Catholic Junior College

JC2 Preliminary Examination

Higher 2

CANDIDATE NAME	
CLASS	**2T**

CHEMISTRY **9729/03**

Paper 3 Free Response **September 2021**

2 hours

Candidates answer on the Question Paper.
Additional Materials: 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.

For Examiner's Use		
Section A	**Q1**	**/18**
	Q2	**/22**
	Q3	**/20**
Section B	**Q4** **OR** **Q5**	**/20** **/20**
TOTAL		**80**

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 **24** printed pages.

Section A

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

1 Fluorine is the most electronegative element and forms many interesting compounds. Antimony, Sb, is in Group 15 of the periodic table and forms two covalent fluorides that exist as simple molecules in gas phase, SbF_3 and SbF_5.
Krypton, Kr, is in Group 18 of the periodic table and its first compound discovered is KrF_2.

(a) Draw 'dot-and-cross' diagrams showing the electrons (outer shells only) in SbF_3, SbF_5, and KrF_2. Use the VSEPR (valence shell electron pair repulsion) theory to predict their shapes and hence state whether the species is polar or non-polar. [8]

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(b) SbF_5 can react as shown in the following reaction and is a useful reagent as an exceptionally strong Lewis Acid.

$$SbF_5 + F^- \rightarrow [SbF_6]^-$$

Explain the term *Lewis Acid*, and suggest the reason why SbF_5 is a *strong* Lewis Acid. [2]

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(c) SbF_3 exists as gaseous molecules at a temperature of 700 K.

(i) Calculate the volume of 0.10 mol of an ideal gas at a temperature of 700 K, at a pressure of 1.01×10^5 Pa. [1]

(ii) The volume of 0.10 mol of SbF_3 measured at 700 K and 1.01×10^5 Pa in a gas syringe was significantly different from your answer in **(i)**.
Suggest **two** possible reasons why this might be the case in terms of the properties of SbF_3. [2]

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(d) KrF_2 is a very reactive compound, undergoing thermal decomposition to give Kr and F atoms at very low temperature.

(i) Suggest what information this gives about the Kr–F bond. [1]

(ii) KrF_2 is a strong oxidising agent, with a standard redox potential of +3.5 V.

State how the reactivity of the halogens as oxidising agents varies down the group. Using relevant data from the *Data Booklet,* arrange KrF_2 and the halogens in increasing order of oxidising power. [2]

(iii) Given the reduction half-equation for krypton fluoride, KrF_2, is as follows:

$$KrF_2 + 2e^- \rightarrow Kr + 2F^-$$

When krypton fluoride, KrF_2, is added to an aqueous solution containing bromide ions, effervescence is observed. The mixture of gas contains Kr gas and another gas that relights a glowing splint.

State another expected observation and suggest a balanced equation for the reaction. [2]

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[Total: 18]

2 The mineral fluorspar consists mainly of calcium fluoride, CaF_2, which is a principal source of hydrogen fluoride.

(a) **(i)** Using calcium fluoride, CaF_2, as an example, define the term *standard enthalpy change of formation*. [1]

(ii) Using the following data and relevant data from the *Data Booklet*, construct a Born-Haber cycle and use it to calculate the enthalpy change of formation of CaF_2(s), stating its units. [2]

	Value / kJ mol^{-1}
lattice energy of CaF_2(s)	–2640
electron affinity of fluorine	–328
enthalpy change of atomisation of calcium	+184

(iii) The solubility product values, K_{sp}, of some Group 2 fluorides, at 25 °C, are given in the table below. Identify the least soluble fluoride from the table and calculate its solubility, in mol dm^{-3}, at 25 °C. [2]

Group 2 fluorides	K_{sp} / mol^3 dm^{-9}
CaF_2	3.9×10^{-11}
SrF_2	2.8×10^{-9}
BaF_2	1.7×10^{-6}

(iv) State and explain how the solubility of the fluoride identified in **(iii)** would change if it is added to an aqueous solution containing sodium fluoride, NaF. [1]

(v) Solution **X** contains 0.100 mol dm^{-3} strontium chloride and 0.100 mol dm^{-3} barium chloride. Predict and explain, with the aid of relevant calculations, what would happen when equal volumes of solution **X** and 0.00500 mol dm^{-3} of sodium fluoride, NaF, are mixed together. [2]

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(b) Morphine, denoted as Mor, is a weak monoacidic alkali and used in small quantities for pain relief.

When 30 cm^3 of 0.30 mol dm^{-3} of morphine solution was titrated against 0.20 mol dm^{-3} hydrochloric acid at room conditions, the end-point was determined using a suitable indicator.

(i) Write the K_b expression for morphine. Use Mor and $MorH^+$ to denote morphine and its conjugate acid respectively. [1]

(ii) Calculate the initial pH of the morphine solution. (Given K_a of $MorH^+$ = 2.09×10^{-12} mol dm^{-3}) [2]

(iii) Determine the concentration of the salt that was formed at the equivalence point. [3]

(iv) Explain, using an appropriate equation, why the end-point of the titration is not neutral. Hence, by using your answer in **(iii)**, determine the pH at the equivalence point. [2]

(v) By using your calculations in **(i)**, **(ii)** and **(iii)**, sketch and label the graph of pH against volume of hydrochloric acid used, indicating the region where the mixture acts as a buffer. [2]

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(c) 1 mole of methane reacts with 1 mole of steam to form carbon monoxide and another gas. The enthalpy change of this reaction is +210 kJ mol^{-1} and the entropy change of this reaction is +216 J mol^{-1} K^{-1}.

Write a balanced chemical equation with state symbols for the above reaction, and explain why the entropy change is positive and why the reaction is spontaneous only at high temperatures.

Hence, determine the minimum temperature, T_s, when the reaction is spontaneous.

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[Total: 22]

3 **(a)** State the electronic configuration of a copper atom. [1]

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(b) Explain why the 1st ionisation energy of the first row transition metals are relatively invariant across the period. [2]

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(c) Copper forms a variety of complex ions, eg. blue $[Cu(H_2O)_6]^{2+}$ which has an octahedral shape.

(i) In the gas-phase transition metal ion, the 5 d orbitals are degenerate, but in the octahedral complex, the d orbitals are split into 2 energy levels.

State and explain which d orbitals have the higher energy level in the complex ion. [2]

(ii) When excess ammonia is added to aqueous copper(II) ions, the blue solution turns deep blue. Describe the reaction that has occurred, and write a balanced equation for the reaction. [2]

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(d) Glycine, $H_2NCH_2CO_2H$, is the simplest stable amino acid, with a single hydrogen atom as its side chain.

Glycinate anions can act as ligands, forming complexes such as copper glycinate, $[Cu(H_2NCH_2CO_2)_2]$, which is used as a source of dietary copper in animal feed.

A synthesis route to form copper glycinate is shown.

$$CH_3CH_2OH \xrightarrow{\text{I}} CH_3CO_2H \xrightarrow{\text{II}} [Cu_2(CH_3CO_2)_4] \xrightarrow{\text{III}} [Cu(H_2NCH_2CO_2)_2]$$

(i) State reagents and conditions for step I. [1]

Step II can be carried out by heating the ethanoic acid, CH_3CO_2H, with copper(II) hydroxide, $Cu(OH)_2$, to form $[Cu_2(CH_3CO_2)_4]$.

(ii) State the oxidation number of copper in $[Cu_2(CH_3CO_2)_4]$. [1]

(iii) Step III is often carried out by adding $[Cu_2(CH_3CO_2)_4]$ in aqueous alcohol to glycine. Given that the shape of copper glycinate is square planar, draw and label the 2 *cis-trans* isomers of copper glycinate that can be formed in step III. [2]

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(e) Glycine can be synthesized from ethanoic acid in the following synthesis route:

$$CH_3CO_2H \xrightarrow{\text{I}} ClCH_2CO_2H \xrightarrow{\text{II}} H_2NCH_2CO_2H$$

(i) In step I, Cl_2 reacts with ethanoic acid in the presence of a catalyst to form chloroethanoic acid.

Suggest a chemical test to distinguish between ethanoic acid and chloroethanoic acid. Include the reagents and conditions used, and the observations for each compound. [2]

(ii) Give reagents and conditions for step II and state the type of reaction that is occurring. [2]

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(f) Another transition element compound, vanadium(V) oxide, V_2O_5, is used as a catalyst in the Contact process to manufacture sulfuric acid.

Sulfur dioxide and oxygen in a 1:1 ratio are passed over the heated V_2O_5 catalyst to form sulfur trioxide. During the reaction, the brown-yellow catalyst changes colour to dark blue, but returns to the original brown-yellow colour at the end of the reaction.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \qquad \Delta H = -196 \text{ kJ mol}^{-1} \qquad \textit{reaction 1}$$

(i) *Reaction 1* takes place via *heterogeneous* catalysis. State what is meant by *heterogeneous* catalysis. [1]

(ii) The mode for this catalysis is unusual, as the catalyst reacts with the reactants that are adsorbed onto its surface. However, throughout *reaction 1*, no vanadium complexes are involved. Suggest a reason for the colour change of the catalyst. [1]

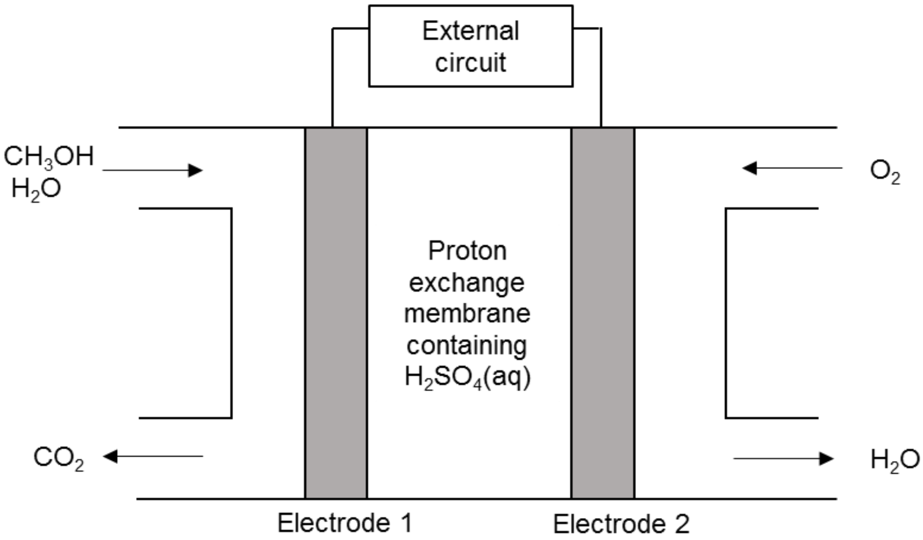
(iii) Use Le Chatelier's principle to explain the optimum temperature and pressure conditions for *reaction 1* in order to maximize yield, and suggest one other consideration in deciding the temperature for *reaction 1* to be carried out commercially. [3]

[Total: 20]

Section B

Answer **one** question from this section.

4 **(a)** The following diagram illustrates the parts of the direct methanol fuel cell (DMFC). Methanol is supplied to Electrode 1 where methanol and water react to form carbon dioxide. Oxygen is supplied to Electrode 2 simultaneously and reacts with the protons at the cathode to form water.



The overall cell reaction of a DMFC can be expressed as follow.

$$CH_3OH(l) + \frac{3}{2}O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$$

Research has shown that the DMFC is an appropriate alternative to rechargeable batteries. The electrons are transported through an external circuit from anode to cathode, providing power to connected devices like mobile phones and laptop computers.

(i) Write the half–equations for the reactions which take place at Electrode 1 and Electrode 2. [2]

(ii) A DMFC is capable of producing a voltage of 1.18 V at standard conditions. Hence, calculate the standard Gibbs free energy change, $\Delta G^{\ominus}$, for the **given** overall cell reaction. [1]

(iii) Predict how the voltage of this cell would change if the [CH_3OH] was decreased. [2]

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(b) The electricity generated by the DMFC can be used to electroplate taps with nickel to give a high lustre finish and resistance to wear and corrosion. The electrolyte used was a solution of nickel(II) sulfate.

Calculate the current produced by the DMFC when a total of 3 hours was used to plate 15 g of nickel. [2]

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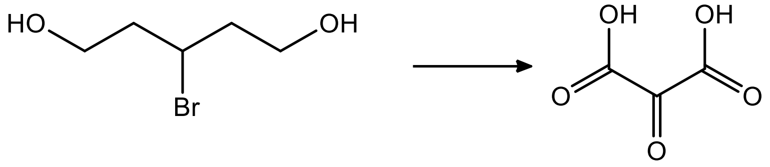
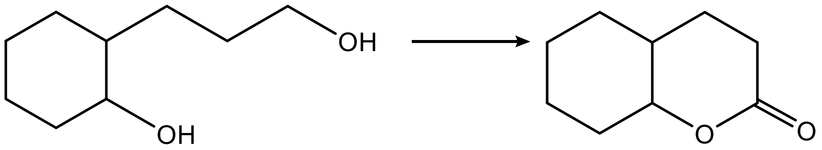
(c) Alcohols can undergo various reactions to form other class of organic compounds like carboxylic acids and esters. Suggest how the following products can be formed from the corresponding alcohol in **three steps**.

You are required to state the reagents and conditions for each step and give the structures of the intermediate compounds.

(i) [3]



(ii) [3]



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(d) Chemists and biochemists use pK_a values to compare the strengths of acids. The use of pK_a values is more convenient for comparing acid strengths than the K_a values.

The pK_a values of two naturally occurring acids are shown below.

name	structural formula	pK_a (at 25 °C)
benzoic acid	C_6H_5COOH	4.19
phenylmethanol	$C_6H_5CH_2OH$	15.1

Explain, in terms of their molecular structures, why benzoic acid and phenylmethanol have significantly different pK_a values. [2]

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(e) Compound **A**, with molecular formula C_5H_8O, decolourises aqueous bromine and gives off white fumes when reacted with PCl_5. Upon heating **A** with acidified potassium manganate(VII), a symmetrical product **B**, $C_5H_6O_5$, is formed.

B does not give a red precipitate with Fehling's solution but an orange precipitate is observed with 2,4-dinitrophenylhydrazine. 1 mol of **B** also reacts with 1 mol of Na_2CO_3 with effervescence observed.

Deduce the structures of compounds **A** and **B**, explaining the chemistry of the reactions involved. [5]

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[Total: 20]

5 **(a)** The pH values of the solutions of two Period 3 chlorides are given below.

compound	pH of a 1.0 mol dm^{-3} solution
NaC*l*	7.0
MgC*l*$_2$	6.0

By using suitable data from the *Data Booklet*, suggest explanations for the pH values of the two chloride solutions. Include appropriate equations in your answer. [4]

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(b) Other Period 3 compounds such as Mg(OH)$_2$ and A*l*(OH)$_3$ are sparingly soluble in water. Their solubility products at 298 K are given in the table below:

compound	numerical value of K_{sp}
Mg(OH)$_2$	1.80 x 10^{-5}
A*l*(OH)$_3$	1.80 x 10^{-11}

Calculate the solubilities of the two compounds, and hence deduce which of the two compounds is more soluble in water at 298 K. [3]

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(c) A zinc-air battery uses oxygen gas in the air as an oxidising agent and zinc metal as a reducing agent. Zinc is oxidised to a soluble zincate, $Zn(OH)_4^{2-}$. The electrolyte circulated through the battery is NaOH(aq).

(i) Write the equations for the reactions that occur at the anode and cathode respectively. [2]

(ii) Given that the $\Delta G^{\ominus}$ for the reaction is –636.9 kJ mol^{-1}.

1. Calculate the standard standard cell potential, $E^{\ominus}_{cell}$. [2]

2. Hence, by the use of suitable data from the *Data Booklet*, calculate a value for the $E^{\ominus}$ of the $Zn(OH)_4^{2-}$ / Zn electrode reaction. [1]

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(d) An aromatic compound **C** has the molecular formula, $C_{10}H_{14}N_2O_2$, and is an amine that dissolves readily in aqueous HCl. Decolourisation is observed when aqueous Br_2 is added to **C**, and a new product **D**, $C_{10}H_{13}BrN_2O_2$, is formed.

C does not give orange precipitate upon reaction with 2,4-dinitrophenylhydrazine (2,4-DNPH) but reacts with excess concentrated H_2SO_4 to form an alkene. **C** also reacts with hot alkaline aqueous iodine to form a yellow precipitate.

Reaction of **C** with hot aqueous sodium hydroxide produces ammonia gas and a salt.

When **C** is subjected to hot acidified $KMnO_4$ followed by a suitable extraction technique, compound **E**, $C_9H_7NO_6$ is obtained. 1 mol of compound **E** requires 1.5 mol of aqueous sodium carbonate for complete neutralisation.

Deduce the structures of compounds **C**, **D**, and **E**, explaining your reasoning. [8]

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[Total: 20]

Additional answer space

If you use the following pages to complete the answer to any question, the question number must be clearly shown.