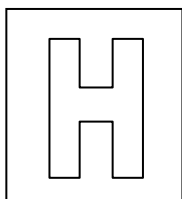


Candidate Name: _____

Class Adm No

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2019 Preliminary Exams Pre-University 3

H2 CHEMISTRY

9729/03

Paper 3 Free Response

20 Sept 2019

2 hours

Candidates answer on separate paper.

Additional materials: Answer Paper
Data Booklet
Graph Paper

READ THESE INSTRUCTIONS FIRST

Do not turn over this question paper until you are told to do so

Write your name, class and admission number on all the work you hand in.

Write in dark blue or black pen.

You may use an HB pencil for any diagrams or graphs.

Do not use staples, paper clips, glue or correction fluid.

Section A

Answer **all** questions.

Section B

Answer **one** question.

A Data Booklet is provided.

The use of an approved scientific calculator is expected, where appropriate.

You are reminded of the need for good English and clear presentation in your answers.

At the end of the examination, fasten all your work securely together.

The number of marks is given in brackets [] at the end of each question or part question.

Question	Section A			Section B		Total
	1	2	3	4	5	
Marks	19	19	22	20	20	80

This question paper consists of **9** printed pages and **1** blank page.

Section A

Answer **all** the questions in this section.

- 1 (a) 3-chloropropanoic acid, $\text{CH}_2\text{ClCH}_2\text{CO}_2\text{H}$, is a weak Brønsted acid. A $0.100 \text{ mol dm}^{-3}$ solution of $\text{CH}_2\text{ClCH}_2\text{CO}_2\text{H}$ has a pH of 2.49.

(i) Calculate the $\text{p}K_{\text{a}}$ of 3-chloropropanoic acid. [3]

(ii) State and explain the differences in the relative acid strength between 3-chloropropanoic acid and propanoic acid. [2]

(iii) 3-chloropropanoyl bromide is the acid derivative of 3-chloropropanoic acid. Propose a 3-step synthetic route for the formation of 3-chloropropanoyl bromide, using 3-hydroxypropanal as the starting reagent. State clearly the reagents and conditions used for each step. [5]

- (b) A student investigated the rate of reaction between 3-chloropropanoic acid and aqueous sodium carbonate. The rate of the reaction may be determined by measuring how long it takes for the gas to be completely released.

A series of experiments were carried out to study the order of reaction with respect to 3-chloropropanoic acid and sodium carbonate. The following results were obtained.

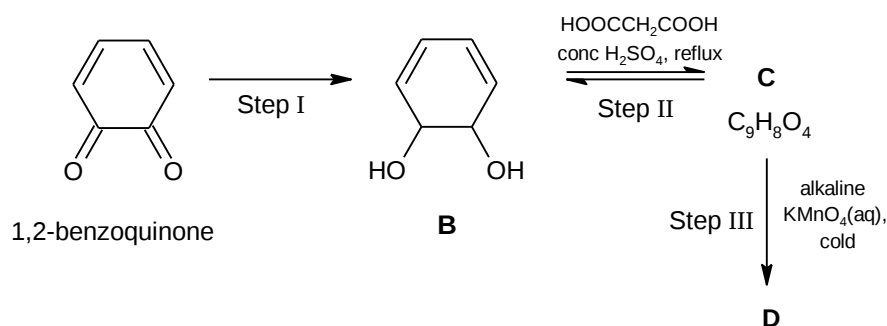
Experiment Number	Volume / cm^3			Time / s
	3-chloropropanoic acid	Na_2CO_3	H_2O	
1	20.0	40.0	40.0	78
2	20.0	30.0	50.0	100
3	5.0	20.0	25.0	75

- (i) Write an equation, including state symbols, for the reaction between sodium carbonate and 3-chloropropanoic acid. [1]
- (ii) State the relationship between time and rate. [1]
- (iii) Determine the order of the reaction with respect to 3-chloropropanoic acid and sodium carbonate. [2]
- (iv) Hence, write the rate equation, stating the units of k . [2]
- (v) With the aid of an appropriate diagram, explain how the addition of a catalyst can increase the rate of a reaction between 3-chloropropanoic acid and sodium carbonate. [3]

[Total: 19]

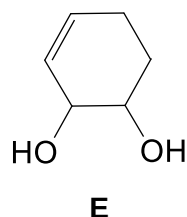
- 2 (a) Using only the elements C, H and O, draw the structural formulae of **two** different **organic** compounds, each containing a **single** carbon atom, with an oxidation state of 0 and +2 respectively. [2]
- (b) A symmetrical organic compound **A**, $C_2H_4N_2O_2$, upon reacting with hot dilute $NaOH(aq)$ produces a colourless, pungent gas that turns moist red litmus paper blue.
- (i) Draw the structure of compound **A** and state the functional group present. [2]
- (ii) The functional group present in compound **A** can be reduced by lithium aluminium hydride, $LiAlH_4$. Draw the dot-and-cross diagram for $LiAlH_4$. [1]
- (iii) Other than $LiAlH_4$, $NaBH_4$ can also be used for the reduction of certain functional groups. $LiAlH_4$ is able to produce hydride ion, H^- more readily than $NaBH_4$. Suggest why $LiAlH_4$ is a more powerful reducing agent than $NaBH_4$. [1]
- (c) Quinones are used in photography as a reducing agent. Quinone compounds are multifunctional as they exhibit properties of both ketones and alkenes.

The following scheme involves 1, 2-benzoquinone, where step I involves the use of $LiAlH_4$.



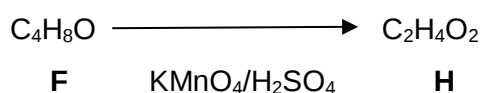
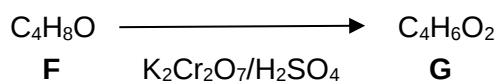
- (i) Draw the structures of **C** and **D**. [2]
- (ii) Identify the chiral centres on **B**. Hence, explain why it does not display optical activity. [2]
- (iii) Using a simple chemical test, suggest how 1,2-benzoquinone can be distinguished from compound **B**. In your answer, state all reagents and conditions used and the expected observations. [2]

(iv) When compound **B** undergoes partial hydrogenation, it forms compound **E**.



Describe the mechanism of the reaction when compound **E** reacts with Br_2 in CCl_4 in the dark. In your answer, show all relevant charges and movement of electrons clearly. [3]

(d) $\text{K}_2\text{Cr}_2\text{O}_7$ and KMnO_4 are common oxidising agents used in organic synthesis where KMnO_4 is the more powerful of the two. Compound **F**, $\text{C}_4\text{H}_8\text{O}$, reacted with $\text{K}_2\text{Cr}_2\text{O}_7$ and KMnO_4 separately to yield different products as shown in the reactions below.



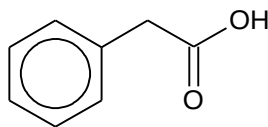
Given the following information,

- All three compounds, **F**, **G** and **H** react with sodium metal.
- **G** and **H** react with Na_2CO_3 , but **F** does not.
- **F** and **G** decolourise aqueous bromine.

Suggest the structures of compounds **F**, **G** and **H**, explaining the chemistry involved. [4]

[Total: 19]

- 3 (a) Phenylethanoic acid is used as a treatment for hyperammonemia, a condition where there is an accumulation of ammonia in the human body.



phenylethanoic acid

- (i) In an experiment, 60 cm^3 of 0.10 mol dm^{-3} of sodium hydroxide was added to 20 cm^3 of 0.20 mol dm^{-3} of phenylethanoic acid in a conical flask. Calculate the pH of the final solution when all 60 cm^3 of sodium hydroxide was added to the flask. [3]
- (ii) 2-amino-2-phenylethanoic acid can be synthesised from phenylethanoic acid through a series of substitution reactions.
- Draw the displayed formula of 2-amino-2-phenylethanoic acid. [1]
- (iii) Write two equations to show how an aqueous solution of 2-amino-2-phenylethanoic acid is able to resist the change in pH upon addition of small amounts of acid and base. [2]
- (iv) Draw the structure of the predominant form when 2-amino-2-phenylethanoic acid is in an aqueous solution of pH 10. [1]
- (b) (i) Predict and explain whether phenylethanoyl chloride or phenylethanoic acid has a higher reactivity towards nucleophilic reagents. [2]
- (ii) Given that phenylethanoyl chloride has a boiling point of 95°C and phenylethanoic acid has a boiling point of 266°C , explain this difference in terms of structure and bonding. [2]
- (iii) State the number of sp^2 and sp^3 hybridised carbon atoms found in one molecule of phenylethanoic acid. [1]
- (iv) State the number of sigma and pi bonds in one molecule of phenylethanoic acid. [1]

- (c) Acid chloride reacts instantly with cold water. The reaction is very exothermic in which steamy white fumes of hydrogen chloride gas are released and the carboxylic acid is formed. The mechanism of the reaction takes place in two stages as described below.

First stage

- The lone pair on the oxygen atom of water molecule attacks the electron deficient carbon atom of the acid chloride, causing the π bond of the C=O bond to break.

Second stage

- The carbon-oxygen double bond reforms and a chloride ion is released.
 - As a result, a hydrogen ion is removed by the chloride ion to give the carboxylic acid and hydrogen chloride.
- (i) Using ethanoyl chloride as an example, illustrate the mechanism of the reaction when ethanoyl chloride reacts with cold water. [3]
- (ii) State the type of reaction occurring in the first stage of the mechanism. [1]

- (d) Compounds **Y** and **Z** are isomers of molecular formula $C_4H_7O_2Cl$. When **Y** and **Z** are added to separate portions of water, solutions are formed with pH values of 0.5 and 2.5 respectively. White precipitate is observed when aqueous silver nitrate is added to **Y**, but not **Z**. Both **Y** and **Z** gives yellow precipitate when heated with aqueous sodium hydroxide and iodine.

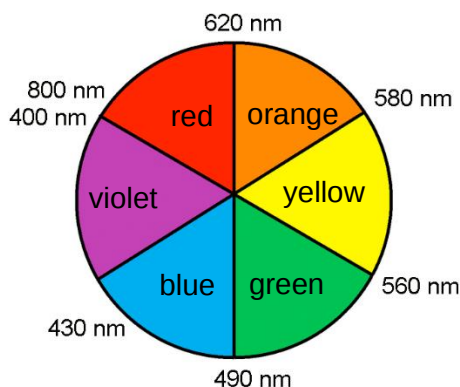
Suggest the structures of compounds **Y** and **Z**. Explain your answers. [5]

[Total: 22]

Section B

Answer **one** question from this section.

- 4 (a) Nickel is a transition metal and can exhibit variable oxidation states. The reducing power of Ni can be determined through its oxidation to Ni^{2+} .
- (i) Define the term *standard electrode potential*. [1]
- (ii) Draw a fully labelled diagram of the electrochemical cell that you would set up in order to measure the standard reduction potential of Ni^{2+}/Ni under standard conditions. [3]
- (iii) Hence or otherwise, suggest what happens to the value of the voltmeter reading when a more concentrated nickel(II) solution is used in part (ii). [1]
- (iv) An electrolytic cell contains $\text{Ni}(\text{NO}_3)_2$ and $\text{Mn}(\text{NO}_3)_2$ in an aqueous electrolyte uses graphite as the electrodes. Determine the products discharged at the cathode and anode and write the overall balanced equation for the electrolytic cell. [3]
- (b) Aqueous nickel salts are coloured. $[\text{Ni}(\text{NH}_3)_6]^{2+}$ ions absorb at 600 nm, whereas $[\text{NiCl}_4]^{2-}$ ions absorbed at 420 nm. The colour and the respective wavelengths are given in the colour wheel below.



- (i) State the oxidation number of nickel in $[\text{NiCl}_4]^{2-}$. [1]
- (ii) Suggest the colour of:
 I: $[\text{Ni}(\text{NH}_3)_6]^{2+}$
 II: $[\text{NiCl}_4]^{2-}$ [2]
- (iii) Explain why the two complexes are coloured. [3]

- (c) The stability of complexes can be determined by the stability constant of the complexes. Consider the formation of $[\text{Ni}(\text{NH}_3)_6]^{2+}$ from $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$. The stability constant, K_{stab} , is given by

$$K_{\text{stab}} = \frac{[\text{Ni}(\text{NH}_3)_6]^{2+}}{[\text{Ni}(\text{H}_2\text{O})_6]^{2+}[\text{NH}_3]^6}$$

Complex	Stability constant
$\text{Ni}(\text{H}_2\text{O})_6]^{2+} + 6\text{NH}_3 \rightleftharpoons [\text{Ni}(\text{NH}_3)_6]^{2+} + 6\text{H}_2\text{O}$	4.8×10^7
$\text{Ni}(\text{H}_2\text{O})_6]^{2+} + 3 \text{ en} \rightleftharpoons [\text{Ni}(\text{en})_3]^{2+} + 6\text{H}_2\text{O}$	2.0×10^{18}

State and explain if the en ligand will replace the NH_3 ligand for the nickel complexes. [2]

- (d) (i) The coordination compound $\text{NiCl}_2(\text{H}_2\text{O})_4$ has an octahedral geometry. Draw and identify the type of isomerism present in the compound. [2]
- (ii) Explain why $[\text{Ni}(\text{en})_3]\text{Cl}_2$ can dissolve in water. [2]

[Total: 20]

- 5 (a) (i) State the structure and describe the bonding present in the chlorides of sodium and aluminium respectively. [2]

- (ii) Construct a fully labelled energy level diagram for the formation of sodium chloride using the following values and relevant values from the *Data Booklet* and calculate the standard enthalpy change of formation of sodium chloride. [3]

Thermochemical term	$\Delta H / \text{kJ mol}^{-1}$
Lattice energy of NaCl(s)	-788
Enthalpy change of atomisation of Na(s)	+108
First electron affinity of Cl(g)	-349

- (iii) Describe what happens when the chlorides of aluminium and silicon are dissolved in water. Write the relevant equations and state the observation when Universal Indicator is added. [4]

- (b) The reactions of different halogens with hydrogen differ due to their reactivity. Explain the relative stability of the hydrogen halides with reference to the Data Booklet. [3]

- (c) The iodine clock reaction involves 2 reactions.
First reaction involves peroxydisulfate ($\text{S}_2\text{O}_8^{2-}$) and excess iodide ions. The second reaction involves thiosulfate ($\text{S}_2\text{O}_3^{2-}$) ion reacting with the iodine produced.

- (i) Write the equations for the two reactions of the clock reaction. [2]

- (ii) If 30 cm^3 of $0.002 \text{ mol dm}^{-3}$ of $\text{S}_2\text{O}_3^{2-}$ is used in the reaction, determine the mass of potassium peroxydisulfate needed for the first step. [2]

- (iii) Iron(II) ions are sometimes added to the reaction between peroxydisulfate and iodide. Write the equations to show how iron(II) ions aid in speeding up the rate of reaction. [2]

- (d) Iron is also used in other reactions, such as the Haber Process.
State the role of iron in the Haber Process and explain why iron is suitable for this role. [2]

[Total: 20]

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