PRELIMINARY EXAMINATIONS
HIGHER 2

TEMASEK
JUNIOR COLLEGE

CANDIDATE NAME									
CIVICS GROUP			/						
CENTER NUMBER	S					INDEX NUMBER				

CHEMISTRY
9729/03

Paper 3 Free Response

13 September 2021
2 hours

Candidates answer on the Question Paper.

Additional materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your Civics Group, Centre number, index number and name in all the work you hand in.
Write in dark blue or black pen.
You may use a 2B 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. If additional space is required, you should use the pages at the end of this booklet. The question number must be clearly shown.

Section A
Answer **all** questions.

Section B
Answer **one** question.

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		
Paper 3 (Section A)	1	
	2	
	3	
Paper 3 (Section B)	4	
	5	
Total		

This document consists of **23** printed pages and **1** blank page.

SECTION A

Answer all the questions in this section.

1 **(a)** The Contact Process is an industrial process for manufacturing sulfuric acid. The key stage in this process is the reaction between sulfur dioxide and oxygen.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \qquad \Delta H = -197 \text{ kJ mol}^{-1}$$

Vanadium(V) oxide, V_2O_5, is used as a heterogeneous catalyst for this process.

With the aid of an energy profile diagram, explain using collision theory why the addition of the catalyst speeds up the reaction. [3]

(b) In an experiment to determine the K_p of the Contact Process in **(a)**, a mixture containing 0.200 mol of SO_2 and 0.100 mol of O_2 was heated in a closed flask and allowed to reach equilibrium at 550 °C and 3.5 atm.

The flask was then rapidly cooled to liquefy the SO_3 so that it can be separated from the gaseous SO_2 and O_2. Excess water was carefully added to the liquid SO_3, causing the following reaction to occur:

$$SO_3(l) + H_2O(l) \rightarrow H_2SO_4(aq)$$

The resulting solution was made up to 250 cm^3 in a standard volumetric flask. 25.0 cm^3 of this solution was titrated with 1.00 mol dm^{-3} NaOH and required 36.00 cm^3 for complete neutralisation.

(i) Calculate the equilibrium amounts of SO_2, O_2 and SO_3 at 550 °C. [3]

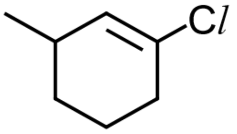
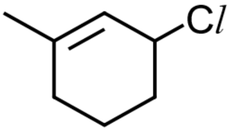
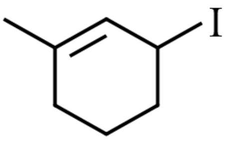
(ii) Write the expression for K_p and calculate the value of K_p at 550 °C and 3.5 atm, including its units. [2]

(iii) In liquefying the SO_3, it was mentioned that the cooling was performed rapidly. Explain how the titre volume would be affected if the cooling had been performed slowly. [2]

(c) Precious metals like platinum and rhodium are fitted into car engines as catalytic converters to reduce the amount of pollutants in the exhaust.

With the aid of equations, show how the pollutants hydrocarbons, C_xH_y, and oxides of nitrogen can be removed from the exhaust. [2]

(d) A student was tasked to investigate the rate of hydrolysis of compounds **A**, **B** and **C** as shown below.

Compound **A**	Compound **B**	Compound **C**
		

(i) State and explain the difference in reactivity of compounds **A, B** and **C** towards hydrolysis. [3]

(ii) Compound **B** reacts with bromine monochloride, BrC*l*, in the presence of an inert organic solvent.

Name and describe the mechanism of this reaction. Show relevant lone pairs and dipoles, and use curly arrows to indicate movement of electron pairs. [3]

(iii) Suggest the structure of another carbocation that can be formed from the mechanism drawn in **(d)(ii)**.

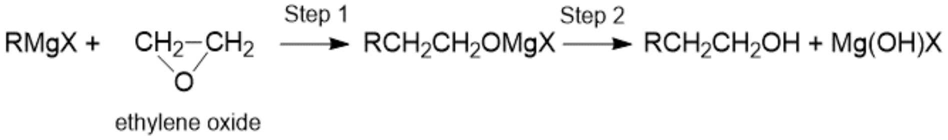
Hence, explain which carbocation is preferentially produced. [2]

[Total: 20]

[Turn over

2 **(a)** Organometallic compounds are compounds that contain carbon-metal covalent bonds. Organometallic compounds of lithium and magnesium are strong bases and are of great importance in organic synthesis.

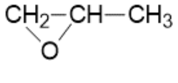
Organomagnesium halides are also known as Grignard reagents. The reaction between an organomagnesium halide and ethylene oxide is shown below.



(i) Suggest the types of reaction for steps 1 and 2. [2]

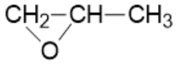
(ii) Explain why the ring opening process in step 1 is favourable. [1]

(iii) Suggest why organomagnesium and organolithium compounds are more reactive than organomercury or organolead compounds. [1]

(b) A student prepared a Grignard reagent, CH_3CH_2MgBr, from bromoethane and magnesium metal in ether solvent. He subsequently reacted the Grignard reagent with  .

(i) Water cannot be used as a solvent as it will react with the Grignard reagent prepared.

Explain how CH_3CH_2MgBr reacts with water, and hence suggest an organic product from the reaction. [2]

(ii) Suggest the structure of the major organic product formed between CH_3CH_2MgBr and  . Explain your answer. [2]

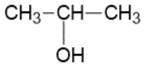
(iii) Describe a simple chemical test you would carry out to confirm the presence of the functional group present in the product in **(b)(ii)**. State what you would observe. [2]

(iv) Use the table of characteristic infra-red absorption frequencies in the Data Booklet to answer this question.

The student suggested testing for the presence of the product in **(b)(ii)** via infra-red spectroscopy, and observing for strong and very broad absorption at 2500–3000 cm^{-1}.

Explain if you agree with the student's suggestion. [1]

Alcohols can also be produced from a reaction between a Grignard reagent and a carbonyl compound.

(v) Suggest the Grignard reagent and carbonyl compound needed to form  $CH_3-\underset{OH}{CH}-CH_3$.

[1]

[Turn over

(c) $LiFePO_4$ can be used in lithium-ion rechargeable batteries which are commonly used in cell phones and laptops.

When the cell is charging, lithium reacts with the graphite electrode to form LiC_6.

(i) Suggest the type of bonding between lithium and carbon in LiC_6. Explain how the bonds are formed during the charging process. [2]

When the cell is discharging, the following processes are observed:

- carbon atoms and lithium ions are formed from solid LiC_6;
- solid $LiFePO_4$ is formed from $FePO_4$.

(ii) Write equations for the reactions at the anode and cathode. [2]

(iii) The cell voltage of $LiFePO_4$ battery is 3.20 V.

Calculate ΔG for the discharging process. [1]

(iv) State one possible advantage of using the lithium-ion rechargeable batteries. [1]

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[Total: 18]

3 **(a)** Hydrogen chloride exists as white fumes under room conditions and dissolves readily in water to form a strongly acidic solution.

$$HCl(g) \rightarrow H^+(aq) + Cl^-(aq) \qquad \Delta H^\ominus = -75 \text{ kJ mol}^{-1}$$

The first electron affinity of $Cl(g)$ is given as –349 kJ mol^{-1}.

(i) Using suitable values from the *Data Booklet* and with the aid of an energy cycle, determine $\Delta H^\ominus_{hyd}{}'$, the sum of standard enthalpy change of hydration of gaseous proton and chloride. [3]

(ii) The standard enthalpy change of reaction when 1 mole of each of the following acids reacts with excess aqueous sodium hydroxide is shown below.

Acid	$\Delta H_r^\ominus$ / kJ mol^{-1}
Nitric acid	–57.3
Sulfuric acid	–114.6
Ethanoic acid	–55.2

Explain the $\Delta H_r^\ominus$ values for the different acids above. [2]

[Turn over

(b) Similar to silver halides, silver carbonate, Ag_2CO_3, is a sparingly soluble salt which is used in the production of microelectronics.

(i) Write an equation to represent the enthalpy change of solution of silver carbonate. [1]

Many thermodynamic properties, such as entropy, are temperature dependent. When temperature changes, the entropy of a species varies according to the following equation,

$$\Delta S = S_{T2} - S_{T1} = C_p \ln \frac{T_2}{T_1}$$

where ΔS is the difference in entropy under temperatures T_2 and T_1;

C_p is the molar heat capacity of the species; and

T_2 and T_1 are temperatures in Kelvin.

The entropies of various species at 398 K, S_{398}, are shown below.

Species	Ag_2CO_3(s)	Ag^+(aq)	CO_3^{2-}(aq)
S_{398} / J K^{-1} mol^{-1}	+199.9	Y	+100.7

(ii) The entropy of Ag^+(aq) at 298 K = 72.7 J mol^{-1} K^{-1}.

Given the molar heat capacity, C_p, of Ag^+(aq) = 35.0 J mol^{-1} K^{-1}, calculate Y, the entropy of Ag^+(aq) at 398 K. [1]

(iii) Hence, calculate the entropy change of solution of silver carbonate at 398 K. [1]

(iv) Assuming the enthalpy change of solution of silver carbonate is a constant value of +41.8 kJ mol^{-1}, calculate the Gibbs free energy change of solution of silver carbonate at 398 K. [1]

(v) The standard Gibbs free energy change of solution of silver carbonate is +44.1 kJ mol^{-1}.

Comment on the effect of increasing temperature on the solubility of silver carbonate. [2]

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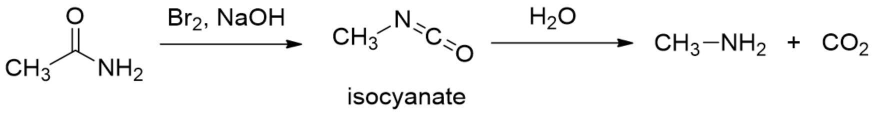
(c) Acids and bases are often used in organic reactions, either as catalysts or to provide an acidic or basic medium.

The Hofmann Degradation reaction is one such reaction which uses an alkaline solution of aqueous bromine to convert an unsubstituted amide to a primary amine, with one less carbon atom.

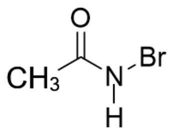
The reaction goes through the formation of an isocyanate intermediate, followed by elimination of carbon dioxide gas, as illustrated using ethanamide.



To form the isocyanate, the ethanamide first undergoes a 2-step reaction described below.

Step 1: The OH^- base abstracts an acidic N-H proton from the amide, yielding an anion.

Step 2: The anion reacts with bromine to form an *N*-bromoethanamide and a bromide anion.



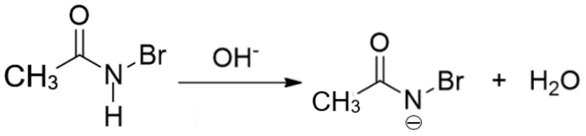
N-bromoethanamide

(i) Suggest why the N-H proton on the ethanamide is acidic. [1]

(ii) Starting with ethanamide, illustrate the 2-step mechanism above to form *N*-bromoethanamide, using appropriate curly arrows to show the movement of electrons.

Show clearly any partial charges and lone pair of electrons on each species. [2]

(iii) The *N*-bromoethanamide produced in Step 2, reacts with more OH^- to form a bromoethanamide anion, which rearranges to form the isocyanate intermediate.



With reference to the strength of the conjugate acid-base pairs, explain why OH^- instead of Br^- ions abstract the acidic N-H proton on the *N*-bromoethanamide. [1]

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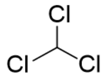
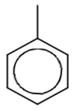
(d) In one experiment, *N*-bromoethanamide is contaminated with bromide leftover from Step 2, in an aqueous solution. A chemist wishes to obtain pure solid *N*-bromoethanamide from the mixture.

You are provided with two solvents below. One of the solvents can be used to extract *N*-bromoethanamide from the impure mixture.

Solvent	Density / g cm^{-3}	Boiling point / °C
 chloroform	1.49	61.2
 toluene	0.87	110.6

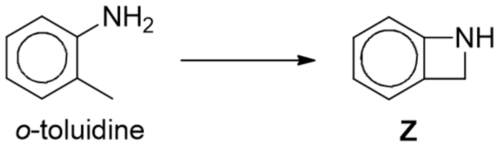
(i) Suggest a suitable solvent to extract *N*-bromoethanamide from the impure mixture and explain your choice. [1]

(ii) Hence, using information from the table above, plan an experiment to purify *N*-bromoethanamide from the impure mixture, using the solvent identified in **(d)(i)**.

Your plan should include details of:

- how *N*-bromoethanamide is obtained in its dry solid form;
- suitable apparatus used; and
- how the purity of the product is determined. [3]

(iii) Starting from *o*-toluidine, suggest a synthesis route to produce **Z**, in the absence of UV light. Show clearly the reagent and conditions for each step as well as the structures of intermediates. [3]



[Total: 22]

[Turn over

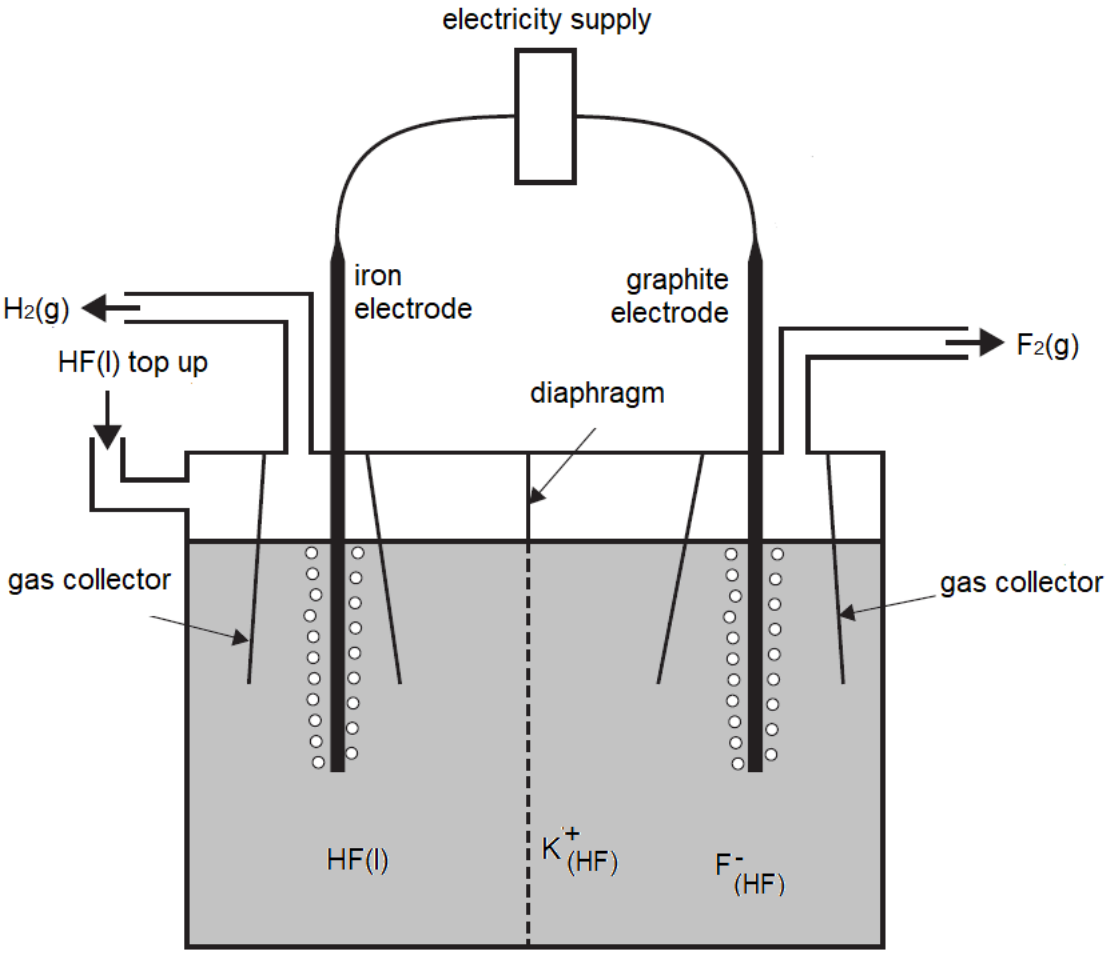
Section B

Answer **one** question from this section.

4 **(a)** Fluorine gas is the most reactive of all non-metals. It can be produced by the electrolysis of liquid hydrogen fluoride using the following set-up.

$$2HF(l) \rightarrow H_2(g) + F_2(g)$$

Potassium fluoride is added to increase electrical conductivity and can be dissolved in hydrogen fluoride.



(i) Suggest which of the electrode is the cathode and state its polarity. [1]

(ii) Write an equation for the reaction occurring at the anode. [1]

(iii) Suggest how a diaphragm was used to ensure the safe operation of the cell. [1]

(iv) A student considered using iron for both the electrodes but decided against it. Suggest and explain if you agree with his decision using relevant data from the Data Booklet. [2]

(v) If some water was added to the above set-up, a colourless triatomic gas was formed at the anode instead of fluorine.

Given that the M_r of the gas is 54, suggest its identity. [1]

(vi) Calculate the time needed to produce 1 dm^3 of fluorine gas using the above set-up where the current was 2.5 A, given that the temperature and pressure in the laboratory was 30 ^{o}C and 101 kPa. [2]

(b) The halogens are oxidising agents.

State and explain the trend in their oxidising ability down the group. [2]

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(c) When a Group 2 metal nitrate is heated strongly, it evolves oxygen and nitrogen dioxide, leaving the metal oxide, **M**O (**M** = Group 2 metal).

(i) Write a balanced equation for this reaction. [1]

(ii) When a particular Group 2 metal nitrate was heated in this way until no further change occurred, it lost 65.8% of its mass. Calculate the A_r of the metal and hence identify it. [2]

(iii) Group 2 nitrates decompose in a similar manner to Group 2 carbonates.

Describe and explain how the thermal stabilities of the Group 2 nitrates vary down the group. [3]

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(d) **(i)** Explain why the melting point of magnesium chloride is lower than that of aluminium oxide. [2]

(ii) State whether:

- $MgSO_4$ or $BaSO_4$ would have the more exothermic lattice energy and
- Mg^{2+} or Ba^{2+} would have the more exothermic enthalpy change of hydration.

Hence, suggest why the solubility of $MgSO_4$ is higher compared to that of $BaSO_4$. [2]

[Total: 20]

5 Heartburn occurs when an excess amount of acid is produced in the stomach, leading to pain. Antacids are substances used to relieve heartburn. A common antacid used is magnesium hydroxide. Although antacids are generally safe, high antacid level in the blood may cause toxicity.

(a) 2 g of solid magnesium hydroxide is shaken in 250 cm^3 of water to reach equilibrium at 25 °C and then filtered. The mass of the residue is 1.998 g.

(i) Write an expression for the solubility product, K_{sp}, of magnesium hydroxide, stating its units. [1]

(ii) Calculate the solubility product of magnesium hydroxide. [2]

(iii) Calculate the pH of the filtrate. [1]

(iv) 2 g of solid magnesium hydroxide is shaken in 250 cm^3 of 0.1 mol dm^{-3} magnesium nitrate to reach equilibrium at 25 °C. Calculate the pH of the resulting solution. [1]

(v) Explain the difference between your calculated values in **(a)(iii)** and **(a)(iv)**. [2]

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(b) **(i)** State how the reactivity of Mg and Ca as reducing agents is different, and relate this difference to relevant $E^\ominus$ values. [2]

(ii) Apart from the basic nature of magnesium hydroxide, suggest another reason why magnesium hydroxide is suitable for the role as an antacid. [1]

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(c) Fluorine gas deviates from an ideal gas and the following equation proposed by J. D. van der Waals can account for the differences.

$$\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$$

where P: actual pressure
V: volume of the container
T: temperature
n: amount of gas
R: molar gas constant
a and *b*: van der Waals constants

The values of *a* and *b* account for the deviation from ideality for a real gas and are dependent on certain molecular properties of the gas.

The values of *a* and *b* for fluorine and the other halogens are given in table 5.1 below.

Table 5.1

Gas	*a* / Pa m^6 mol^{-2}	*b* / m^3 mol^{-1}
Fluorine	0.117	2.90×10^{-5}
Chlorine	0.634	5.42×10^{-5}
Bromine	0.975	5.91×10^{-5}

(i) For each of the constants a and b, suggest a molecular property of the gas that will directly affect its value. [2]

(ii) Explain the differences in the values of a for the halogens. [2]

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(d) Halogens form many interhalogen compounds. One such compound is bromine monochloride, BrC*l*, which have similar properties to the halogens.

Suggest an equation for the reaction between BrC*l* and KI. [1]

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(e) Halogens are also found in organic compounds which can be used to synthesise amino acids.

Table 5.2 shows some naturally occurring α-amino acids found in the body. The isoelectric point is the pH at which an amino acid exists as a zwitterion.

Table 5.2

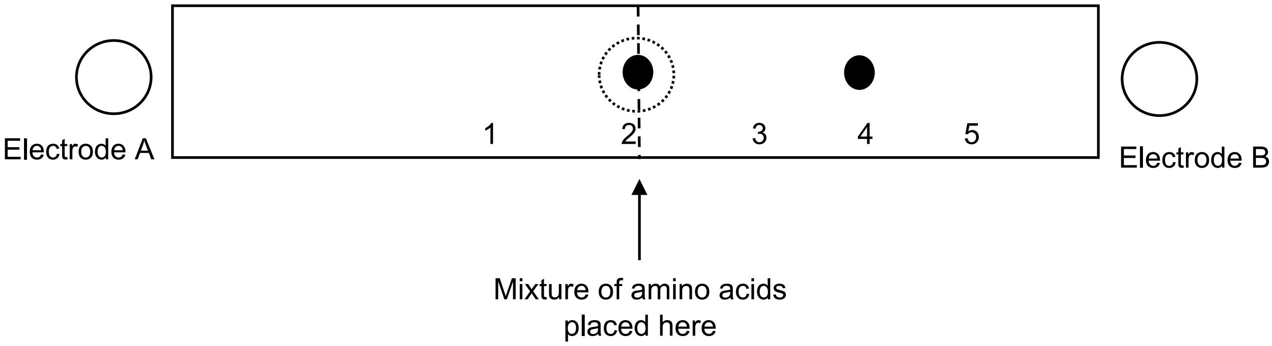
Amino acid	Abbreviation	R group	M_r	Isoelectric point
Serine	Ser	$-CH_2OH$	105	5.68
Asparagine	Asn	$-CH_2CONH_2$	132	5.43
Lysine	Lys	$-(CH_2)_4NH_2$	146	9.74

(i) Draw the dipeptide Asn-Ser, showing the peptide bonds in displayed formula. [1]

Electrophoresis is a technique used to separate mixtures of amino acids. Ions of higher charge to mass ratio will migrate towards the electrode of opposite charge at a faster rate.

A mixture of the three amino acids in table 5.2 were placed at position 2 and subjected to electrophoresis in a buffer at pH 9.74.

The positions of two of the amino acids, serine and lysine, relative to the electrodes were as follows:



(ii) Draw the structure of the species at positions 2 and 4. [2]

(iii) State the number which correspond to the likely position of asparagine and explain your answer. [2]

[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.

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