YISHUN INNOVA JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE NAME			
CG		INDEX NO	

CHEMISTRY 9729/03

Paper 3 Free Response **12 September 2022**

Candidates answer on the Question Paper. **2 hours**
Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, class and index number on all the work you hand in.
Write in dark blue or black pen on both sides of the paper.
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. 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** the 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		
Section A		
1		**/ 17**
2		**/ 18**
3		**/ 25**
Section B		
4 or 5		**/ 20**
Penalty	**units**	**significant figures**
Overall		**/ 80**

This document consists of **31** printed pages and **1** blank page

Section A

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

1 (a) Describe and explain the trend in the thermal stability of the hydrogen halides, HC*l*, HBr and HI. Include an equation for the thermal decomposition reaction in your answer. [3]

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(b) Alkanes are generally considered to be unreactive compounds, showing an inertness to common reagents such as NaOH, H_2SO_4, and $K_2Cr_2O_7$.

(i) Suggest a reason why these reagents do not react with an alkane such as propane. [1]

Propane can be converted into 2-chloropropane when it reacts with chlorine in ultraviolet (UV) light.

(ii) Describe the mechanism of the reaction between propane and chlorine in UV light. [3]

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(c) **(i)** Define the term *lattice energy*. [1]

(ii) Use the data in Table 1.1, together with data from the *Data Booklet*, to calculate a value for the lattice energy of silver iodide, AgI(s). Show your working.

Table 1.1

	value / kJ mol^{-1}
electron affinity of iodine, $I(g) + e^- \rightarrow I^-(g)$	−295
enthalpy change of sublimation of iodine molecules, $I_2(s) \rightarrow I_2(g)$	+62
standard enthalpy change of atomisation of Ag(s)	+285
standard enthalpy change of formation of AgI(s)	−62

[3]

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(d) Air bags in car inflate rapidly during an accident to protect the front passengers. The air bag contains sodium azide, NaN_3, silicon dioxide, SiO_2, and potassium nitrate, KNO_3.

On impact, three reactions take place.

The sodium azide first decomposes to sodium and nitrogen.

$$2NaN_3(s) \rightarrow 2Na(s) + 3N_2(g)$$

The nitrogen formed inflates the air bag while the sodium formed reacts with potassium nitrate to form sodium oxide, potassium oxide and additional nitrogen gas, which may be used to fill the air bag.

Potassium oxide and sodium oxide then react with silicon dioxide to form harmless metal silicates.

$$K_2O(s) + Na_2O(s) + SiO_2(s) \rightarrow K_2Na_2SiO_4(s)$$

(i) Write an equation, with state symbols, for the reaction between sodium and potassium nitrate. [1]

(ii) Calculate the mass of sodium azide needed to inflate an air bag of capacity 60 dm^3 at room temperature and pressure. [2]

(iii) To determine the amount of sodium azide in an impure sample, the azide present is first reacted with excess iodine.

$$2N_3^- + I_2 \rightarrow 3N_2 + 2I^-$$

The amount of unreacted iodine is then titrated with a standard solution of sodium thiosulfate.

$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$$

0.120 g of an impure sample of sodium azide was dissolved in water. The mixture was reacted with 25.0 cm^3 of 0.050 mol dm^{-3} of aqueous iodine. The excess iodine was found to require 23.10 cm^3 of 0.040 mol dm^{-3} aqueous sodium thiosulfate for reaction. Calculate the percentage purity of sodium azide in the sample. [3]

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[Total: 17]

2 (a) Ammonia is manufactured by the following reaction.

equation 2.1 $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

The value of the equilibrium constant, K_p, measured at two different temperatures is shown in Table 2.1.

Table 2.1

temperature / K	K_p / atm^{-2}
600	1.33×10^{-2}
750	1.33×10^{-4}

(i) Write the expression for the equilibrium constant, K_p, for this reaction. [1]

(ii) A plant is designed to convert, at equilibrium, 50% of the reactants into ammonia. Assuming that the reactants are a mixture of N_2 and H_2 in a 1 : 3 ratio by volume, calculate the total equilibrium pressure necessary to bring about a 50% conversion at

- 600 K, and
- 750 K. [2]

(iii) Discuss the relative advantage and disadvantage of using plants designed to run at 600 K instead of 750 K. [2]

Theory shows that K_p varies with temperature according to the equation below.

$$\log_{10} \frac{K_p \text{ (at temperature } T_1)}{K_p \text{ (at temperature } T_2)} = \frac{-\Delta H}{2.30R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

where: T_1 and T_2 are the temperatures in Kelvins,

ΔH is the enthalpy change of the reaction,

R is the molar gas constant.

(iv) Use the data in Table 2.1, together with data from the *Data Booklet*, and to calculate the enthalpy change, ΔH, in kJ mol^{-1}, for the reaction in equation 2.1. [1]

(v) The standard enthalpy change of formation of ammonia is –46 kJ mol^{-1}, given that ΔH for the reaction in equation 2.1 to be –92 kJ mol^{-1}.

Suggest one reason why this differs from the value calculated in **(iv)**. [1]

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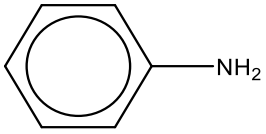
(b) The K_b values of three bases, at 25 ^oC, are shown in Table 2.2.

Table 2.2

base	formula	K_b / mol dm^{-3}
ammonia	NH_3	1.8×10^{-5}
ethylamine	$CH_3CH_2NH_2$	4.5×10^{-4}
phenylamine		7.4×10^{-10}

(i) Calculate the pH of 0.25 mol dm^{-3} solution of ethylamine. [2]

(ii) Explain the relative magnitudes of the K_b values in Table 2.2. [2]

(iii) Explain why amides, $RCONH_2$, are neutral, rather than basic. [1]

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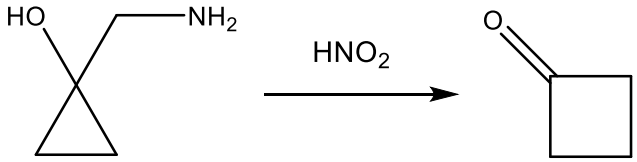
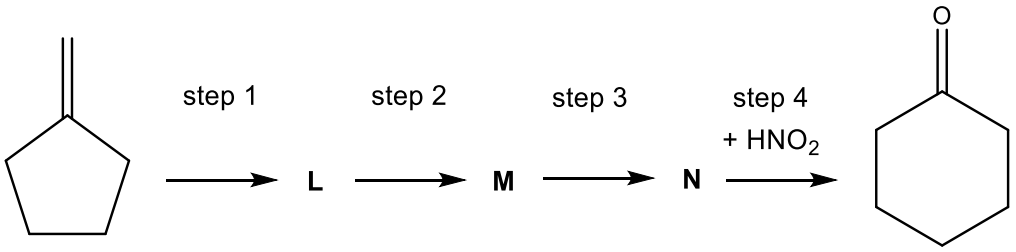
(c) Nitrous acid, HNO_2, can be used to react with aminoalcohol to form an enlarged cycloketone via the Tiffeneau-Demjanov Rearrangement, as shown below.



cyclic aminoalcohol cycloketone

Methylenecyclopentane can be used to synthesise cyclohexanone by the four-step route shown in Fig. 2.1.



methylenecyclopentane cyclohexanone

Fig. 2.1

State the reagents and conditions required for step 1, 2 and 3 and suggest structures for the organic compounds **L**, **M** and **N**. [6]

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[Total: 18]

3 (a) (i) Explain what is meant by the term *transition element*. [1]

(ii) State the electronic configuration of the Cu atom and Ni^{2+} ion. [2]

(iii) Explain why transition element complexes are usually coloured. [3]

(b) **(i)** Draw a fully labelled diagram of the experimental set-up used to measure the standard electrode potential of the $Ni^{2+}(aq)/Ni(s)$ half-cell. Indicate clearly the positive and negative electrodes. [3]

Another cell composing of a standard $Ni^{2+}(aq)/Ni$ half-cell and a standard $Cr_2O_7^{2-}(aq)/Cr^{3+}(aq)$ half-cell was set up.

(ii) Calculate $\Delta G^{\ominus}$, in kJ mol^{-1}, for the reaction that occurs [2]

(iii) Predict how the voltage of this cell would change, if at all, if the pH of the $Cr_2O_7^{2-}(aq)/Cr^{3+}(aq)$ half-cell was increased. Explain your answer. [1]

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(c) Table 3.1 give data about some physical properties of the elements calcium, iron and copper.

Table 3.1

property	calcium	iron	copper
relative atomic mass	40.1	55.8	63.5
atomic radius (metallic) / nm	0.197	0.126	0.128
ionic radius (2+) / nm	0.099	0.076	0.069
melting point / K	1112	1808	1358
density / g cm^{-3}	1.54	7.86	8.92
electrical conductivity / × 10^6 S cm^{-1}	0.298	0.100	0.596

(i) Explain why the atomic radii of iron and copper are similar to each other. [2]

(ii) Explain why the densities of iron and copper are significantly greater than that of calcium using relevant data from Table 3.1. (No calculations are required.) [2]

When solid copper(II) carbonate is heated, it behaves in a similar way to the Group 2 carbonates.

(iii) Write an equation, with state symbols, for the decomposition of the carbonate ion, CO_3^{2-}. [1]

(iv) Copper(II) carbonate decomposes at 300 °C while calcium carbonate decomposes at 830 °C.

Suggest an explanation for the difference in the temperature at which the two metal carbonates will decompose. [2]

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(d) Describe and explain what you would see when $NH_3(aq)$ is added slowly to a solution containing $Cu^{2+}(aq)$ ions, until the $NH_3(aq)$ is in excess.

Write equations for any reactions that occur. [4]

(e) An alkaline solution of complexed $Cu^{2+}(aq)$ is used in organic chemistry to test for a particular functional group.

Draw the displayed formulae of **one** compound with the molecular formula C_4H_8O that would show a positive result in this test, and the displayed formulae of **one** compound with the same molecular formula that would not. Label your structures clearly. [2]

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[Total: 25]

Section B

Answer **one** question in this section.

4 (a) Table 4.1 shows the melting points of these four elements found in Period 3 of the Periodic Table.

Table 4.1

element	melting point / ^{o}C
sodium	97
silicon	1410
sulfur	112
chlorine	−100

These four elements differ greatly in their melting points. Explain this variation. [4]

(b) Beams of charged particles are deflected by an electric field.

(i) State two ways in which the behaviour of electrons in an electric field differs from that of protons. [1]

(ii) In a particular experimental set-up, protons are deflected through an angle of $+15^{o}$.

Assuming an identical set of experimental conditions, by what angles will the following particles be deflected?

- $^{2}H^{-}$
- $^{3}He^{2+}$ [2]

(c) (i) State three basic assumptions of the kinetic theory as applied to an ideal gas. [2]

(ii) Diving tanks store a mixture of oxygen, nitrogen and helium gas at high pressures for deep-water diving for long periods of time.

When air bubbles are released underwater, they expand in size.
A 10 cm^3 bubble was released from a diver, 120 m below the water surface at a pressure of 1300 kPa and temperature of 10 °C.
It was estimated that pressure increases by 101 kPa with each 10 m depth.

Calculate the volume of the air bubble when it ascends towards the water surface by 60 m where the water temperature is 20 °C. [1]

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(d) Buttercups contain a poisonous cyclic compound called *protoanemonin*, $C_5H_4O_2$.

On catalytic hydrogenation, *protoanemonin* gives compound **A**, $C_5H_8O_2$. When **A** is heated with an acid, compound **B**, $C_5H_{10}O_3$, is formed. On standing, **B** slowly loses water and is converted back to **A** again.
Compound **B** gives a yellow precipitation with aqueous alkaline iodine and compound **C**, $C_4H_6O_4$, can be isolated.

Protoanemonin is an unstable oil which when treated with an acid or alkali, it is converted to compound **D**, $C_5H_6O_3$. Unlike *protoanemonin*, **D** effervesces with aqueous sodium hydrogencarbonate and gives a precipitate with 2,4-dinitrophenylhydrazine but does not react with Tollens' reagent.

Suggest possible structures for **A**, **B**, **C**, **D**, and *protoanemonin*. For each reaction, state the *type of reaction* described and explain what the information tells you about the functional group present in each compound. [10]

[Total: 20]

5 (a) (i) Describe the reactions, if any, of the chlorides NaC*l*, A*l*C*l*$_3$ and SiC*l*$_4$ with water. Write equations for all reactions that occur, and suggest the pH of the resulting solutions. [3]

(ii) Aluminium oxide is amphoteric.

Write equations to illustrate the acid-basic behaviour of aluminium oxide. [2]

(b) Hydrogen selenide can act as a weak acid.

$$H_2Se(aq) \rightleftharpoons H^+(aq) + HSe^-(aq)$$

NaHSe is a weak base. The pH of a solution of 0.10 mol dm^{-3} NaHSe is 8.45.

Calculate the pK_a of H_2Se. [3]

(c) The Gattermann–Koch reaction is used to produce benzaldehyde as shown in Fig. 5.1.

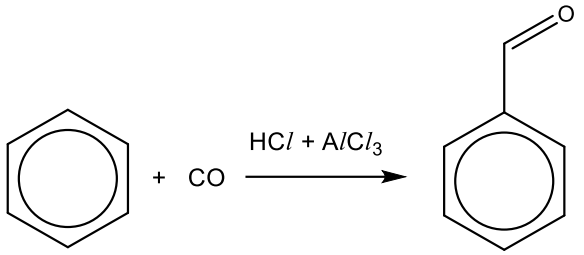

Fig. 5.1

(i) Name the *type of reaction* in the Gattermann-Koch reaction. [1]

Fig. 5.2 shows the synthesis of compound **U**, which involves the Gattermann-Koch reaction.

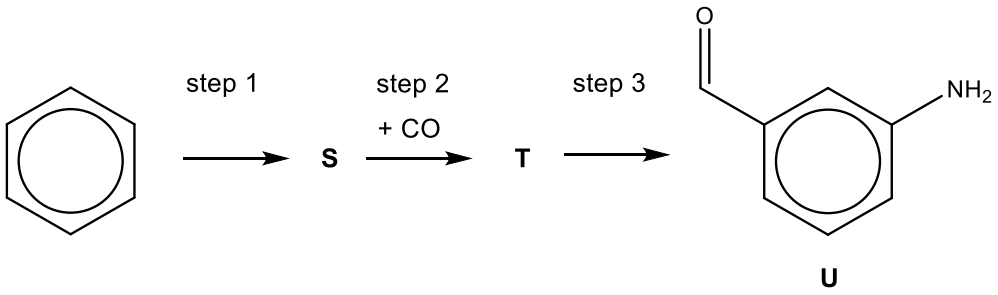

Fig. 5.2

(ii) Suggest the structures of the intermediate organic products **S** and **T**. [2]

(iii) Suggest the reagents and conditions for step 1 and step 3. [2]

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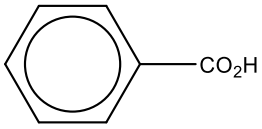
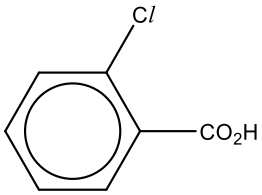
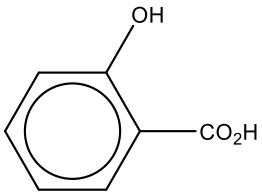
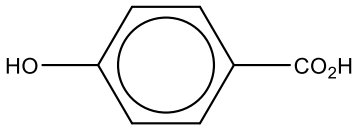
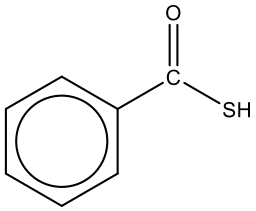
(d) Table 5.1 lists the pK_a values for some other weak acids.

Table 5.1

acid	formula	pK_a
benzoic acid		4.20
2-chlorobenzoic acid		2.89
2-hydroxybenzoic acid		2.97
4-hydroxybenzoic acid		4.54
thiobenzoic acid		3.61

(i) Explain the difference in the pK_a values between 2-chlorobenzoic acid and benzoic acid. [1]

(ii) Suggest a reason why the pK_a value of 2-hydroxybenzoic acid is so much less than the pK_a of 4-hydroxybenzoic acid. [1]

(iii) Thiobenzoic acid is related to benzoic acid by the replacement of one of the oxygen atoms with a sulfur atom.

Suggest a reason why the pK_a for thiobenzoic acid is lower than benzoic acid. [1]

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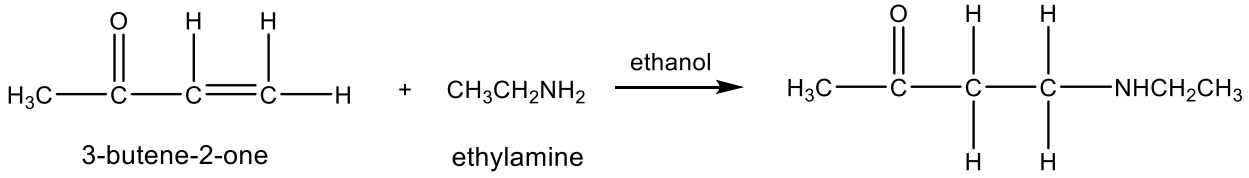
(e) Enones are ketones having a neighbouring C=C double. Enones undergoes a reaction called conjugate addition, a type of nucleophilic addition reaction, with a primary amine.

The reaction of 3-butene-2-one, an enone, with ethylamine via conjugate addition is as shown.

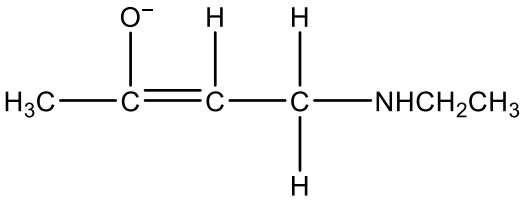


3-butene-2-one + ethylamine → 4-N-ethylamino-2-butanone

In this reaction, an amine is added directly to an alkene carbon.

The reaction takes place in 3 steps.

step 1 The amine attacks the terminal alkene carbon to form an enolate ion intermediate.



enolate ion

step 2 The intermediate will undergo rearrangement to form back the ketone and a carbanion.

step 3 The carbanion is then protonated to form the product.

(i) Suggest the mechanism for the conjugate addition reaction between 3-butene-2-one and ethylamine to form 4-N-ethylamino-2-butanone.

Show all charges and relevant lone pairs and show the movement of electron pairs by using curly arrows. [3]

(ii) In the absence of the carbonyl group, –C=O, there will be no reaction between butene and ethylamine.

Suggest why this is so. [1]

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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.

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