RIVER VALLEY HIGH SCHOOL
JC 2 PRELIMINARY EXAMINATION

CANDIDATE NAME									
CLASS	2	2	J						
CENTRE NUMBER	S					INDEX NUMBER			

H2 CHEMISTRY 9729/03

Paper 3 Free Response **20 September 2023**

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your Centre number, index number, class and name on all the work that 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.
DO **NOT** WRITE IN ANY BARCODES.

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. **Circle** the question number of the question you attempted.

The use of an approved scientific calculator is expected, where appropriate.
A Data Booklet is provided.

The number of marks is given in brackets [ ] at the end of each question or part question.

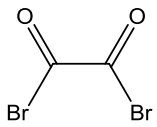
For Examiner's Use								
Question Number	**1**	**2**	**3**	**4**	**5**	**units**	**s.f.**	**Total**
Marks	/19	/24	/17	/20	/20			/80

This document consists of **28** printed pages.

Section A

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

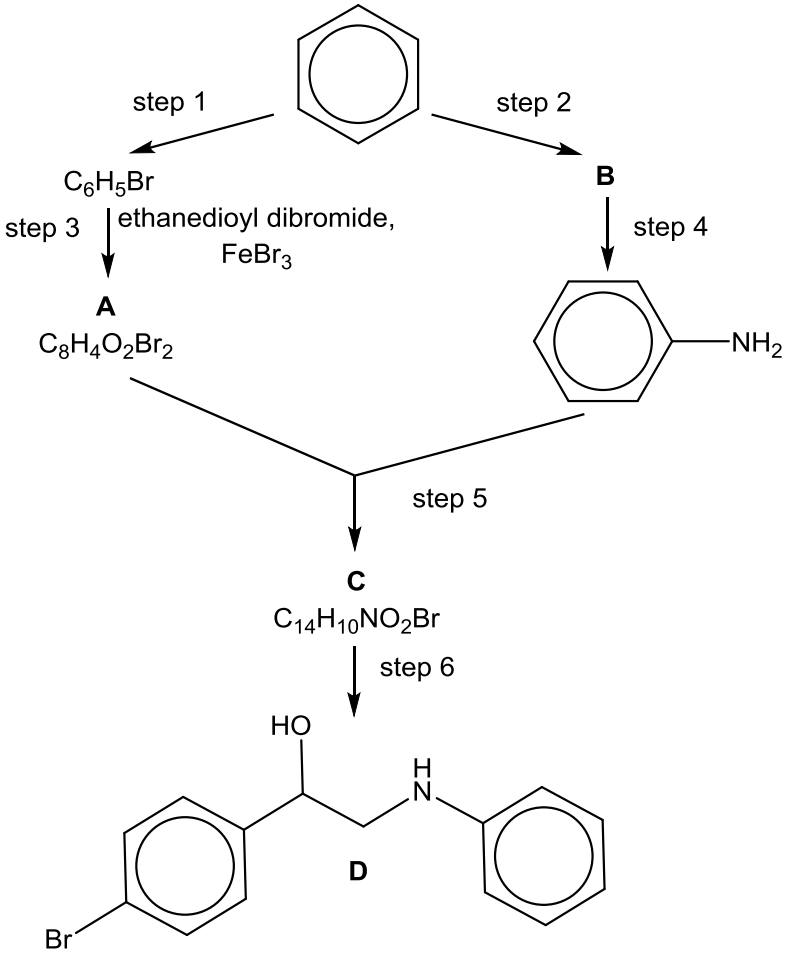
1 (a) Ethanedioyl dibromide, BrCOCOBr, is a useful reagent in organic synthesis.



ethanedioyl dibromide

Ethanedioyl dibromide is used in the following synthesis of compound **D**.

It reacted in a 1:1 stoichiometric ratio with C_6H_5Br in step 3.



(i) Suggest the identities of **A**, **B** and **C**. [3]

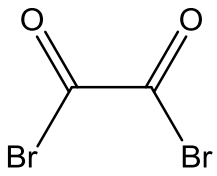
(ii) State the reagents and conditions for steps 2, 4 and 6. [3]

(iii) If the amount of ethanedioyl dibromide used in step 3 is decreased, another compound is formed. The compound has the molecular formula $C_{14}H_8O_2Br_2$.

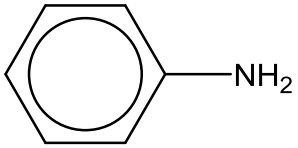
Suggest the structure of this compound. [1]

(iv) A student has 3 unlabelled bottles, each containing a chemical found in the above synthesis pathway.

These chemicals are as shown:



C_6H_5Br



Suggest 2 simple chemical tests that will allow the student to identify the chemical in each bottle, stating clearly the observations in each test. [4]

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(b) Like ethanedioyl dibromide, Period 3 chlorides such as $MgCl_2$ and PCl_5 are halogen–containing compounds.

Write equations for the reactions of these two chlorides with water. In each case, state the pH of the resulting solution. [4]

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(c) Phenylamine, $C_6H_5NH_2$, is a product in step 4.

Another nitrogen–containing compound, $(CH_3)_2N_2H_2$, known as UDMH, is used in *Aerozine 50*.

Aerozine 50 is a 50/50 mix of hydrazine, N_2H_4, and UDMH. It is used as a rocket fuel, typically mixed with dinitrogen tetroxide, N_2O_4, as the oxidising agent.

The equation for the reaction of the UDMH with dinitrogen tetroxide is given in equation 1 and relevant thermodynamic data under standard conditions is in Table 1.1.

Equation 1 $(CH_3)_2N_2H_2(l) + 2N_2O_4(l) \rightarrow 2CO_2(g) + 4H_2O(g) + 3N_2(g)$

Table 1.1

Substance	$\Delta H_f^\ominus$ / kJ mol^{-1}	$S^\ominus$ / J K^{-1} mol^{-1}
$(CH_3)_2N_2H_2(l)$	+83.3	304.7
$N_2O_4(l)$	+9.1	304.4
$CO_2(g)$	–393.5	213.8
$H_2O(g)$	–241.8	188.8
$N_2(g)$	0.0	191.6

(i) Calculate the enthalpy change, $\Delta H_{r}^{\ominus}$, for the reaction in equation 1. [1]

(ii) The entropy change, $\Delta S_{r}^{\ominus}$, for the reaction in equation 1 is a large and positive value.

Explain, without calculation, why this entropy change has such a large, positive value. [1]

(iii) Calculate the free energy change, $\Delta G_{r}^{\ominus}$, in kJ mol^{-1}, at 298 K for the reaction in equation 1.

$\Delta S_{r}^{\ominus}$ can be used in the same manner as $\Delta H_{r}^{\ominus}$ in a Hess' law cycle. [2]

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[Total: 19]

2 (a) The solubility product, K_{sp} of a sparingly soluble salt can be determined by measuring the cell potential.

An electrochemical cell comprising of the standard Ni^{2+}/Ni half-cell and a Ag^{+}/Ag half-cell where a saturated solution of silver dichromate(VI) is used as the electrolyte is set up. The silver ions oxidise nickel metal to nickel(II) ions.

The electrochemical cell is not under standard conditions, as the $[Ag^{+}]$ in a saturated solution of $Ag_2Cr_2O_7$ is significantly less than 1.0 mol dm^{-3}. The E_{cell} was measured at +0.924 V. The $E_{electrode}$ in the Ag^{+}/Ag half-cell is related to the $[Ag^{+}]$ by the following equation.

$$E_{electrode} = E^{\ominus}_{electrode} + 0.0592 \log [Ag^{+}]$$

(i) Write an ionic equation for the reaction in the electrochemical cell. [1]

(ii) Calculate the Gibbs free energy, ΔG, for the reaction, per mole of nickel(II) ions formed. [1]

(iii) Write an expression for the solubility product, K_{sp}, of silver dichromate(VI), $Ag_2Cr_2O_7$. [1]

(iv) Calculate the $E_{electrode}$ for the Ag^{+}/Ag electrode in this experiment. [1]

(v) Use your answer to **(iv)** to calculate the concentration of silver ions in the saturated solution, and hence, the K_{sp} of $Ag_2Cr_2O_7$.

If you were unable to obtain an answer in **(iv)**, use $E_{electrode}$ = +0.50 V. [2]

(vi) Determine the concentration of silver ions when a silver electrode is immersed in 0.5 mol dm^{-3} of $K_2Cr_2O_7$ containing some $Ag_2Cr_2O_7$ precipitate. [1]

(vii) Given that $NiCO_3$ is sparingly soluble, predict and explain how the E_{cell} in **(a)** would change, if at all, when a few cm^3 of concentrated Na_2CO_3(aq) were added to the beaker containing Ni^{2+}/ Ni half-cell. [2]

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(b) (i) Define, using sodium dichromate(VI) as an example, what is meant by the term *lattice energy*. [1]

(ii) Suggest and explain the difference in lattice energies of sodium dichromate(VI), $Na_2Cr_2O_7$, and sodium chromate(VI), Na_2CrO_4. [2]

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(c) Sodium dichromate, $Na_2Cr_2O_7$, is generated on a large scale from ores containing chromium(III) oxides. The ore is typically fused with sodium carbonate in the presence of oxygen, as described in equation 1.

Equation 1 $2Cr_2O_3(s) + 4Na_2CO_3(aq) + 3O_2(g) \rightarrow 4Na_2CrO_4(aq) + 4CO_2(g)$

$\Delta H_r = -99.2 \text{ kJ mol}^{-1}$

Further treatments are carried out and the enthalpy changes of reactions are shown in Table 2.1.

Table 2.1

	ΔH_r / kJ mol^{-1}
$2CrO_3(s) \rightarrow Cr_2O_3(s) + \frac{3}{2}O_2(g)$	*y*
$Na_2CrO_4(aq) + H_2SO_4(aq) \rightarrow CrO_3(s) + Na_2SO_4(aq) + H_2O(l)$	−109.6
$Na_2CO_3(aq) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + CO_2(g) + H_2O(l)$	−122.4

(i) Draw the 'dot-and-cross' diagram of chromate(VI) ion, CrO_4^{2-}.

Assume that chromium behaves as a Group 16 element. [1]

(ii) Use the data above to calculate *y*.

Show your working. [3]

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(d) (i) Ammonium dichromate decomposes to give nitrogen gas, water vapour and chromium(III) oxide.

$$(NH_4)_2Cr_2O_7 \rightarrow Cr_2O_3(s) + N_2(g) + 4H_2O(g)$$

When 20.0 g of $(NH_4)_2Cr_2O_7$ is ignited, it inflates an empty airbag to a volume of 5.00 dm^3. Calculate the final pressure in the airbag, at a temperature of 225 °C. [1]

(ii) Under what conditions of temperature and pressure is the behaviour of real gases most nearly ideal? Explain your answer. [3]

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(e) Atmospheric NO_2 is involved in the oxidation of atmospheric sulfur dioxide through the formation of nitrogen oxide, NO, intermediate.

With the aid of equations and a labelled Boltzmann distribution diagram, explain how the oxidation occurs. [4]

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[Total: 24]

3 (a) Compound **A**, $C_9H_8O_3$ (molar mass: 164 g mol^{-1}) is found in plants, fruits and vegetables. It contains three different functional groups, and it exhibits stereoisomerism.

Compound **A** decolourises bromine water and gives compound **B** as the major product. Compound **B** is a white precipitate, and it has a molar mass 497.6 g mol^{-1}.

When treated with PCl_5, compound **A** gives compound **C**, $C_9H_7O_2Cl$.

An acid anhydride can be used to convert a hydroxy compound into an ester and carboxylic acid, as shown in Fig. 3.1.

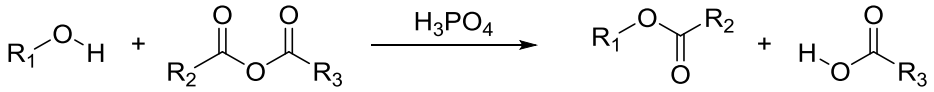

Fig. 3.1

Compound **A** reacts with a symmetrical acid anhydride to give two compounds, **D**, $C_{11}H_{10}O_4$, and $C_2H_4O_2$ only.

Compound **A** gives violet colouration with neutral iron(III) chloride.

When treated with hot acidified $KMnO_4$, compound **D** give only two organic products. The organic product with a larger molar mass is compound **E**.

Suggest possible structures for **A, B, C, D** and **E**, explaining the reactions described. [10]

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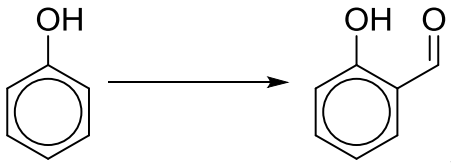
(b) The Reimer-Tiemann reaction is a reaction that forms salicylaldehyde from phenol.



salicylaldehyde

(i) Draw a labelled diagram to show the hybridised orbitals of the carbonyl carbon atom in salicylaldehye.

(ii) State the oxidation number of carbonyl carbon in salicylaldehye.

(iii) The oxidation of salicylaldehyde can be carried out by addition of acidified potassium manganate under suitable conditions.

Construct the ion-electron equation for the oxidation of salicylaldehyde, hence construct the balanced redox equation for this reaction.

$$MnO_4^{\#} + 8H^+ + 5e^{\#} = Mn^{2+} + 4H_2O$$

[4]

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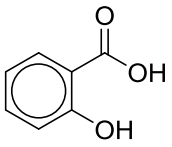
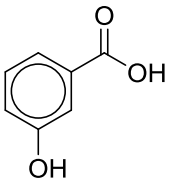
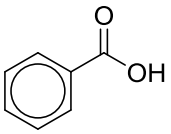
(c) The Reimer-Tiemann reaction can be modified to form salicylic acid from phenol.

State and explain, with the aid of an appropriate diagram, the relative acidities of the three acids.

Name	salicylic acid	3-hydroxybenzoic acid	benzoic acid
Structure			
pK_{a1}	2.98	4.08	4.19

[3]

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[Total: 17]

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Section B

Answer **one** question from this section.

4 The halogens and their compounds are useful laboratory reagents.

(a) **(i)** Describe the trends in the volatility and colour of the halogens from F_2 to I_2. [3]

(ii) Describe the reactivity of hydrogen with fluorine, chlorine and bromine. [2]

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(b) Pseudohalogens are polyatomic analogues of halogens, whose chemistry resembles that of the true halogens. Thiocyanogen, $(SCN)_2$, is one example of a pseudohalogen.

Thiocyanogen reacts with water to form hydrogen cyanide, sulfuric acid and thiocyanic acid, HSCN.

(i) Given that the mole ratio of $(SCN)_2$ to H_2SO_4 is 3:1, write a balanced equation for the reaction of thiocyanogen with water. [1]

(ii) Thiocyanogen undergoes addition reactions with alkenes, very much like how true halogens, such as Cl_2 and Br_2, do.

A hydrocarbon, of relative molecular mass 68.0, does not exhibit any stereoisomerism. It undergoes an addition reaction with thiocyanogen that can form an achiral product of relative molecular mass of 300.4.

Draw the structual formulae of the hydrocarbon and the achiral product. [2]

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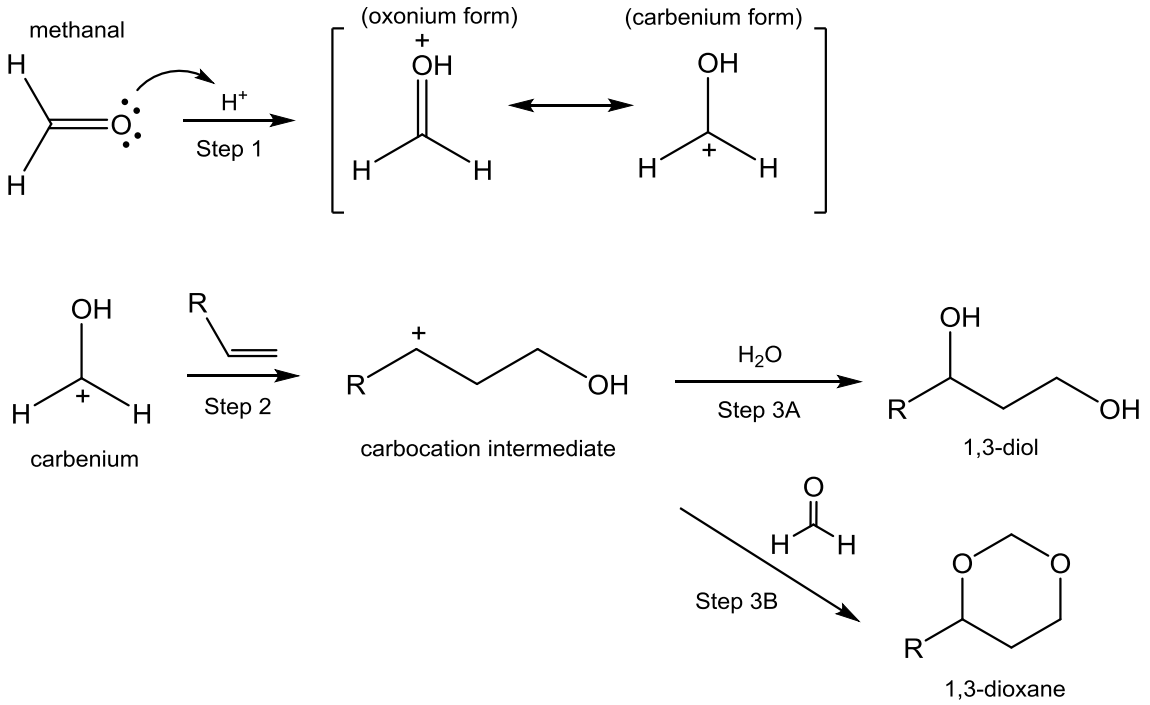
(c) The Prins reaction, discovered in 1919, is an acid-catalysed addition of aldehydes to alkenes. It is an important process that has been used extensively in the fragrance industry to synthesise flavour and fragrance ingredients.

Depending on the reaction conditions, different products can be generated. A schematic diagram displaying two possible reaction outcomes, with methanal as the starting aldehyde, is shown below.



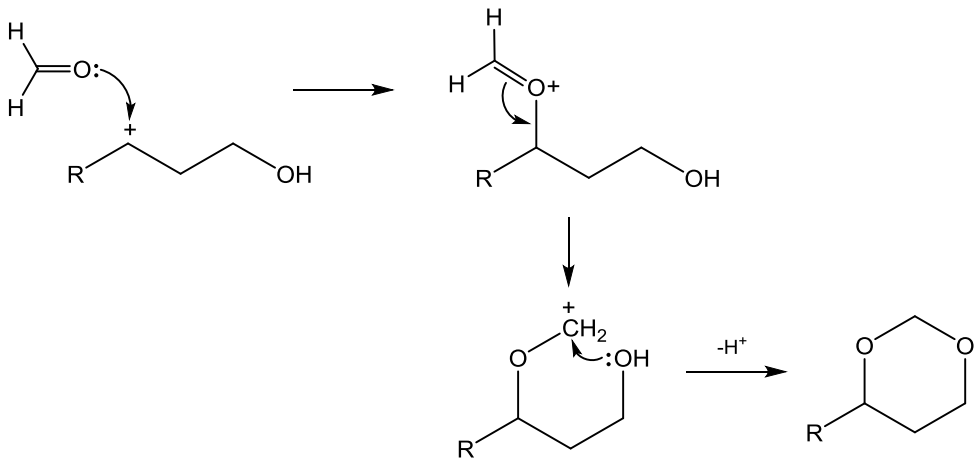
(i) State the type of reaction in Step 1. [1]

(ii) Name and describe the mechanism of the reaction of the carbenium ion with an alkene to form the diol, from Step 2 to Step 3A.

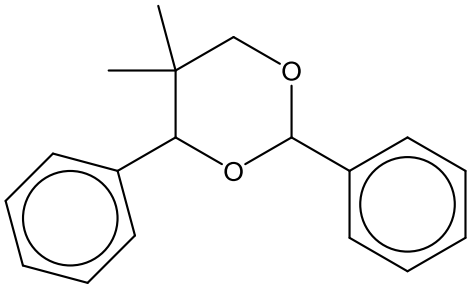
You may use RCH∃CH_2 as the alkene in reference. [3]

(iii) In the presence of an *excess* of the starting aldehyde, methanal, the carbocation intermediate undergoes further reaction, i.e., Step 3B, to form 1,3-dioxane.

The mechanism of Step 3B is shown below.



Using the information given, identify the starting alkene and aldehyde that form dioxane **Y**.



dioxane **Y**

[2]

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(d) When solid ammonium chloride is decomposed, ammonia and hydrogen chloride are formed.

$$NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$$

The standard enthalpy change, $\Delta H^{\ominus}$, is +177 kJ mol^{-1} and the standard entropy change, $\Delta S^{\ominus}$, is +285 J mol^{-1} K^{-1}.

Using the information given,

- explain why the reaction will only occur at high temperatures,
- determine the minimum temperature at which the reaction will take place. [2]

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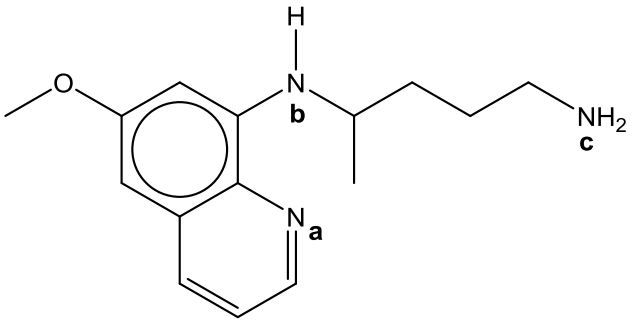
(e) Primaquine is an antimalaria drug used to prevent relapse of malaria infections.



primaquine

The hybridisation of the nitrogen atoms in ∃N_a# and #N_bH# are like that of the carbon atoms in benzene. The hybridisation of #$N_c H_2$ is like that of the carbon atoms in ethane.

Suggest and explain the relative basicities of the following pairs of nitrogen–containing groups:

- #N_bH# and #$N_c H_2$,
- ∃N_a# and #$N_c H_2$. [4]

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[Total: 20]

5 In a Periodic table, elements are arranged in order of increasing proton number.

Elements, such as carbon, nitrogen and chlorine, in Period 2 and 3 are common elements used in reactions.

(a) Describe and explain how the electrical conductivities varies across the third period of the Periodic Table from sodium to argon. [3]

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(b) The simplest chemical reactions are those that occur in the gas phase in a single step, such as the transfer of a chlorine atom from C*l*NO_2 to NO.

$$C\mathit{l}NO_2(g) + NO(g) = NO_2(g) + C\mathit{l}NO(g)$$

(i) An equimolar mixture of C*l*NO_2(g) and NO(g), at total initial pressure of 3.00 atm, is allowed to react in a closed vessel at 1000 K. When equilibrium is attained at the 5th minute, 38.0% of C*l*NO_2 is left in the vessel.

Write the K_p expression and hence calculate the value for the equilibrium constant, K_p, of this system. [2]

(ii) Hence, sketch 2 graphs on the same axes to show how the partial pressures of C*l*NO_2 and NO_2 change with time when

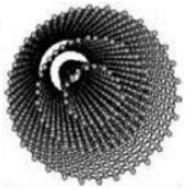
- the above gaseous system first reaches equilibrium at the 5th minute,
- more C*l*NO_2 gas was added into the vessel at the 10th minute and a new equilibrium is attained at the 15th minute,
- helium gas was added into the vessel at the 15th minute. [3]

(c) A carbon nanotube (CNT) is a tube made of graphene, which is a single layer of carbon atoms arranged in interconnecting hexagonal planar rings.

Carbon nanotubes are useful materials that increase the tensile strength of a material. Tensile strength is a measurement of the resistance of a material to break when pulled at both ends (under tension).

A single-walled carbon nanotubes behave like cylindrical graphene. Multi-walled carbon nanotubes consist of multiple–rolled layers of graphene.

Single-walled carbon nanotube



Multi-walled carbon nanotube

(i) Describe the structure and bonding of a carbon nanotube. [1]

(ii) Suggest whether a single-walled carbon nanotube or a multi-walled carbon nanotube has higher tensile strength. [1]

(iii) Carbon nanotubes can conduct electricity.

The carbon atom in graphene is sp^2 hybridised. Explain how carbon nanotubes can conduct electricity. [2]

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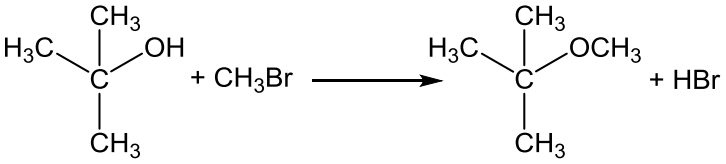
(d) The Williamson ether synthesis is an organic reaction which forms an ether from a halogenoalkane and alcohol in the presence of sodium hydride, NaH.

An example of the reaction is shown below.



In the reaction, sodium hydride first reacts with the alcohol.

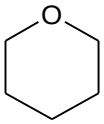
(i) State the purpose of NaH used in the Williamson ether synthesis. [1]

(ii) Phenol reacts with 1-bromopropane to give only one product.

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

(iii) Using the information given in **(d)**, suggest suitable reactants to synthesise each of the following ethers using Williamson ether synthesis.

(I) $CH_3CH_2OCH_2CH_3$

(II) 

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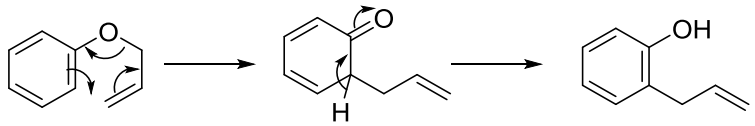
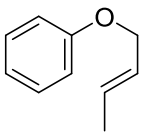
(e) The Claisen arrangement reaction takes place through a pericyclic mechanism as shown below.



Predict the intermediate and product that is formed when but-2-enyl phenyl ether undergoes the Claisen arrangement.



but-2-enyl phenyl ether [2]

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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.