HWA CHONG INSTITUTION
C2 Preliminary Examinations
Higher 2

CANDIDATE NAME		**CT GROUP**	**19S**
CENTRE NUMBER		**INDEX NUMBER**	

CHEMISTRY

9729/02

Paper 2 Structured Questions

31 August 2020

2 hours

Candidates answer on the Question Paper

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your **name**, **CT group, centre number** and **index number** clearly in the spaces above.

Write in dark blue or black pen.

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

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

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

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

A Data Booklet is provided.

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.

For Examiner's Use	
1	/ 11
2	/ 14
3	/ 15
4	/ 13
5	/ 22
Deductions	
Total	/ 75

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

For Examiner's use

1 This question concerns the reactions of Group 17 hydrides.

(a) HC*l*, HBr and HI exhibit different behaviour on heating.

(i) Describe the differences in decomposition behaviour for these three hydrides.

HC*l*: ……

……

HBr: ……

……

HI: ……

…… [2]

(ii) Explain the variation in the thermal stabilities of these hydrides.

……

……[1]

(b) Using HC*l* and a **different** base in each case, write equations, with state symbols, to illustrate:

(i) the Arrhenius theory of acids and bases,

……[1]

(ii) the Lewis theory of acids and bases.

……[1]

(c) HF and HC*l* have different acid strengths when dissolved in water.

(i) Given that the pH of 0.100 mol dm^{-3} HF is 2.10, explain, with the aid of relevant calculations, why HF is a weak acid.

……

……

……[2]

(ii) Hence, calculate a value for the K_a of HF.

[1]

For Examiner's use

25.0 cm^3 of 0.0500 mol dm^{-3} NaOH was placed in a conical flask. 0.100 mol dm^{-3} HF was then added from a burette.

The changes in pH for the titration was monitored throughout the experiment until 50.0 cm^3 of HF(aq) was added from the burette.

The experiment was then repeated by replacing HF(aq) with HC*l*(aq) of the same concentration.

(iii) Describe **one** way in which the pH titration curves are **similar** for these two experiments, apart from their initial pH.

……

……[1]

(iv) Describe **two** ways in which the pH titration curves are **different**. Briefly explain your answers.

1 ……

……

……

……

2 ……

……

……

……[2]

[Total: 11]

For Examiner's use

2 (a) The graph in Fig. 2.1 shows the successive ionisation energies for the removal of the first 15 electrons of Fe^{x+}.

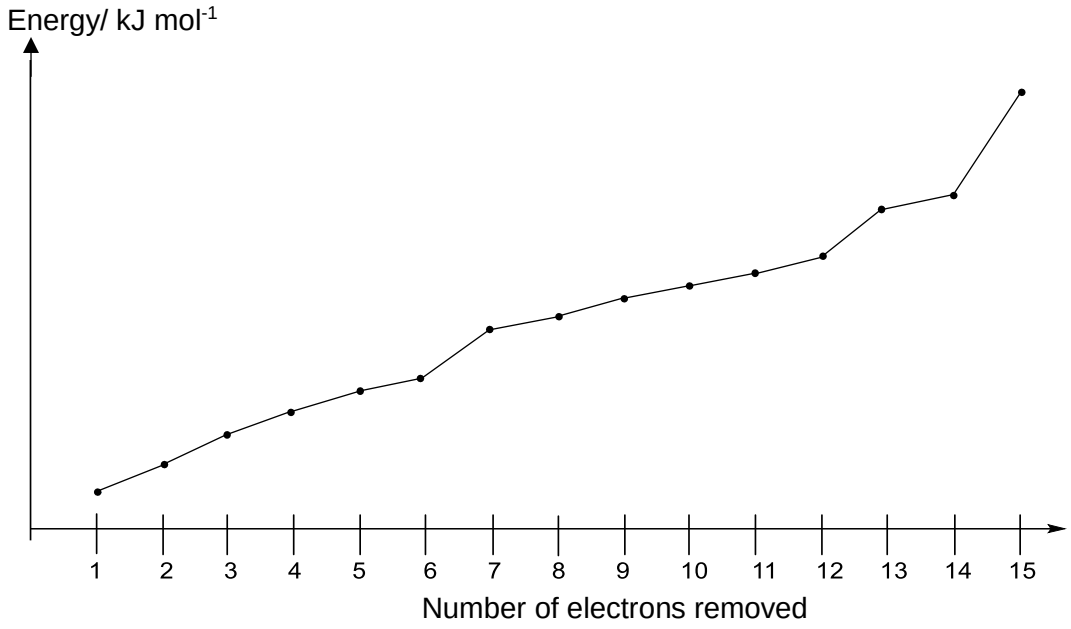

Fig. 2.1

Deduce the value of **x**.

……

……..……..……

……..……[2]

(b) (i) The standard reduction potential for the following electrode system is -1.02 V.

$$2CO_2(g) + 2HCO_2^-(aq) + 6H^+(aq) + 6e^- \ll C_4H_4O_6^{2-}(aq) + 2H_2O(l)$$

methanoate ion tartrate ion

Draw a fully labelled diagram of the set-up you would use to measure the above standard reduction potential.

[3]

For Examiner's use

(ii) Peroxodisulfate(VI) ions, $S_2O_8^{2-}$, are capable of oxidising $C_4H_4O_6^{2-}$ ions to CO_2 and HCO_2^-.

Explain why this reaction is expected to be slow.

……

……[1]

(iii) By considering relevant $E^\ominus$ values from the *Data Booklet*, show by means of balanced equations, how $Fe^{2+}(aq)$ ions can act as a homogeneous catalyst in the reaction.

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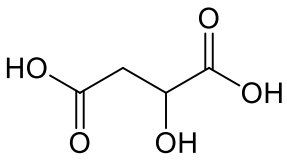
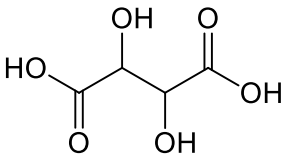
……[3]

(c) Wine contains a mixture of organic acids, such as tartaric acid and malic acid. These acids produce a prickling sensation on the tongue during wine-tasting.



malic acid



tartaric acid

Which of the two acids has a lower pK_{a1}? Explain.

……

……

……[2]

For Examiner's use

(d) Tartaric acid can undergo selective hydrodeoxygenation to form compound **K**. When **K** is heated strongly, compound **L** is formed, according to the scheme in Fig. 2.2.

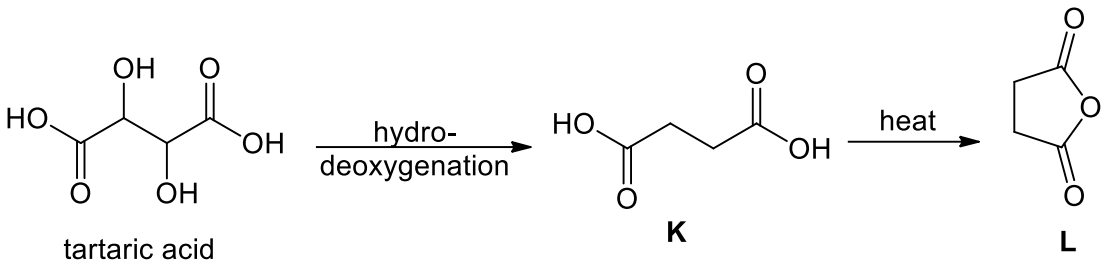


Fig. 2.2

Fig. 2.3 shows the mechanism of conversion of **K** to **L**.

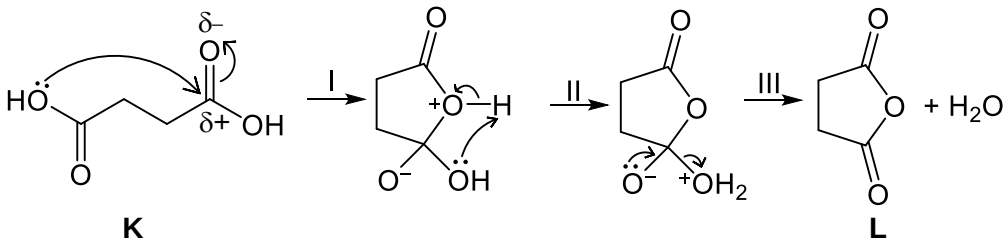


Fig. 2.3

(i) With reference to Fig. 2.3, suggest why the conversion of **K** to **L** can be described as *addition-elimination*.

……

……

……

……[2]

(ii) **L** slowly reacts with water, giving **K** again.

Draw the structural formula of product **M** ($C_6H_{10}O_4$) formed if **L** were to react with ethanol instead of water.

[1]

[Total: 14]

For Examiner's use

3 (a) 0.200 mol PCl_5 and 3.00 mol PCl_3 were left in a 10.0 dm^3 sealed container and allowed to reach equilibrium at 500 K. At equilibrium, there was 0.0500 mol Cl_2 gas.

$$PCl_5(g) \ll PCl_3(g) + Cl_2(g)$$

(i) Determine the total number of moles of gas at equilibrium.

[1]

(ii) Calculate the total pressure at equilibrium, giving your answer in Pa.

[1]

(iii) Hence, calculate the value of the equilibrium constant, K_p, for the reaction.

[2]

(iv) Explain how the position of equilibrium would be affected if the volume of the container above is decreased to 5.0 dm^3.

.....

.....

.....

.....[2]

For Examiner's use

(v) Using the value of K_p calculated in **(a)(iii)**, deduce the sign of ΔG_r for the above reaction at 500 K.

.....

.....[1]

(vi) Explain the effect of a catalyst on the value of K_p.

.....

.....[1]

(vii) Sketch and label on Fig. 3.1, a graph of variation of pV against 1/V at constant temperature for 1 mol of:

(I) Cl_2, and

(II) PCl_3.

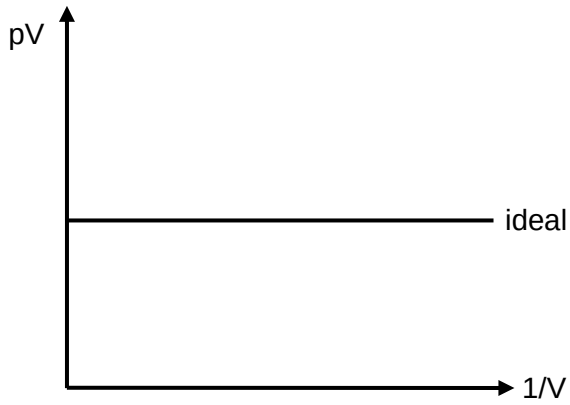


Fig. 3.1

[1]

(viii) Explain whether the gaseous equilibrium mixture in **(a)** will behave more or less ideally when temperature is lowered to 300 K.

.....

.....

.....[2]

For Examiner's use

(b) Alcohol **A** can be converted to nitrile **C** via the scheme shown in Fig. 3.2.

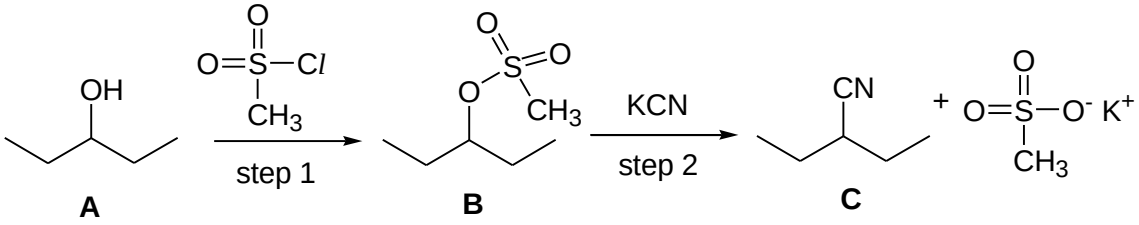


Fig. 3.2

(i) Draw the **skeletal formulae** of two constitutional isomers of **A**, one with an unbranched structure and the other with a branched structure, and name them.

Isomer with unbranched structure	**Isomer with branched structure**
Name……	Name……

[2]

Alcohol **A** cannot be converted to nitrile **C** via one step.

(ii) Given that the pK_a of H_2O is 15.6 and pK_a of CH_3SO_3H is –1.9, state whether OH^- or $CH_3SO_3^-$ is a weaker base.

……[1]

(iii) Hence, suggest why step 1 is necessary.

……

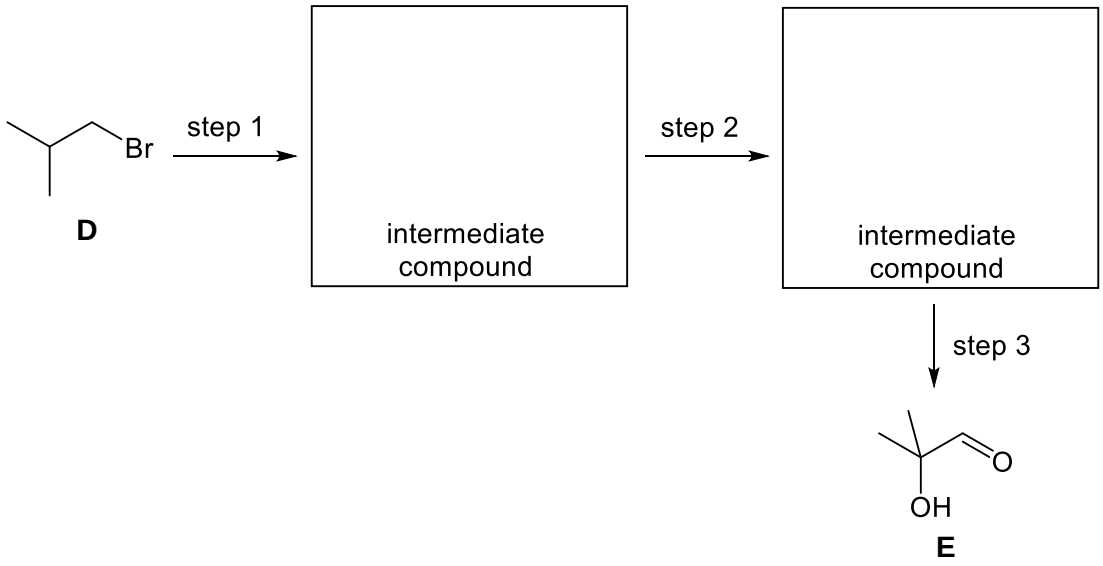
……[1]

[Total: 15]

For Examiner's use

4 Hydroxyaldehydes are common organic compounds, widely used in the fragrance industry and as precursors to many other organic molecules.

(a) (i) Complete the reaction scheme in Fig. 4.1 to show how hydroxyaldehyde **E** could be synthesised from compound **D** in **three** steps using inorganic reagents. Show the structures of the intermediate compounds and state the reagents and conditions for each step.



D **E**

Fig. 4.1

step 1: .....

step 2: .....

step 3: .....

[5]

(ii) A few drops of 2,4-dinitrophenylhydrazine was added to **E**. Draw the organic product of this reaction.

[1]

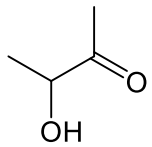
For Examiner's use

(b) Adding HCN with trace amounts of KCN to **E** at low temperatures would produce $(CH_3)_2C(OH)CH(OH)CN$.

(i) Draw the mechanism of this reaction. Show all charges and relevant lone pairs and show the movement of electron pairs by using curly arrows.

[3]

(ii) Explain why the rate of reaction would decrease if **E** was replaced with compound **F**.



F

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.....

..... [1]

For Examiner's use

(c) In 2019, a group of researchers from Singapore published an article in *Science*, one of the world's top academic journals, about the discovery of an unusual nucleophilic substitution reaction involving tertiary halogenoalkanes.

This new reaction, named halogenophilic nucleophilic substitution (S_N2X), is an unconventional method of synthesising a chiral product with a large excess of one enantiomer over the other. A simplified overall scheme of the S_N2X reaction, as well as the conventional unimolecular nucleophilic substitution (S_N1), are shown in Fig. 4.2.

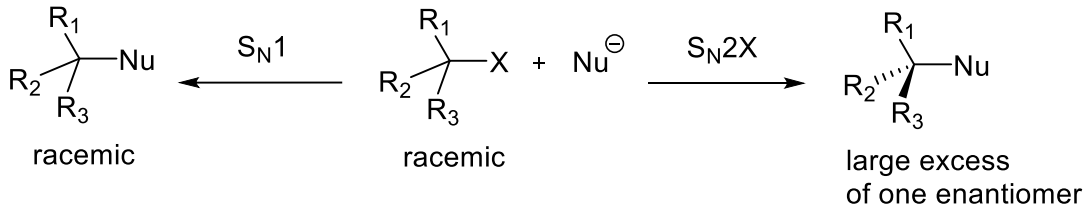

Fig. 4.2

(i) Suggest why tertiary halogenoalkanes typically do not undergo S_N2 reactions.

……

……

…… [1]

(ii) Instead, tertiary halogenoalkanes undergo S_N1 reactions to produce racemic product mixtures.

Explain why this is so.

……

……

…… [1]

For Examiner's use

Fig. 4.3 shows the mechanism of the S_N2X reaction which involves the generation of a carbanion intermediate and an uncharged Nu-X intermediate.

The carbanion intermediate and Nu-X interact with an enantiomerically-pure chiral cation (shown by the dotted lines) in the second step before undergoing a reaction. This results in a product mixture with a large excess of one enantiomer.

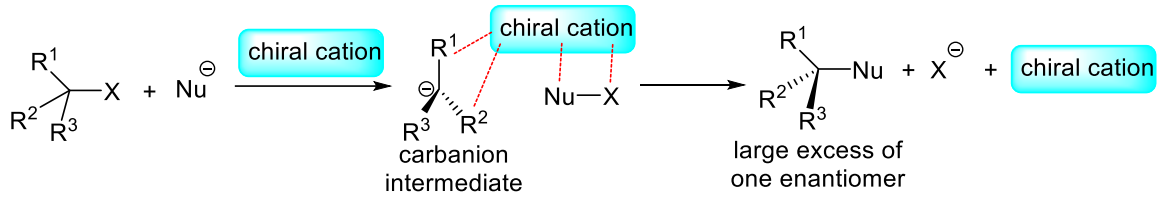

Fig. 4.3

(iii) Suggest why a chiral cation is crucial in the S_N2X reaction to obtain a product mixture with a large excess of one enantiomer.

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..... [1]

[Total: 13]

For Examiner's use

5 Titanium dioxide, TiO_2, is a brilliant white pigment which imparts whiteness and opacity for paints, plastics, sunscreens, toothpaste, and food colouring. It is also coated on the paper you are reading now.

(a) In the industrial manufacture of TiO_2, titanium(IV) chloride, $TiCl_4$, is oxidised by oxygen according to the equation:

$$TiCl_4(g) + O_2(g) \rightarrow TiO_2(s) + 2Cl_2(g) \qquad \Delta H^{\ominus} = -175 \text{ kJ mol}^{-1}$$

Use the following data, together with appropriate data from the *Data Booklet*, to calculate the average bond energy of the Ti–C*l* bond in $TiCl_4$.

standard enthalpy change of formation of $TiO_2(s)$ = –939 kJ mol^{-1}
standard enthalpy change of atomisation of Ti(s) = +473 kJ mol^{-1}

[3]

(b) Sidewalks in many cities are paved with Noxer blocks, which are cement mortar coated with TiO_2 to a thickness of 5 to 7 mm. The photocatalytic properties of TiO_2 enables it to remove pollutants from the air, particularly nitrogen dioxide, NO_2, and nitrogen monoxide, NO, both of which are radicals.

(i) Draw a dot-and-cross diagram to show the bonding in NO_2.

[1]

(ii) The bond angle in NO_2 is experimentally observed to be 135°. Apply the principles of the VSEPR theory to account for this observation.

……

……

……[2]

(c) The Noxer blocks essentially work by first using ultra-violet light to split water on the surface of the TiO_2 to give the hydroxyl radical, a proton, and an electron:

$$H_2O \rightarrow HO^{\bullet} + H^+ + e^-$$

Each hydroxyl radical can then react with one NO_2 molecule to form a single product. Each electron can react with an oxygen molecule from the air to form the superoxide ion, O_2^-, which can then react with NO to form a single, charged species. The four reactions may be combined to give an overall reaction showing the formation of a solution that can be washed away by rain water.

(i) Write equations for the three reactions described above, and hence, construct the equation for the overall reaction which takes place on the TiO_2 surface to remove both oxides of nitrogen. Identify the species being reduced in the overall equation.

Overall equation:

……

Species that is reduced:

…… [4]

(ii) Suggest, with a reason, whether the nitrogen-containing products in **(c)(i)** constitute the same compound or two different compounds.

……

……

……[1]

For Examiner's use

(d) At high temperatures, NO reacts with H_2 to produce nitrous oxide, N_2O, a greenhouse gas.

$$2NO(g) + H_2(g) \rightarrow N_2O(g) + H_2O(g)$$

To study the kinetics of this reaction at 820 °C, initial rates for the formation of N_2O were measured using various initial partial pressures of NO and H_2, as shown in Table 5.1.

Table 5.1

experiment	initial partial pressure / kPa		initial rate of formation of N_2O / kPa s^{-1}
	P_{NO}	P_{H_2}	
1	16	8	1.15×10^{-2}
2	8	8	2.88×10^{-3}
3	8	24	8.78×10^{-3}

(i) Determine the experimental rate equation for the reaction.

[2]

(ii) Hence, calculate a value for the rate constant. Include units in your answer.

[2]

(iii) In another experiment, NO at a pressure of 106 kPa and H_2 at 10 kPa are mixed at 820 °C. Calculate the time elapsed to reduce the partial pressure of H_2 to the half of its initial value.

[1]

For Examiner's use

(iv) A proposed mechanism for the reaction between NO and H_2 is given below.

$$2NO(g) \ll N_2O_2(g)$$

$$N_2O_2(g) + H_2(g) \xrightarrow{\text{slow}} N_2O(g) + H_2O(g)$$

Determine whether this mechanism is consistent with the experimental rate equation found in **(d)(i)**.

[2]

(e) When titanium(III) chloride is heated, it undergoes disproportionation.

$$2TiCl_3(s) \rightleftharpoons TiCl_2(s) + TiCl_4(g)$$

(i) The standard Gibbs free energy change, $\Delta G^{\ominus}$, at 25 ^{o}C for this reaction is +112.5 kJ mol^{-1}, and the standard enthalpy change, $\Delta H^{\ominus}$, is +155.8 kJ mol^{-1}.

Calculate the standard entropy change, $\Delta S^{\ominus}$, and comment on its sign with respect to the reaction.

……

……

……[2]

For Examiner's use

(ii) Using your answer to **(e)(i)**,

- explain why the reaction will only occur at high temperatures,
- determine the minimum temperature at which the reaction will take place.

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……[2]

[Total: 22]