Catholic Junior College

JC2 Preliminary Examinations

Higher 2

CANDIDATE NAME	
CLASS	**2T**

CHEMISTRY **9729/03**

Paper 3 Free Response **Friday 30 August 2019**

2 hours

Candidates answer on separate paper.

Additional Materials: Answer Paper
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and class 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.

At the end of examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

This document consists of **11** printed pages and **1** blank page.

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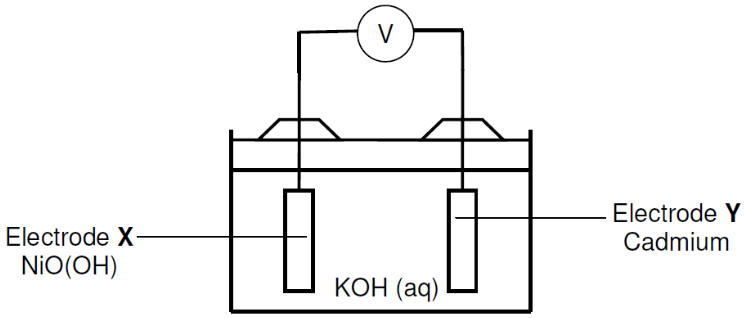
Section A

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

1 **(a)** Chemical energy can be directly converted to electrical energy in batteries and fuel cells. Fuel cells require a continuous source of fuel and oxygen to sustain the chemical reaction, whereas in batteries, the chemical energy is usually derived from reactions of metals or metal oxides present in the battery.

The nickel-cadmium (NiCd) battery is a rechargeable battery used in many devices such as handphones and laptops. A simplified diagram of the NiCd electrochemical cell is as shown:



Electrode **X** is made of a solid nickel compound, NiO(OH), and electrode **Y** is made of solid cadmium. The electrolyte is aqueous potassium hydroxide. During discharge, $Ni(OH)_2(s)$ and $Cd(OH)_2(s)$ are formed at the respective electrodes.

(i) Construct the half-equations at the electrodes of this alkaline NiCd electrochemical cell. Hence, give the balanced overall equation for the reaction that occurs during discharge. [2]

(ii) Write a cell representation for the NiCd electrochemical cell, indicating clearly the direction of electron flow in the external circuit. [2]

(iii) NiCd batteries can be recharged by applying a current across the two electrodes. How long would it take to recharge a NiCd battery at a current of 2.0 A, if 5.6 g of cadmium was converted to $Cd(OH)_2$? [2]

(b) Methane gas, CH_4, is the simplest alkane used to power a fuel cell. The methane-oxygen fuel cell has recently been shown to be an efficient source of electrical energy. In the simplest version of this fuel cell, an acid is used as the electrolyte and methane undergoes reaction at one of the electrodes while oxygen undergoes reaction at the other electrode.

$$CO_2 + 8H^+ + 8e^- \rightleftharpoons CH_4 + 2H_2O \qquad E^\theta = +0.17\text{ V}$$

$$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$$

(i) By using the half-equations above and relevant data from the *Data Booklet,* calculate the E^θ_{cell} of this fuel cell. [1]

(ii) Draw a fully labelled diagram of the electrochemical cell you could use to measure this E^{θ}_{cell}. [3]

(c) An alternative fuel used in fuel cells is dimethyl oxalate, $(CH_3)_2C_2O_4$, which is obtained by the esterification of ethanedioic acid, $H_2C_2O_4$, with methanol, CH_3OH. The ethanedioate ion, $C_2O_4^{2-}$, is commonly found in ionic salts such as **X**C_2O_4. When these ethanedioate salts, **X**C_2O_4, are oxidised by acidified potassium manganate(VII), $KMnO_4$, both the $\mathbf{X}^{2+}$ and $C_2O_4^{2-}$ ions are oxidised. Carbon dioxide gas is formed as one of the products in the reaction.

(i) Write a balanced equation for the reaction between MnO_4^{-} and $C_2O_4^{2-}$ under acidic conditions. [1]

(ii) 25.0 cm^3 of 0.1 mol dm^{-3} **X**C_2O_4 solution was titrated with 0.1 mol dm^{-3} of acidified $KMnO_4$. Determine the volume of $KMnO_4$ needed to oxidise $C_2O_4^{2-}$ only. [2]

(iii) Given that 15.00 cm^3 of acidified $KMnO_4$ was required to completely oxidise 25.0 cm^3 of 0.1 mol dm^{-3} **X**C_2O_4 solution, and using your answer in **(c)(ii)**, find the oxidation state of **X** in the product. [3]

(d) Potassium manganate(VII), $KMnO_4$, can be used to oxidise alkenes in different ways. Alkene **P**, C_8H_{16}, reacts with hot acidified $KMnO_4$ to form one organic product only, which gives a yellow precipitate with hot aqueous alkaline iodine. **P** also reacts with cold alkaline $KMnO_4$ to form an optically inactive diol, **Q**. When **P** is treated with chlorine in ultraviolet light, it produces a mixture of chlorinated compounds, including **R**, $C_8H_{14}Cl_2$, which does not have any chiral carbon. When **R** is reacted with ethanolic NaOH, compound **S**, C_8H_{12}, is the only product formed. **S** produces two compounds, CO_2 and CH_3COCO_2H in equimolar amounts when it is oxidised by hot acidified $KMnO_4$.

(i) Suggest the structural formulae for compounds **P**, **Q**, **R** and **S**. [4]

(ii) Draw the structural formula of an isomer of **R**, $C_8H_{14}Cl_2$, that could give **S** on dehydrochlorination. [1]

(iii) Suggest, with a reason, the number of stereoisomers for compound **S**. [1]

[Total:22]

2 With the prospect that fossil fuels will become increasingly scarce in the future, many compounds are being considered for use in internal combustion engines. One of these is DME or dimethyl ether, CH_3OCH_3. DME is a gas which can be synthesised from methanol. Methanol can be obtained from biomass, such as plant waste from agriculture.

(a) Write a balanced equation to define the term *standard enthalpy change of combustion*, $\Delta H_c^{\ominus}$, of DME. [1]

(b) A 0.31 g sample of DME was completely burnt in air. The heat produced raised the temperature of 200 g of water by 11.7 °C. Assume no heat losses occurred during this experiment.

(i) Use relevant data from the *Data Booklet* to calculate the amount of heat released in this experiment. [1]

(ii) Hence calculate the enthalpy change of combustion, $\Delta H_c^{\ominus}$, of DME. [1]

(c) **(i)** Use the bond energies given in the *Data Booklet* to calculate another value for the *enthalpy change of combustion*, $\Delta H_c^{\ominus}$, of DME. [2]

(ii) Suggest a reason for the discrepancy, if any, between this $\Delta H_c^{\ominus}$ value and that calculated in **(b)(ii)**. [1]

(d) DME may be synthesised from methanol according to the following equation.

$$2CH_3OH(l) \rightarrow CH_3OCH_3(g) + H_2O(l) \qquad \Delta H^{\ominus} = +7.10 \text{ kJ mol}^{-1}$$

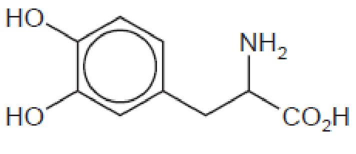
(i) The entropy change for this reaction, $\Delta S^{\ominus}$, is $+83.62$ J K^{-1} mol^{-1}.
Explain the significance of the sign of $\Delta S^{\ominus}$. [1]

(ii) Use the value of $\Delta S^{\ominus}$ and $\Delta H^{\ominus}$ given above to calculate a value for the standard Gibbs Free energy, $\Delta G^{\ominus}$, for this reaction. [1]

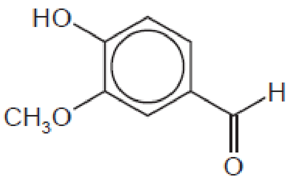
(iii) By considering the effect of temperature on the spontaneity of this reaction, suggest and explain whether high or low temperature should be used to produce DME. [2]

(iv) Explain, in molecular terms, how the rate of the above reaction is affected by changing the concentration of methanol. [2]

(e) Methanol is also a reagent to synthesise vanillin. Vanillin is an important raw material for the production of L-DOPA used in the treatment of Parkinson's disease.



L-DOPA



vanillin

A student carried out some reactions with samples of L-DOPA and vanillin using reagents **X**, **Y** and **Z**.

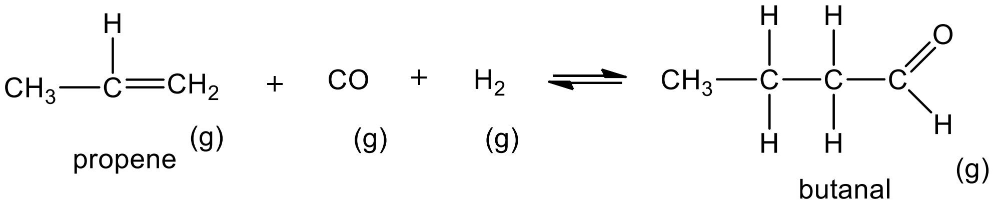
- Reagent **X** reacted with L-DOPA **and** with vanillin.
- Reagent **Y** reacted with L-DOPA but **not** with vanillin.
- Reagent **Z** reacted with vanillin but **not** with L-DOPA.

Assume that the CH_3O– group in vanillin is inert and does not react.

Suggest possible identities of reagents **X**, **Y** and **Z** and give the structures of the organic products formed in each case. [7]

[Total: 19]

3 **(a)** The hydroformylation reaction is an industrial process for the production of aldehydes from alkenes. For example, butanal can be synthesised from propene, C_3H_6, as follows:



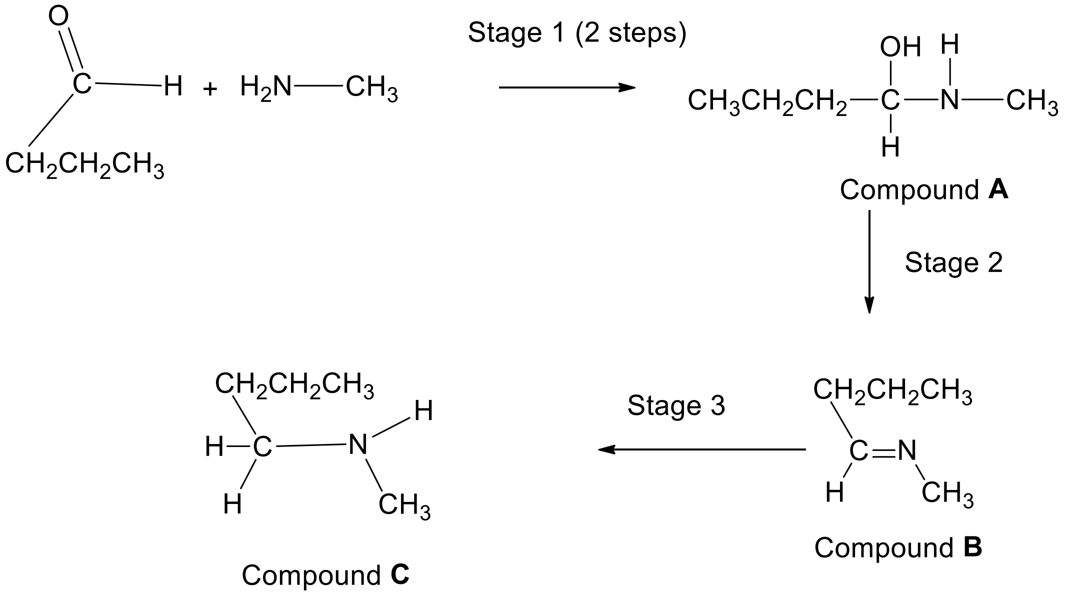
(i) Write an expression for K_p of the reaction, including units. [2]

(ii) Given that the magnitude of K_p for the above reaction is 775, deduce what the K_p value indicates about the position of equilibrium. Hence, state the sign of $\Delta G^{\ominus}$ for the reaction. [2]

(iii) Given that the above reaction is exothermic, suggest, with a reason, the effect of an increased temperature on the amount of butanal formed at equilibrium. [1]

(iv) The mechanism of hydroformylation of propene resembles the electrophilic addition of alkenes and can result in the formation of two isomeric products. Apart from butanal, suggest the structure of the other isomer that can be formed. [1]

(b) In the Leuckart-Wallach reaction, a carbonyl compound reacts with a primary amine to form a secondary amine.



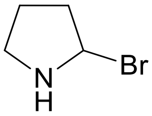
(i) Stage 1 occurs in 2 steps. The first step involves a nucleophilic attack while in the second step, a proton transfer occurs within the intermediate to form the alcohol group.

Name and outline the 2-step mechanism for Stage 1, to form Compound **A**. Show relevant lone pairs and dipoles, and use curly arrows to indicate the movement of electron pairs. [3]

(ii) Compound **B** undergoes reduction in Stage 3. Describe the change in oxidation state of carbon which occurs in this stage. [1]

(iii) Unlike primary amines, amides cannot be used in the Leuckart-Wallach reaction. Explain why this is so. [1]

(iv) 2-bromopyrrolidine, a cyclic amine, can be synthesised via the Leuckart-Wallach reaction.



2-bromopyrrolidine

Draw the displayed formula of the starting compound used in the synthesis of 2-bromopyrrolidine. [1]

(v) State and explain the relative basicities of 2-bromopyrrolidine and compound **C**. [2]

(c) Carbon also forms compounds with other Group 16 elements like sulfur and selenium. The properties of some of these compounds are given in the table below.

Compound	Structure	Dipole moment	Boiling point / °C
CS_2	S=C=S	0	46
COS	S=C=O	0.71	–50
COSe	Se=C=O	x	–22

(i) Explain, in terms of structure and bonding, the difference in the boiling point of CS_2 and COS. [2]

(ii) Predict a value for the dipole moment of COSe, x, and explain. [1]

(iii) Aside from the common oxides, carbon forms a series of straight-chained reactive oxocarbons. One such compound is tricarbon monoxide, C_3O, a reactive molecule found in space. Suggest a displayed structure of tricarbon monoxide. Indicate clearly any lone pairs of electrons present in your structure. [1]

(iv) Tricarbon monoxide is isoelectronic to cyanogen, $(CN)_2$. The molecule of cyanogen contains a C–C single bond.
Draw the dot-and-cross diagram of cyanogen. In your diagram, you should distinguish the electrons originating from each of the two carbon atoms and those from the two nitrogen atoms. [1]

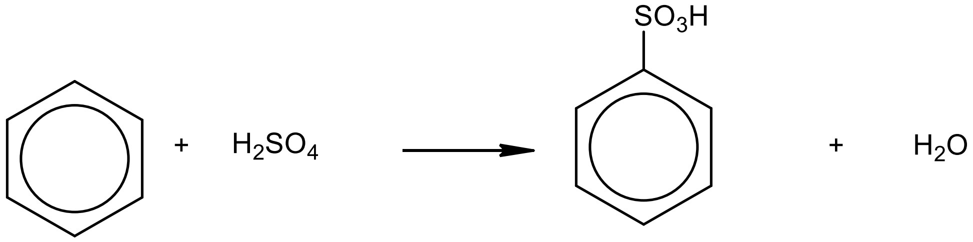
[Total: 19]

Section B

Answer **one** question from this section.

4 **(a)** Benzene is a widely used starting organic compound to synthesize other chemicals, such as benzenesulfonic acid and 2-methylphenol.

Benzenesulfonic acid can be produced by heating benzene under reflux with concentrated sulfuric acid for several hours. This process is similar to the nitration of benzene.

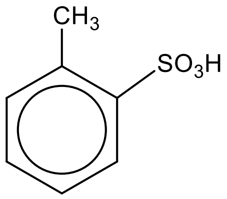


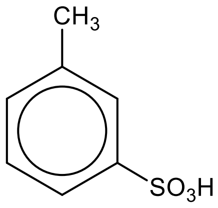
benzenesulfonic acid

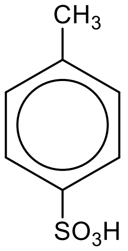
The first step of the mechanism involves the protonation of one molecule of sulfuric acid by another and the loss of a molecule of water.

(i) Describe the mechanism for the above reaction. Show relevant lone pairs and charges, and use curly arrows to indicate the movement of electrons. [4]

(ii) Similarly, methylbenzene also reacts with concentrated sulfuric acid to form a mixture of the three isomers, in equilibrium.

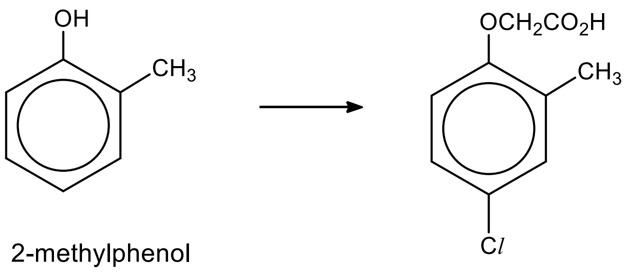






Suggest why there is a lower concentration of 1,2-isomer than that of 1,4-isomer in the equilibrium mixture. [1]

(iii) The chlorinated compound MCPA, widely used as a weed killer, can be synthesized from 2-methylphenol.



2-methylphenol

MCPA

Using **not** more than 3 steps, draw a reaction scheme to show how MCPA can be synthesised from 2–methylphenol. [5]

(b) The chemical reactions of benzene sometimes require iron as a catalyst. Iron is a hard grey transition metal which is resistant to corrosion at ordinary temperatures. In contrast, calcium is a fairly soft, silvery-grey Group 2 metal which quickly tarnishes in air.

(i) By considering relevant electronic configurations, explain why the atomic radius of iron is smaller than that of calcium, even though iron has more electrons. [2]

(ii) Iron can exist in different oxidation states whereas calcium does not. Explain why. [2]

(iii) Explain why iron(II) complexes are green in colour. [3]

(iv) Iron(III) ions catalyse the reaction between I^- ions and $S_2O_8^{2-}$ ions through homogeneous catalysis.
Explain why iron(III) ions can be described as a homogeneous catalyst. By considering relevant $E^\ominus$ values from the *Data Booklet*, show by means of balanced equations, how the iron(III) ions carry out its role in this reaction. [3]

[Total: 20]

5 **(a)** Aluminium oxide, Al_2O_3, and aluminium chloride, $AlCl_3$, are widely used in various industrial and commercial applications.

(i) Aluminium oxide has a melting point of 2072 °C while aluminium chloride sublimes at 180 °C. Explain the difference in melting points in terms of structure and bonding in each compound. [2]

(ii) Describe the reactions, if any, of aluminium oxide and aluminium chloride with water, suggesting the pH of the resulting solutions and writing equations, where appropriate. [4]

(b) The reaction between chlorine gas and hot sodium hydroxide is as follows.

$$3Cl_2 + 6NaOH \rightarrow 5\,NaCl + NaClO_3 + 3H_2O$$

(i) State the type of reaction occuring. [1]

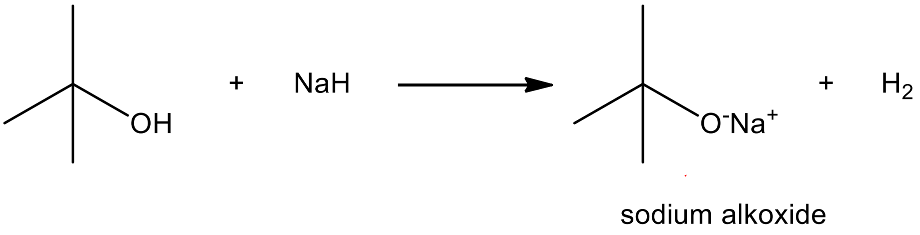
(ii) State the change in oxidation numbers of chlorine that occur during this reaction. [2]

(c) Ethers are a class of organic compounds that has two organic groups bonded to the same oxygen atom, R-O-R'. The organic groups could be alkyl and aryl groups. Williamson synthesis could be used to synthsise ethers by a reaction between primary alkyl halides and metal alkoxides.

A typical example of the Williamson synthesis is a two-step reaction to synthesize *tert*-butyl methyl ether.

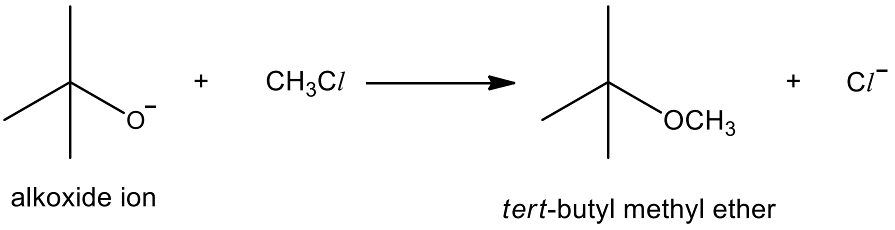
The first step of the reaction involved the preparation of sodium alkoxide in the presence of sodium hydride, NaH.

Step 1:



The second step of the reaction involved the reaction between the alkoxide ion and the primary alkyl halide.

Step 2:

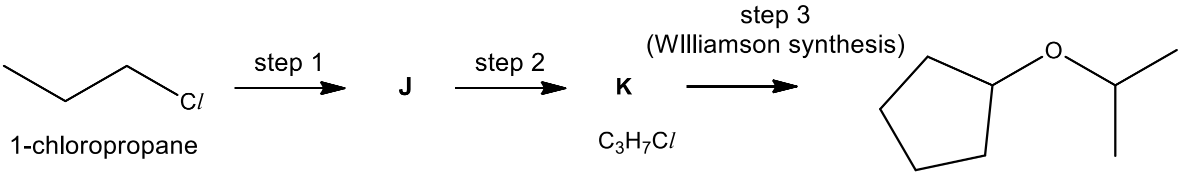


(i) Suggest the role of sodium hydride in step 1. [1]

(ii) Suggest the type of reaction which occurs in step 2. [1]

(iii) Suggest why primary alkyl halide is used in Williamson synthesis instead of secondary or tertiary alkyl halide. [1]

(iv) The following scheme shows a three-step synthesis of compound **L** from 1-chloropropane. Given that step 3 involves Williamson synthesis, suggest the reagents and conditions you would use for each step and identify the intermediates **J** and **K**.

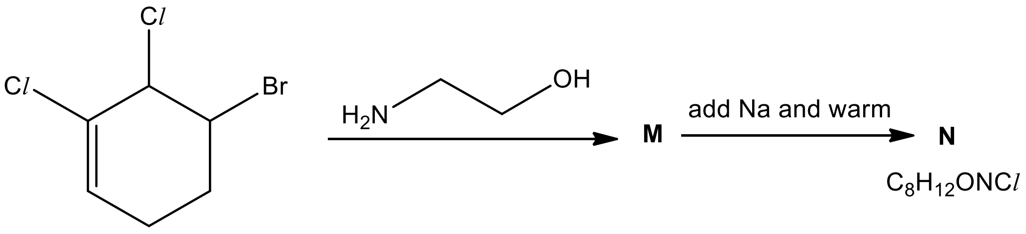


Compound **L**

[5]

(d) **(i)** Using monohalogenethanes, C_2H_5X, as examples, describe and explain the relative reactivities of chloro- and bromo-compounds with respect to hydrolysis. [1]

(ii) There are other methods to synthesise ethers. A cyclic ether **N** could be formed as shown below. Predict the outcomes of the following transformations, drawing the structures of the intermediate **M** and the product **N**.



[2]

[Total: 20]

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