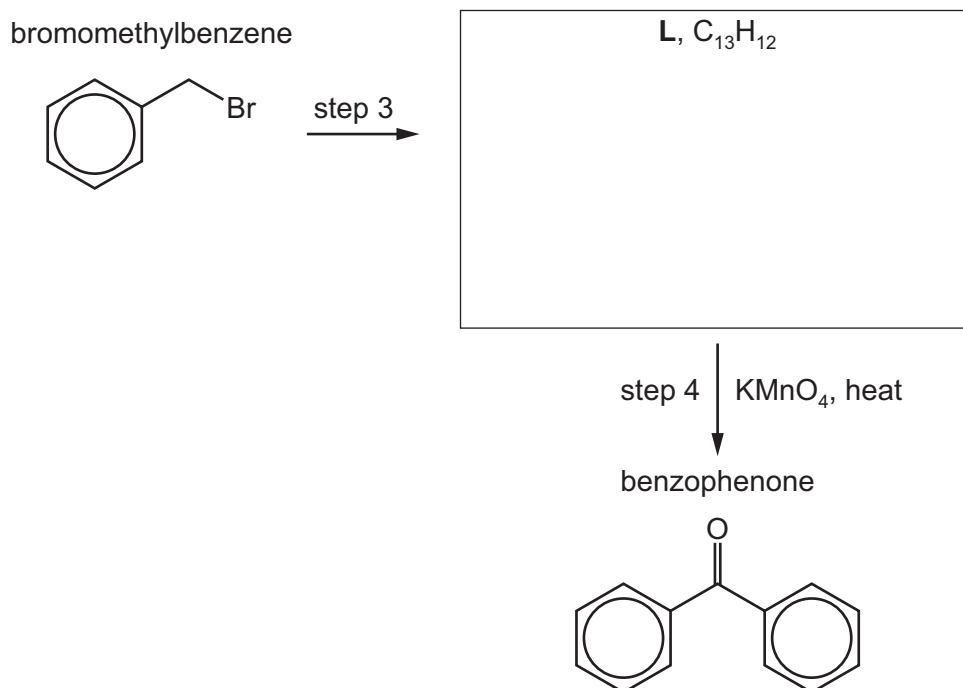


(i) Deduce the identities of organic compounds **J** and **K** and draw their structures in the boxes. [2]

(ii) Suggest reagents and conditions for step 1.

..... [1]

(d) Benzophenone can also be synthesised in two steps from bromomethylbenzene.



(i) Deduce the identity of compound **L** and draw its structure in the box. [1]

(ii) Name the mechanism of step 3 and suggest reagents and conditions for step 3.

mechanism of step 3

reagents and conditions

[2]

(iii) Deduce the *type of reaction* in step 4.

..... [1]

(e) (i) Deduce the number of peaks that would be present in the carbon-13 NMR spectrum of benzophenone.

number of peaks [1]

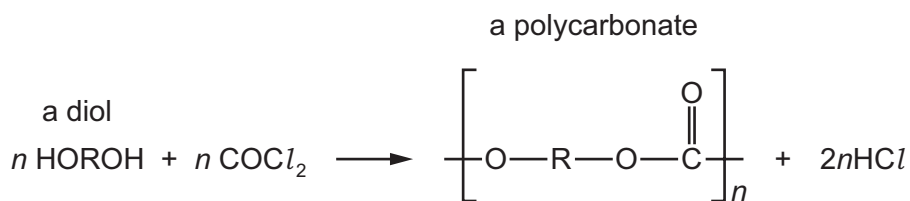
(ii) Identify **two** different environments of carbon atom that would result in different chemical shift ranges in this carbon-13 NMR spectrum of benzophenone.

environment of carbon atom	chemical shift range (δ)

[2]

[Total: 15]

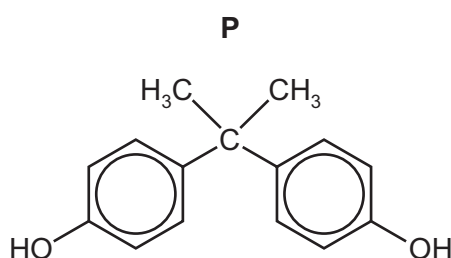
- 6 The class of polymers called polycarbonates are made by the reaction of carbonyl dichloride, COCl_2 , with a diol.



- (a) (i) Deduce the *type of polymerisation* shown here.

..... [1]

Nalgene® is a polycarbonate formed from the diol **P** and COCl_2 .



- (ii) Draw **one** repeat unit of Nalgene®.

[1]

- (iii) Nalgene® is a strong and tough polymer.

Identify **two** types of intermolecular force that are responsible for these properties of Nalgene®.

1

2

[1]

- (b) Proteins are polymers of amino acids.

Complete the table to show how the secondary and tertiary structures of proteins are stabilised.

	one intermolecular force responsible	groups involved
secondary structure		
tertiary structure		

[2]

- (c) Explain the significance of hydrogen bonding in DNA in relation to the accurate replication of genetic information.

.....

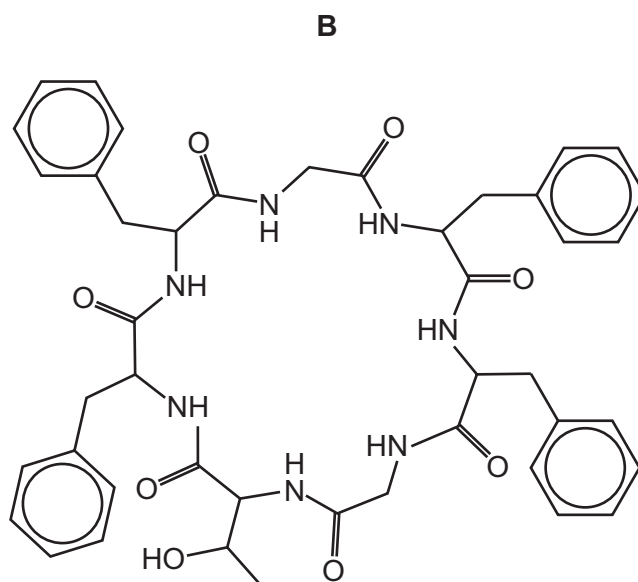
 [2]

- (d) Many polymers are degradable.

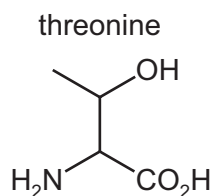
State **two** different processes by which some polymers can be degraded.

.....
 [1]

- (e) The cyclic peptide **B** is shown.



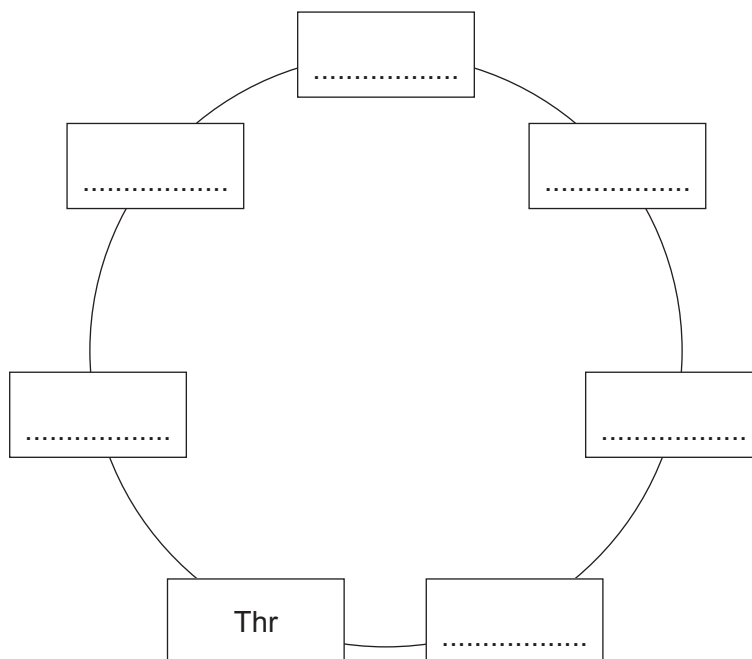
Cyclic peptide **B** is broken into its monomers by heating under reflux with dilute hydrochloric acid. The amino acid threonine, Thr, and two other organic products are formed.



- (i) Draw the structures of the two other organic products formed.

[2]

- (ii) Using the 3-letter abbreviations for the amino acids as given in the *Data Booklet*, complete the sequence for the cyclic peptide, **B**.



[1]

- (iii) Name **two** analytical techniques that could be used to separate these amino acids.

..... and [1]

[Total: 12]

7 (a) (i) Define the term *electron affinity*.

.....

.....

..... [2]

(ii) Define the term *lattice energy*.

.....

.....

..... [2]

(b) Use the following data and relevant data from the *Data Booklet* to calculate a value for the enthalpy change of formation of zinc bromide, $\text{ZnBr}_2(\text{s})$.

You might find it helpful to construct an energy cycle.

electron affinity of $\text{Br}(\text{g})$	$= -325 \text{ kJ mol}^{-1}$
enthalpy change of atomisation of $\text{Zn}(\text{s})$	$= +131 \text{ kJ mol}^{-1}$
enthalpy change of vaporisation of $\text{Br}_2(\text{l})$	$= +31 \text{ kJ mol}^{-1}$
lattice energy of $\text{ZnBr}_2(\text{s})$	$= -2678 \text{ kJ mol}^{-1}$

enthalpy change of formation of $\text{ZnBr}_2(\text{s}) = \dots\dots\dots \text{ kJ mol}^{-1}$ [4]

(c) The lattice energies of ZnBr_2 , ZnCl_2 and ZnO are shown.

compound	lattice energy / kJ mol^{-1}
ZnBr_2	-2678
ZnCl_2	-2734
ZnO	-3971

(i) Explain why there is a difference between the lattice energies of ZnBr_2 and ZnCl_2 .

.....
 [1]

(ii) Explain why there is a difference between the lattice energies of ZnCl_2 and ZnO .

.....
 [1]

[Total: 10]

- 8 (a) (i) Define the term *standard cell potential*.

.....

 [2]

An electrochemical cell is set up to measure the standard electrode potential of a cell, $E_{\text{cell}}^{\ominus}$, made of a $\text{Co}^{3+}/\text{Co}^{2+}$ half-cell and a Cl_2/Cl^- half-cell.

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

half-cell	electrode
$\text{Co}^{3+}/\text{Co}^{2+}$	
Cl_2/Cl^-	

[1]

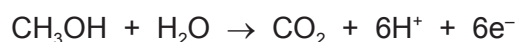
- (iii) Use data from the *Data Booklet* to calculate the $E_{\text{cell}}^{\ominus}$.

$$E_{\text{cell}}^{\ominus} = \dots\dots\dots \text{V} \quad [1]$$

- (iv) Write the equation for the overall cell reaction.

..... [1]

- (b) A fuel cell is an electrochemical cell that can be used to generate electrical energy. A methanol-oxygen fuel cell can be used as an alternative to a hydrogen-oxygen fuel cell. When the cell operates, the carbon atoms in the methanol molecules are converted into carbon dioxide.



Calculate the volume of CO_2 , in cm^3 , formed when a current of 2.5A is delivered by the cell for 30 minutes. Assume the cell is operated at room conditions.

$$\text{volume of CO}_2 = \dots\dots\dots \text{cm}^3 \quad [2]$$

[Total: 7]

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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.



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*.

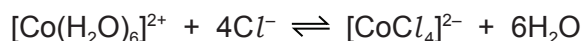
.....
 [1]

(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.

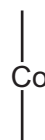
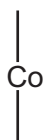
.....

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

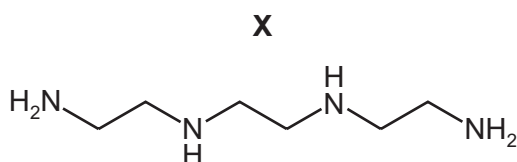
Suggest the type of stereoisomerism.



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.

.....

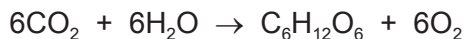
.....

.....

..... [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 $E^\ominus_{\text{cell}}$ 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.

S $\text{C}_6\text{H}_5\text{CONH}_2$

T $\text{C}_6\text{H}_5\text{NH}_2$

U $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$

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

..... > >
 most basic least basic

.....

.....

.....

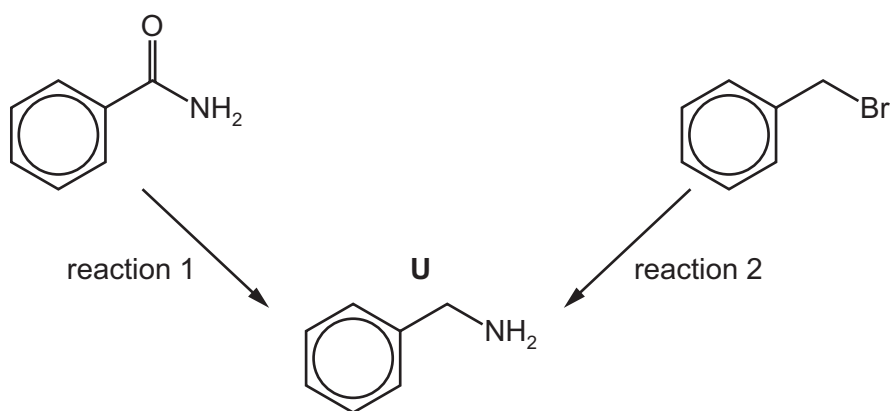
.....

.....

.....

[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.

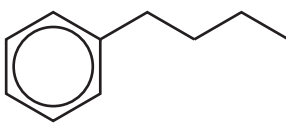
structure 1	structure 2	structure 3	structure 4
$CH_3CH_2CH_2CH_2^+$			

[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

.....

.....

.....

.....

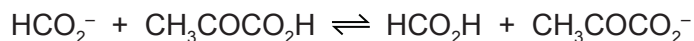
.....

[3]

- (b) (i) The numerical values of K_a for methanoic acid, HCO_2H , and pyruvic acid, $\text{CH}_3\text{COCO}_2\text{H}$, are given.

acid	K_a
HCO_2H	1.78×10^{-4}
$\text{CH}_3\text{COCO}_2\text{H}$	4.07×10^{-3}

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



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

$K_{\text{eq}} = \dots\dots\dots$ [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, $\text{HO}_2\text{CCO}_2\text{H}$, has two dissociation constants, $K_{\text{a}1}$ and $K_{\text{a}2}$, whose $\text{p}K_{\text{a}}$ values are 1.23 and 4.19.

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

$\text{p}K_{\text{a}1}$ 1.23

$\text{p}K_{\text{a}2}$ 4.19

[2]

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

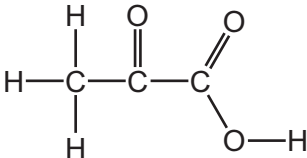
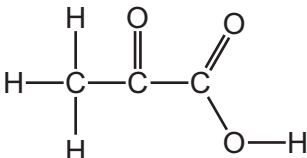
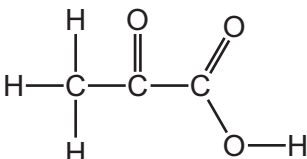
test	reagent(s) and conditions	HCO_2H	$\text{CH}_3\text{COCO}_2\text{H}$	$\text{HO}_2\text{CCO}_2\text{H}$	observed change
1		✓	x	x	
2		x	✓	x	
3		✓	x	✓	

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.

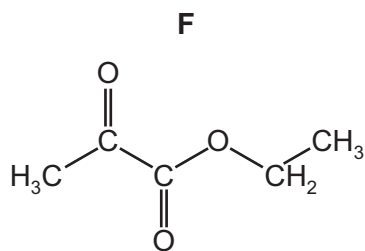
Complete the table by:

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

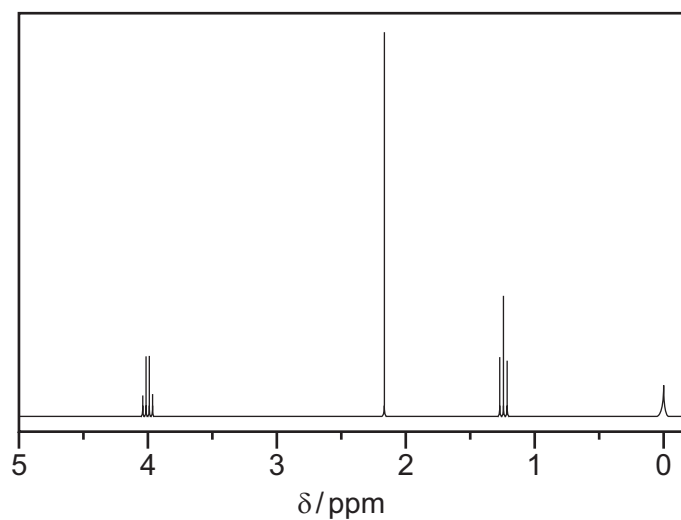
chemical shift (δ)	carbon atom responsible for chemical shift	hybridisation of the circled carbon atom
27		
163		
192		

[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.



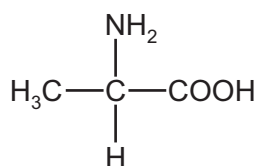
Use the proton NMR spectrum of **F** to complete the table.

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.

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.

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.

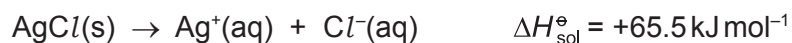
$$[\text{CO}_3^{2-}] = \dots\dots\dots \text{mol dm}^{-3} \quad [1]$$

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

- (i) Calculate the standard entropy change of solution, ΔS° .

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

- (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]

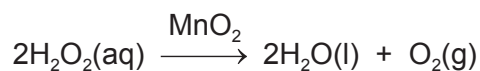
- (iii) The numerical value of K_a for $\text{NH}_4^+(\text{aq})$ is 5.6×10^{-10} at 298 K.
 A buffer solution was prepared by adding 0.80 dm^3 of 0.25 mol dm^{-3} ammonia, an excess, to 0.20 dm^3 of 0.20 mol dm^{-3} hydrochloric acid.

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.

.....

.....

.....

.....

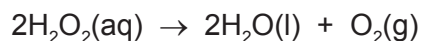
.....

equation 1

equation 2

[3]

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

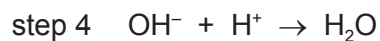
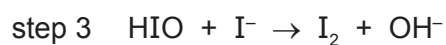
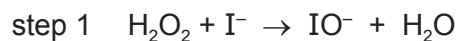


Under certain conditions this reaction is found to be first order with respect to hydrogen peroxide, with a rate constant, k , of $2.0 \times 10^{-6} \text{ s}^{-1}$ at 298 K.

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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