Name:		Centre/Index Number:		Class:	

DUNMAN HIGH SCHOOL
Preliminary Examination
Year 6

H2 CHEMISTRY

9729/02

Paper 2 Structured Questions

13 September 2022

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your centre number, index number, name and class at the top of this page.
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.

Answer **all** questions in the spaces provided on the Question Paper.

The use of an approved scientific calculator is expected, where appropriate.
You may lose marks if you do not show your working or if you do not use appropriate units.

A Data Booklet is provided.

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

For Examiner's Use	
1	/12
2	/12
3	/14
4	/16
5	/21
Total	/75

This document consists of **21** printed pages and **3** blank pages.

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

1 **(a)** Describe the thermal decomposition of the hydrogen halides HC*l*, HBr and HI and explain any variation in their thermal stabilities.

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(b) Tert-butyl alcohol reacts with hydrogen chloride according to the equation shown.

$$(CH_3)_3COH + HCl \rightarrow (CH_3)_3CCl + H_2O$$

This reaction occurs in three steps.

step 1 protonation of –OH group in $(CH_3)_3COH$ to produce $(CH_3)_3COH_2^+$ cation

step 2 loss of H_2O molecule from $(CH_3)_3COH_2^+$ to produce a carbocation

step 3 chloride ion reacts with carbocation to produce $(CH_3)_3CCl$

(i) Describe the mechanisms which occur in **steps 2 and 3**. Use curly arrows to show the movement of electrons and label the slow step.

[3]

(ii) An enantiomerically pure alcohol, where the carbon atom bonded to the –OH group is chiral, was used for the reaction in **(b)**.

Use your answer in **(b)(i)** to deduce the stereochemical outcome of this reaction. Explain your reasoning.

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……. [2]

Tert-butyl alcohol also reacts with solid phosphorus pentachloride, PCl_5, to produce $(CH_3)_3CCl$.

(iii) With the aid of a suitable equation, explain why the reaction is not carried out in aqueous medium.

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……. [2]

(c) $(CH_3)_3CCl$ is one of the two monochlorinated products of the reaction between an alkane, **X**, and chlorine gas in the presence of UV light.

(i) Draw the structure of the alkane, **X**, and state the IUPAC name of the other monochlorinated product.

IUPAC name ……

[1]

(ii) The rate of formation of $(CH_3)_3CCl$ is faster than that of the other monochlorinated product.

Suggest an explanation for the different rates of reaction.

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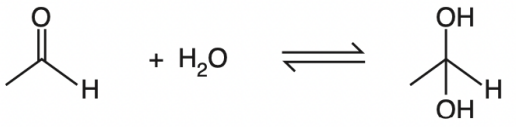
……. [1]

[Total: 12]

2 (a) The following equilibrium occurs when ethanal is mixed with water.



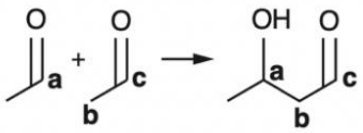
$\Delta G^{\ominus} = -0.282$ kJ mol^{-1}

Use relevant data from the *Data Booklet* to calculate the equilibrium constant, *K*, for the reaction.

[2]

(b) The aldol reaction is a useful reaction that forms a carbon–carbon bond between two carbonyl compounds. For example, two ethanal molecules can be combined using the aldol reaction.

The carbonyl carbon, **a**, of one ethanal molecule forms a covalent bond with a carbon atom, **b**, of another ethanal molecule. Carbon atom, **b,** must be adjacent to carbonyl carbon, **c**.



(i) When different carbonyl compounds are used in an aldol reaction, a mixture of structural isomers is formed.

Suggest two possible structural isomers that can be formed if propanone, CH_3COCH_3, and propanal, CH_3CH_2CHO, are mixed.

structural isomers	

[2]

(ii) Both propanal and propanoic acid can be formed from propan–1–ol in the same reaction.

Describe the reagents and conditions needed to ensure that the reaction yields propanal as the major product.

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……..... [2]

(c) Some tin reagents are useful in organic chemistry.

Tin forms two chlorides, $SnCl_2$ and $SnCl_4$.

(i) A mixture of these chlorides was found to contain 50.0% by mass of tin. Calculate the percentage by mass of $SnCl_2$ in the mixture.

[3]

(ii) Tin exists in +2 or +4 oxidation states in many of its compounds. Great care must be taken to ensure the correct oxidation state of tin is formed.

A student proposed the following preparation methods to prepare the two chlorides, $SnCl_2$ and $SnCl_4$.

Preparation method for $SnCl_2$

Heating tin with hydrochloric acid produces hydrogen gas. Careful evaporation of the water and dehydration produces white solid $SnCl_2$.

Preparation method for $SnCl_4$

Passing chlorine gas over heated tin produces colourless liquid $SnCl_4$ as the only product.

Explain if the preparation methods proposed above are feasible without reference to any calculation. Use relevant standard electrode potentials from the *Data Booklet*.

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[Total: 12]

3 (a) Compound **N**, $C_3H_4O_3$, liberates a gas when treated with aqueous sodium carbonate.

(i) Identify the gas and state the functional group that is present in compound **N**.

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……..... [1]

When 0.10 cm^3 of liquid compound **N** was dissolved in an inert solvent and an excess of sodium metal added, 15 cm^3 of gas was produced at 303 K and 1 atm.
[Density of compound **N** = 1.093 g cm^{-3}]

(ii) Calculate the ratio of the amount of compound **N** reacted to the amount of gas that is produced.

[1]

(iii) Use your answers in **(a)(i)** and **(a)(ii)** to suggest **two** possible structures of compound **N**. Explain your reasoning.

possible structures of compound **N**	

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……..... [3]

Compound **N**, $C_3H_4O_3$, is formed as the only organic product when a neutral organic compound **M**, $C_4H_8O_3$, is heated with acidified $KMnO_4$. **M** does not decolourise aqueous bromine.

(iv) Use the information provided and your answer in **(a)(iii)** to
- identify the structure of **N** and
- deduce the structure of **M**.

Explain your reasoning and the chemistry of the reactions involved.

N	**M**

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……..... [3]

(b) Phenylethene, $C_6H_5CH=CH_2$, can be used to synthesise three different aromatic compounds **R**, **S** and **T** as shown in Fig. 3.1.

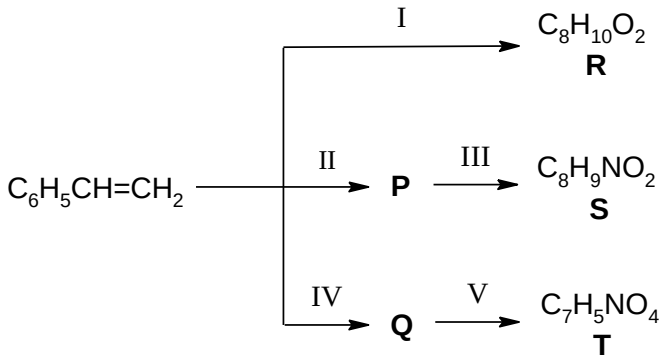

Fig. 3.1

(i) State the reagents and conditions required for reaction I.

……..... [1]

Compounds **S** and **T** have the following features.

- Each compound contains a disubstituted benzene ring.
- They have an identical substituent on their benzene rings.
- **S** has its substituents at positions 1 and 2 on the benzene ring.
- **T** has its substituents at positions 1 and 3 on the benzene ring.

(ii) Using the information provided and given that the same type of reaction is occurring in III and V, suggest structures for the intermediates **P** and **Q**.

Hence state the reagent and conditions required for reaction II.

P	**Q**

reagent and conditions for reaction II ……

…….... [3]

(iii) Suggest and explain how the conditions for reactions III and V would differ despite the same type of reaction occurring.

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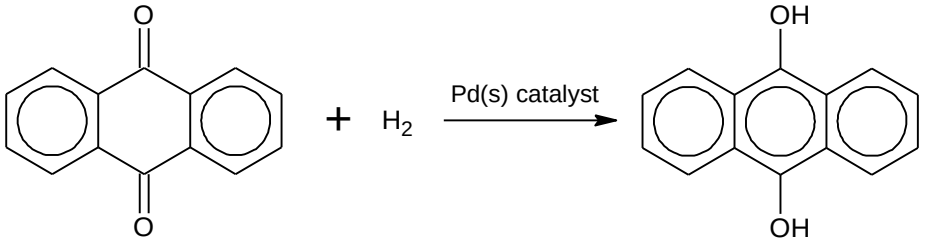
……..... [2]

[Total: 14]

4 Hydrogen peroxide, H_2O_2, finds its applications in a diversity of fields. Amongst many uses, it is an important precursor for the synthesis of organic peroxides and polymers. As such the manufacture of hydrogen peroxide has been an important industrial process since the 20th century.

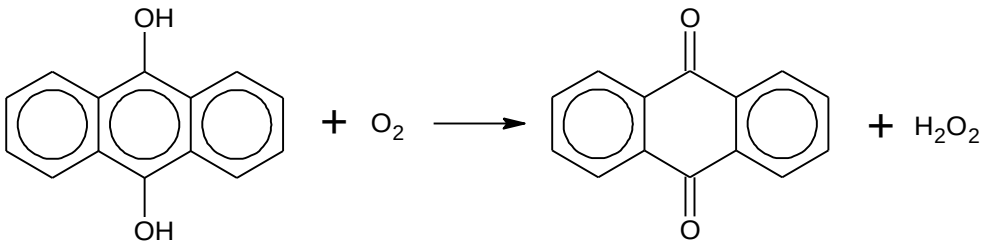
Today, most of the world's hydrogen peroxide is manufactured by the anthraquinone process. This process involves the two steps shown below.

step 1:



anthraquinone anthrahydroquinone

step 2:



anthrahydroquinone anthraquinone

(a) Step 1 involves the adsorption of H_2 gas onto the surface of the palladium metal catalyst.

(i) State the property that palladium possesses that allows it to act as a catalyst in step 1, and explain how the adsorption of H_2 gas onto palladium increases the rate of reaction.

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……. [2]

(ii) A study of the kinetics of step 1 revealed that at low pressures, the rate of reaction increases with increasing pressure of H_2. However, at high pressures, increasing the pressure of H_2 has no effect on the rate of reaction.

Explain these observations.

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……..... [2]

Although palladium and nickel belong to Group 10 of the Periodic Table, both elements have different ways of filling up their d orbitals. For palladium, it has a fully filled 4d subshell.

(iii) Draw, on the Cartesian axes provided in Fig. 4.1, the orbital from which the first electron of palladium is removed. Label the axes and orbitals clearly.

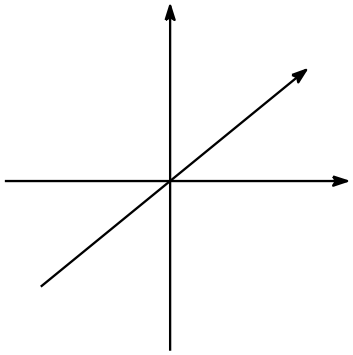

Fig. 4.1

[1]

(iv) It is observed that the first ionisation energies of the Period 4 transition elements remain relatively invariant. Explain this observation.

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……..... [2]

(b) At the end of step 1, anthrahydroquinone is extracted from the reaction mixture before reacting it with O_2 in step 2.

It is observed that step 2 follows the rate equation below.

$$\text{rate} = k[\text{anthrahydroquinone}][O_2]$$

In this step, a large excess of O_2 is required to ensure that anthrahydroquinone is completely oxidised back to anthraquinone, producing hydrogen peroxide.

(i) Explain why the rate equation for step 2 can be rewritten as rate = k'[anthrahydroquinone].

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……..... [1]

(ii) Hence sketch, on Fig 4.2, a labelled graph to show how the concentration of H_2O_2 in step 2 will vary over time.

Fig 4.2

[2]

(iii) Step 2 was repeated with different initial pressures of O_2 and different initial concentrations of anthrahydroquinone.

Table 4.1 shows the initial quantities of reactants used for each experiment and the time required for the initial concentration of anthrahydroquinone to be halved for experiment 1.

Table 4.1

experiment	initial pressure of O_2(g) / Pa	initial [anthrahydroquinone] / mol dm^{-3}	time required for initial [anthrahydroquinone] to be halved / min
1	4×10^5	1.00	12.0
2	4×10^5	0.50	
3	8×10^5	1.00	

Complete Table 4.1 and explain your answer.

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……..... [2]

(c) At the end of step 2, the reaction mixture contains only anthraquinone and H_2O_2. H_2O_2 can be separated out from the reaction mixture by adding water to the reaction mixture.

With reference to the bonding between relevant molecules, explain how the addition of water allows this to happen.

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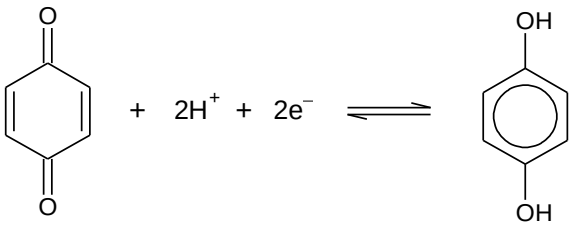
…….. [2]

(d) Quinone and hydroquinone have similar structures to anthraquinone and anthrahydroquinone respectively.

The standard reduction potential of the quinone–hydroquinone system is +0.70 V.



$E^{\ominus}$ = +0.70 V

quinone hydroquinone

An electrolytic cell was set up under standard conditions with a mixture of aqueous quinone and dilute sulfuric acid as the electrolyte and platinum rods as electrodes.

State the products formed at the anode and the cathode.

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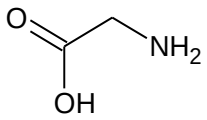
[Total: 16]

5 (a) Glycine has the following structure.



The pK_a values of glycine are shown in Table 5.1.

Table 5.1

pK_a of α–carboxyl group	pK_a of α–amino group
2.30	9.60

(i) Glycine exists as a zwitterion at pH 5.95.

State what is meant by the term *zwitterion*.

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……..... [1]

(ii) A 15 cm^3 solution of 0.05 mol dm^{-3} glycine is prepared in which glycine is fully protonated. The initial pH of this solution is 1.87.

Sketch the pH–volume added curve you would expect to obtain when 11.25 cm^3 of 0.10 mol dm^{-3} NaOH is added to this solution.

Use the information provided, and data from **(a)(i)** and Table 5.1 to label the various key points on the curve.

Show your working.

[3]

(iii) Write an equation to show the reaction occurring when 1.75 cm^3 of 0.10 mol dm^{-3} NaOH is **further** added to the resulting solution in **(a)(ii)**.

Hence calculate the pH of the solution obtained.

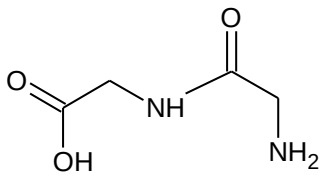
equation ……

[2]

(iv) Draw the structure of the predominant species of glycine at pH 10.0.

[1]

(v) Name the type of reaction occurring when **Q** is formed from two glycine molecules.



Q

……..... [1]

(b) The presence of some amino acids has been linked to the precipitation of calcium ethanedioate (CaC_2O_4), a component of kidney stones, in the body. Research studies have been performed to better understand the effect of pH on the solubility of CaC_2O_4.

(i) Predict and explain the effect of pH on the solubility of CaC_2O_4.

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……..... [2]

One research study on the effect of pH on the solubility of CaC_2O_4 involves adding excess powdered CaC_2O_4 to water that has its pH value adjusted. The suspension was filtered and the filtrate was titrated against acidified potassium manganate(VII) of a known concentration. The results are shown in Table 5.2.

Table 5.2

experiment	pH of filtrate	volume of $KMnO_4$ added / cm^3
1	1.56	30.00
2	1.76	24.55
3	2.45	13.40
4	3.20	8.00
5	5.37	3.70
6	6.16	3.50

(ii) Construct balanced ion-electron equations for the reaction between CaC_2O_4 and potassium manganate(VII) which produces a gas.

Hence write the overall equation for the reaction.

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……..... [2]

(iii) Using the data in Table 5.2, comment on your prediction in **(b)(i)**.

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……..... [2]

(iv) In experiment 1, 200 cm^3 of the filtered solution was titrated against 0.00100 mol dm^{-3} potassium manganate(VII).

Calculate the mass of Ca^{2+}, in mg, present in the filtrate.

[2]

(c) Thermogravimetric analysis is an analytical technique used to determine a substance's thermal stability by monitoring the change in mass that occurs as a sample is heated at a constant rate.

(i) Calcium ethanedioate monohydrate, $CaC_2O_4.H_2O$, has been used to calibrate equipment that performs thermogravimetric analysis because of its well-defined three-step decomposition process.

Complete the following equations which describe the decomposition process of $CaC_2O_4.H_2O$. Include state symbols.

Step 1: $CaC_2O_4.H_2O(s) \rightarrow CaC_2O_4(s) + H_2O(g)$

Step 2: $CaC_2O_4(s) \rightarrow$ …… + ……

Step 3: $CaCO_3(s) \rightarrow$ …… + ……

[2]

(ii) A thermogram from a thermogravimetric analysis plots mass of carbonate against temperature.

Given the same initial mass of carbonate, state and explain how the thermogram of magnesium carbonate will differ from that of calcium carbonate in terms of

- the final mass of carbonate obtained,
- the temperature at which the mass of carbonate starts to change significantly.

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[Total: 21]

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