ST ANDREW'S JUNIOR COLLEGE
PRELIMINARY EXAMINATIONS
HIGHER 1

CANDIDATE NAME	
CLASS	2 3

H1 CHEMISTRY

8873 / 02

Paper 2 Structured Questions

27 August 2024
2 hours

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

READ THESE INSTRUCTIONS FIRST

Write your centre number, index number, name and class at the top of this page.
Write in dark blue or black pen.
You may use a HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Section A
Answer **all** the questions.

Section B
Answer **one** question.

The use of an approved scientific calculator is expected, where appropriate.

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

Question Number	Total Marks	Marks Obtained
SECTION A		
1	14	
2	7	
3	9	
4	30	
SECTION B		
5	20	
6	20	
TOTAL	80	

This document consists of **XX** printed pages (including this cover page).

Section A

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

1 This is a question about Group 14 elements and its compounds.

(a) **(i)** A sample of silicon contains three isotopes, as shown in **Table 1.1**. **[2]**

Table 1.1

Isotope	Relative Isotopic mass	Percentage abundance. %
^{28}Si	27.976	92.22
^{29}Si	28.976	4.69
^{30}Si	29.973	3.09

Calculate the relative atomic mass of silicon in this sample, giving your answer to **two decimal places**.

Relative atomic mass of silicon
= (27.976 x 92.22 + 28.976 x 4.69 + 29.973 x 3.09) / 100
= 28.08 (to two decimal places)

(ii) Complete the electronic configuration for silicon. **[1]**

$1s^2$ ……………………………

$1s^2$ $2s^2 2p^6 3s^2 3p^2$

(iii) Explain why second ionisation energy of silicon is lower than that of aluminium. **[2]**

2^{nd} I.E. of Si is lower than that of Al.

Al^+: $1s^2$ $2s^2$ $2p^6$ $3s^2$

Si^+ : $1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^1$

- In Al^+, the electron is removed from the 3s orbital, whereas for Si^+, the electron is removed from the 3p orbital.

- The **electron in the 3p orbital** is **further from the nucleus** √ than the electron in the 3s orbital and experiences **additional shielding effect**√ by the two 3s electrons.
- These factors **outweigh the effect of increase in nuclear charge** √ from Al^+ to Si^+, resulting in a **weaker attraction by nucleus** √
- Hence **less energy** is required to remove the electron from the 3p orbital in Si^+ than that in the 3s orbital in Al^+.

(b) When carbon tetrachloride, CCl_4, and silicon tetrachloride, $SiCl_4$, were added to water, the following observations were seen.

carbon tetrachloride	Forms two immiscible layers
silicon tetrachloride	White solid and steamy fumes

(i) Write a balanced equation for the reaction of $SiCl_4$ with water. **[1]**

$SiCl_4(l) + 2H_2O(l) \rightarrow SiO_2(s) + 4HCl\ (aq)$ **(State symbols not required)**

(ii) CCl_4 has no reaction with water. Suggest an explanation for the inertness of CCl_4 to water. **[1]**

CCl_4 **does not have any empty and energetically accessible 3d orbitals** that can accept lone pair of electrons from water molecules, hence, it is inert to water.

(iii) Explain why CCl_4 forms two immiscible layers with water when they are mixed. **[2]**

The energy released to form the **instantaneous dipole-induced dipole interactions between CCl_4 and water** √ is **insufficient**√ to overcome the **hydrogen bonding between water molecules** √ and the **instantaneous dipole-induced dipole interactions between CCl_4 molecules**√ . Hence,

CCl_4 is insoluble in water and forms two immiscible layer when added to water.

(c) Due to carbon's ability to form strong multiple bonds, it can form different allotropes like graphene and fullerene.

Graphene is an allotrope of carbon that occurs as two-dimensional sheets while fullerenes are molecules of carbon atoms with hollow shapes. An example of a spherical fullerene is buckminsterfullerene, C_{60}, while carbon nanotube (CNT) is a type of cylindrical fullerene.

Buckminsterfullerene has low melting point and is slippery while CNT, like graphene, has high tensile strength and is an excellent conductor of electricity.

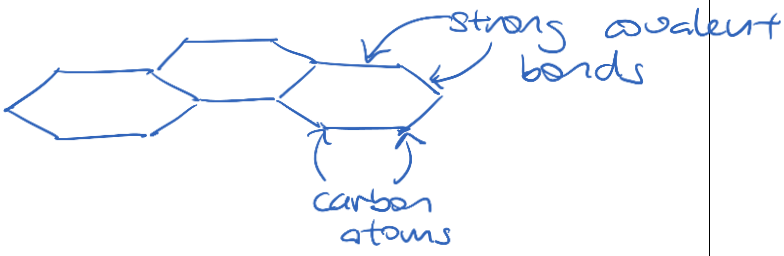
(i) Graphene is a *nanomaterial*. **[1]**

Define what is meant by the term *nanomaterial*.

Nanomaterials are defined as a material containing particles where there is **at least one dimension** between **1-100 nm on the nanoscale**.

(ii) Draw a diagram to illustrate the structure of graphene. **[1]**

Structure of graphene.



(iii) Explain how carbon nanotube is an excellent conductor of electricity and has high tensile strength. **[2]**

In CNT, there is **delocalisation of the electron in the p orbital on each carbon ,** forming an **extended π-electron cloud** √above and below the layer within the tube allows it to be good electrical conductors.

			Carbon atoms in graphene form a single layer hexagonal lattice structure, resulting in an **extensive network of many strong covalent bonds between carbon atoms** give a single carbon nanotube high tensile strength.	
		(iv)	Suggest why buckminsterfullerene is a good lubricant.	**[1]**
			The **spherical shape** of the buckminsterfullerene allows it to **roll/move between the moving parts**, reducing contact and friction between parts.	
			[14 marks]	

2 Propanone, CH_3COCH_3, reacts with iodine, I_2, in the presence of an acid catalyst.

An experiment is performed using 1.00 mol dm^{-3} of I_2 and 1.00 mol dm^{-3} H^+(aq) where concentration of CH_3COCH_3 is monitored over time. The same experiment was then repeated using 0.500 mol dm^{-3} H^+(aq) instead.

The results obtained are used to plot the graph below.

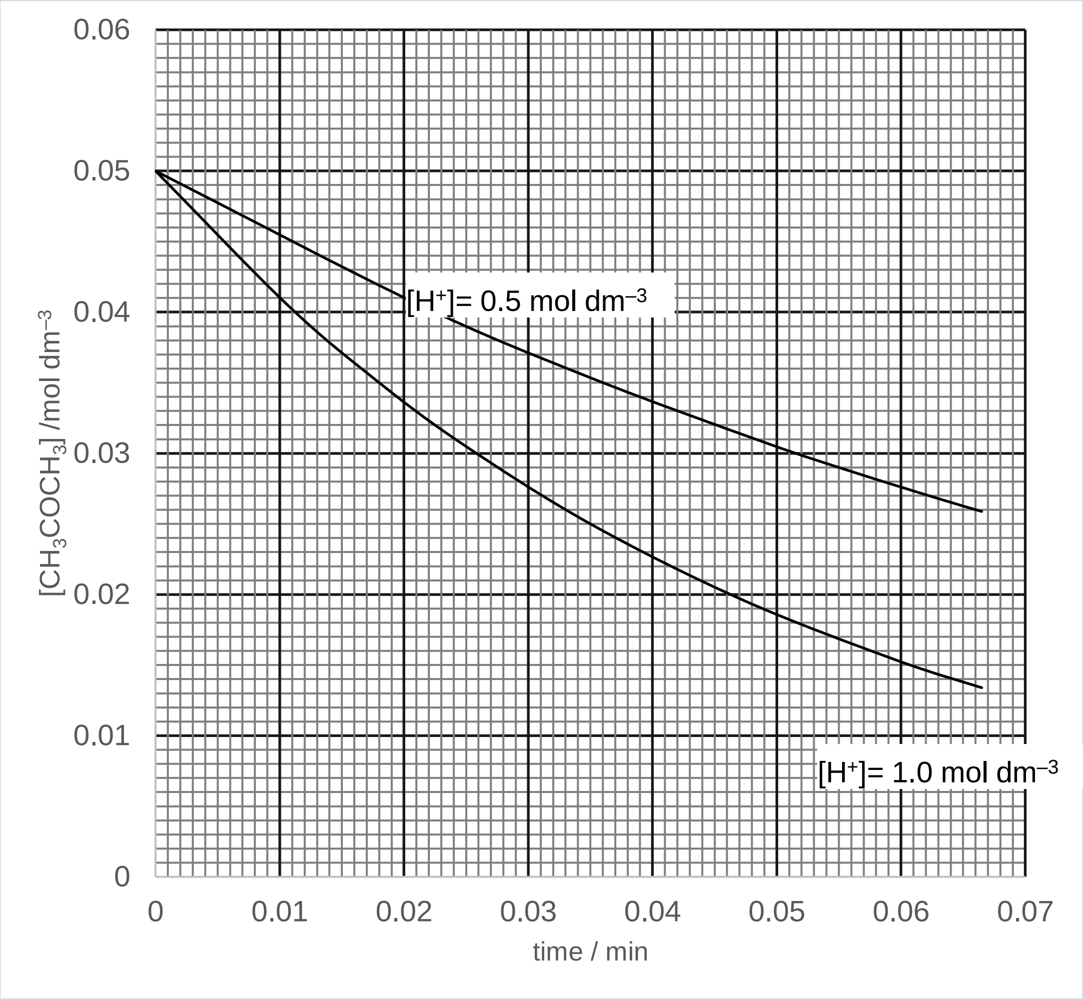
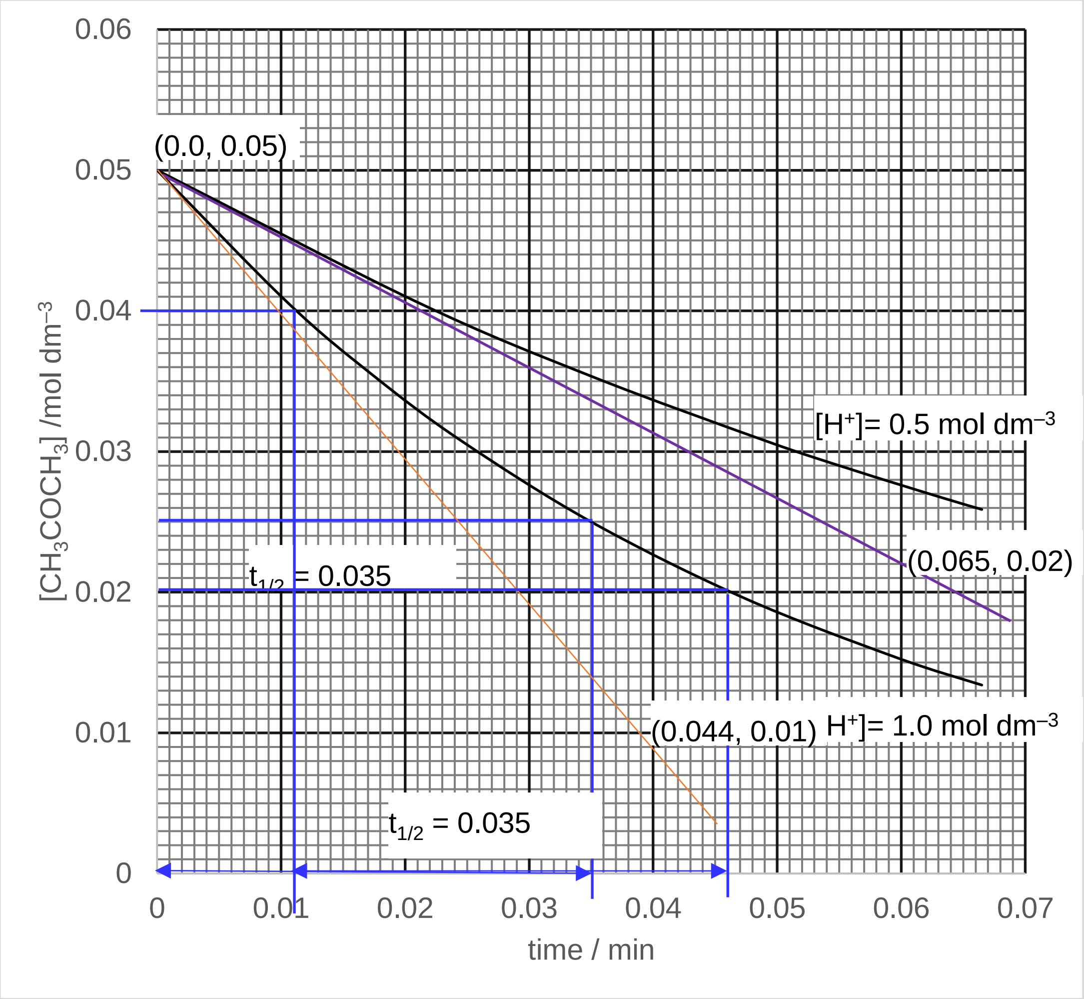
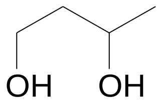
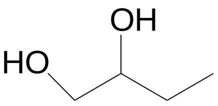
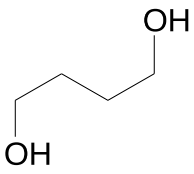
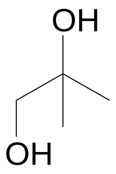


Fig 2.1

	 **Fig 2.1**			
	(a)	**(i)**	It was found that the reaction is zero order with respect to $[I_2]$. Define the term *order of reaction*.	**[1]**
			Order of reaction is the **power to which the concentration of the reactant is raised in the rate equation.**	
	(b)	**(i)**	Use the graph, Fig 2.1, to determine the order of reaction with respect to $[CH_3COCH_3]$ and $[H^+]$ respectively.	**[2]**
			Since first $t_{1/2}$ = second $t_{1/2}$ = 0.035 min, **$t_{1/2}$ is constant at 0.035 min.** Order of reaction wrt $[CH_3COCH_3]$ = **1** Don't award if no working shown on the graph for the 2 $t_{1/2}$ interval	

			When $[H^+]$ = 1.0 moldm^{-3}, initial rate = $\left\lvert\frac{0.01-0.05}{0.044-0}\right\rvert$ = 0.909 When $[H^+]$ = 0.5 moldm^{-3}, initial rate = $\left\lvert\frac{0.02-0.05}{0.065-0}\right\rvert$ = 0.462 **When $[H^+]$ x 2, rate x 2,** Order of reaction wrt $[H^+]$ = **1**	
		(ii)	Write the rate equation for this reaction. Hence, calculate the value of rate constant, *k*. Include the units.	**[2]**
			Rate = k $[H^+][CH_3COCH_3]$ k = $\frac{0.0909}{0.05}$ = **18.2 mol^{-1}dm^{3}min^{-1}**	
	(c)		Other halogens, like chlorine and bromine, can also react with propanone in similar reactions as iodine. Describe and explain how the reactivity of halogens varies down the group. Include relevant data from the *Data Booklet* in your answer.	**[2]**
			Atomic radius of C*l* = 0.099nm **Atomic radius of Br = 0.114nm** **Atomic radius of I = 0.133 nm** Down the group, the **oxidising power of halogens decreases** √ because its **atomic radius increases** and its **electron affinity decreases** √. Hence, there is **less tendency for halogens to gain electrons** √ to be reduced to form halide ions. **OR** Down the group, the **oxidising power of halogens decreases** √ because **valence electrons of halogens are further away from nucleus**, and hence, **are less attracted to the nucleus**√. As a result, it is **harder for halogens to gain electrons** √ to be reduced to form halide ions.	

			[7 marks]	
3	A sample of sodium nitrite, $NaNO_2$, was analysed by titrating with yellow aqueous cerium(IV) ions, Ce^{4+}. The experimental procedures for this analysis were as follows. • 0.140 g of impure $NaNO_2$ was dissolved in deionised water to form a colourless solution. It was then transferred to a 100 cm^3 volumetric flask and top up to the mark with more deionised water. • 25.0 cm^3 of this solution required 22.05 cm^3 of 0.0400 mol dm^{-3} $Ce^{4+}(aq)$ to reach the end-point. During the titration, Ce^{4+} was reduced to colourless Ce^{3+} while nitrite ion was oxidised to form colourless nitrate ion, NO_3^-.			
	(a)	**(i)**	Draw a dot-and-cross diagram of $NaNO_2$.	**[2]**
				
		(ii)	Construct the ionic equation for the reaction between sodium nitrite and cerium(IV) ions.	**[1]**
			$Ce^{4+} + e^- \rightarrow Ce^{3+}$ -- (1) $H_2O + NO_2^- \rightarrow NO_3^- + 2H^+ + 2e^-$ -- (2) (1) x 2 + (2): **$2Ce^{4+}(aq) + H_2O(l) + NO_2^-(aq) \rightarrow NO_3^-(aq) + 2H^+(aq) + 2Ce^{3+}(aq)$** (state symbols not required)	
		(iii)	Calculate the percentage purity of this sample of $NaNO_2$.	**[3]**
			Amount of Ce^{4+} = 0.02205 x 0.04 = 0.000882 mol Amount of NO_2^- in 25 cm^3 = 0.000882 / 2 = 0.000441 mol Amount of NO_2^- in 100 cm^3 = 0.000441 x 4 = 0.001764 mol Mass of $NaNO_2$ = 0.001764 x [(23.0 + 14.0 + 2(16.0)] = 0.121716 g % purity = 0.121716 / 0.14 x 100% = 86.94% ≈ 86.9% (to 3 sf)	

		(iv)	Predict the colour change at the end-point of this titration.	**[1]**
			Colourless to (pale) **yellow**.	
	(b)	Suggest and explain the difference in the ionic radii of Ce^{4+} and Ce^{3+}.		**[2]**
		Both Ce^{4+} and Ce^{3+} have **same nuclear charge**√. Ce^{4+} have **one less electron**√ and hence the **valence electrons are** **more strongly attracted**√ to the nucleus and thus Ce^{4+} has a **smaller ionic radius**√ than Ce^{3+}.		
			[9 marks]	
4	Diol is an organic compound with 2 –OH groups. The following are some examples of diol.  Compound **A**  Compound **B**  Compound **C**  Compound **D**			
	(a)	**(i)**	Compounds **A** to **D** are constitutional isomers. Define the term *constitutional isomers*.	**[1]**
			Constitutional isomers are compound with the **same molecular formula** but **different structural formula**.	
		(ii)	Give the systematic name of compound **A**.	**[1]**
			Butane-1,3,-diol OR **1,3-butanediol** OR **Butan-1,3-diol**	
		(iii)	Both compound **A** and butane are made up of four carbon atoms. Despite this, butane is less reactive than **A**. Explain briefly why this is so.	**[1]**
			Butane is non-polar while **A is polar**.	

(iv) **Table 4.1** shows the boiling points of compounds **A** to **D**.

Table 4.1

Compound	Boiling point / °C
A	210
B	192
C	230
D	176

With reference to structure and bonding, explain why compound **C** has a higher boiling point than compound **B**. **[2]**

Both **B** and **C** are polar **simple covalent molecules** with **intermolecular hydrogen bonds**. Within molecules of **B**, there are **intramolecular hydrogen bonds,** which **reduce the extent of intermolecular hydrogen bonds**. This is unlike **C** which only has intermolecular hydrogen bonds. Hence, more energy is needed to overcome the more extensive intermolecular hydrogen bonds of C.

(v) With reference to **(a)(iv)**, explain why compound **D** has the lowest boiling point. **[2]**

Compounds **A** to **D** are **polar simple covalent molecules** with **intermolecular hydrogen bonds**. Unlike **A** to **C**, **D** is branched and therefore, it has the **smallest surface area**, resulting in the **smallest extent of / least extensive intermolecular instantaneous dipole-induced dipole interactions**. Hence, less energy is needed to overcome it.

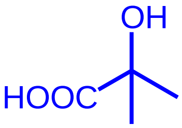
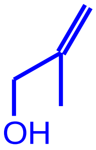
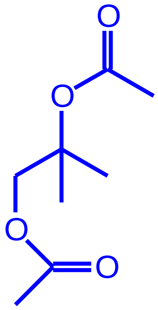
(b) **(i)** In the spaces provided below, draw the structure of the organic product obtained when compound **D** is reacted with the following reagents and conditions. State the type of reaction for each reagent and condition.

I) $K_2Cr_2O_7$, H_2SO_4, heat

II) Concentrated H_2SO_4, 170 °C

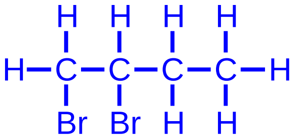
III) excess CH_3COOH, concentrated H_2SO_4, heat

[6]

Reagent and condition	I	II	III
Structure of organic product			
Type of Reaction	Oxidation	Elimination	Condensation

(ii)	With reference to **(b)(i)**, state the role of concentrated H_2SO_4 in reaction III.	**[1]**
	Catalyst OR **dehydrating agent**	
(iii)	Compound **B** can be synthesised from a bromoalkane. Draw the **displayed** formula of this bromoalkane. State the reagents and conditions for this synthesis.	**[2]**

NaOH(aq), heat



$CH_2BrCHBrCH_2CH_3$

Reagents and conditions: ……………………………………………………………...

(c) When 2 –OH groups are bonded to the same carbon atom, the compound is known as geminal diol. Geminal diol is unstable and will spontaneously lose water to form a carbonyl compound. An equation to represent this is as shown.

$$R_2C(OH)_2 \rightleftharpoons R_2C{=}O + H_2O$$

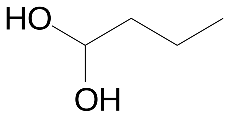
(i) Explain what is meant by a *reversible reaction*. **[1]**

A reversible reaction is one that **does not go to completion** and can **proceed in both the forward and backward reaction**.

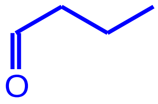
(ii) For the conversion between geminal diol and carbonyl compound, suggest whether the ratio of $\frac{[\text{products}]}{[\text{reactants}]}$ at equilibrium will be less than, equal to or greater than 1. **[1]**

Greater than 1

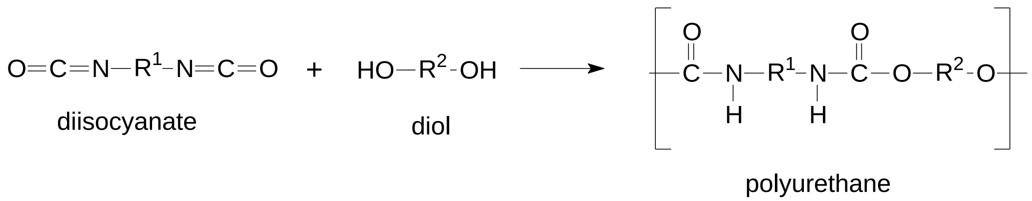
(iii) For the following compound, draw the structure of the carbonyl compound that it will form.



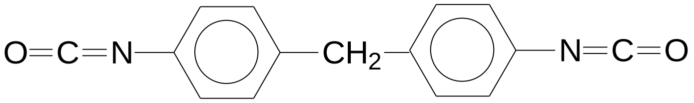
[1]



(d) Diol can react with diisocyanate to form polyurethane, which is a polymer. The equation representing this reaction is as shown.



Spandex is a fabric that contains polyurethane formed from compound **E** and $HOCH_2CH_2OH$.



Compound **E**

Unlike nylon which is derived from coal and petroleum, all the constituent parts of polyurethane in spandex are synthesised in the laboratory. Spandex is non-biodegradable. When polyurethane in spandex is heated, a variety of harmful products can be produced, such as carbon monoxide, CO, and hydrogen cyanide, HCN.

The properties of spandex and nylon are shown in **Table 4.2**.

Table 4.2

Property	Spandex	Nylon
Stretchability	High	Moderate
Durability	High	High
Retention	High	Low to moderate
Breathability	High	High

(i) State the molecular formula of **E**. **[1]**

$C_{15}H_{10}N_2O_2$

(ii) Spandex fibres are strong due to the intermolecular forces between the polymer chains.

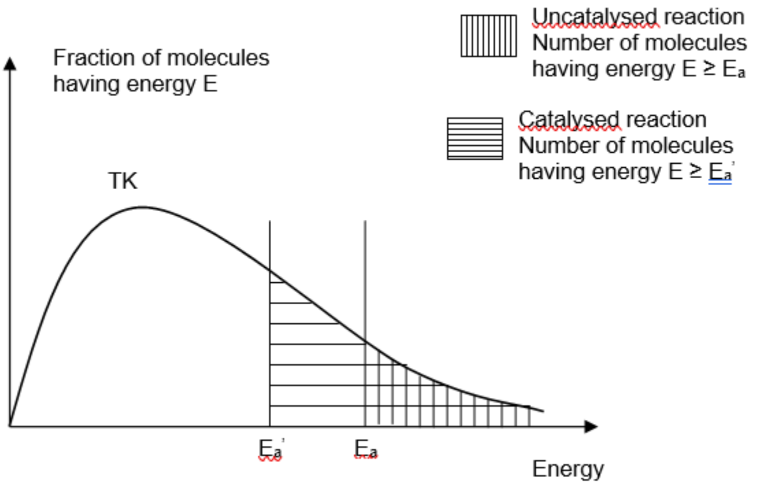
			State the two types of intermolecular forces responsible for this property and the group(s) of atoms involved.	**[3]**
			Hydrogen bonds ; ester and amide. **Instantaneous dipole-induced dipole interactions; benzene**	
		(iii)	Explain why spandex fabric dissolves slowly when placed in aqueous alkali.	**[1]**
			The **ester and amide** in spandex will undergo **hydrolysis**.	
		(iv)	Deduce whether spandex is classified as a thermoplastic or thermoset. Explain your answer. Hence, state whether it can be recycled.	**[2]**
			Spandex is a **thermoset as it decomposes on heating** to form products like CO and HCN. Hence, it **cannot be recycled**.	
		(v)	Suggest a preferred method to dispose spandex. State a disadvantage associated with this method.	**[1]**
			Dispose in **landfill**. Landfills are **scarce** OR **will eventually be used up**.	
		(vi)	In high performance sports, such as running, strenuous movements are involved and therefore, a large amount of sweat is produced. It is important for the sportsperson to feel comfortable when wearing the sportswear. Between spandex and nylon, state which polymer will be more suitable to make the sportswear for high performance sports. Explain your choice by considering the properties listed in **Table 4.2**.	**[3]**
			Spandex. Spandex has **higher stretchability** than nylon and this allows the sportsperson to **perform movements with ease**.	

			Spandex has **<u>higher retention</u>** than nylon and this allows the sportswear to be **<u>worn repeatedly</u>**.	
			[30 marks]	

Section B

Answer one question from this section in the spaces provided.

5	**(a)**	New car exhaust systems are fitted with a catalytic converter where it converts harmful gases like carbon monoxide and nitrogen dioxide to harmless gases like carbon dioxide and nitrogen before the exhaust gases are being released into the atmosphere.		
		(i)	Write an equation to represent the chemical reaction taking place in the catalytic converter as described in **(a)**.	[1]
			$4\ CO + 2\ NO_2 \rightarrow N_2 + 4\ CO_2$	
		(ii)	State the type of catalyst involved and explain the mode of action of this type of catalyst.	[4]
			Heterogenous Catalyst • **Adsorption** of reactant molecules on catalyst surface **weaken the bonds** within the reactants. • **Activation energy is reduced**, **reactant surface concentration increased** and the reactants **break down and react** to form products. • **Products desorb** from the catalyst surface.	
	(a)	**(iii)**	Explain, with the aid of a Boltzmann distribution diagram, on how this catalyst affects the rate of reaction.	[3]



- Catalyst provides an alternative pathway with lower activation energy.
- Number of particles with $E \geq E_a^{I}$ increases
- Frequency of effective collisions increases
- Rate increases.

(b) An industrial process in the production of a fuel, N_2O_3 involved the following equilibrium system.

$$N_2O_4\,(g) + 2\,NO\,(g) \rightleftharpoons 2\,N_2O_3\,(g) \qquad \Delta H = -31.0 \text{ kJ mol}^{-1}$$

In one of such processes, 4 mol of dinitrogen tetraoxide, N_2O_4, and 9 mol of nitrogen monoxide, NO, was heated in a 3.0 dm^3 vessel at 450 ºC. The two gases reacted slowly to produce N_2O_3. The amount of N_2O_3 at equilibrium was found to be 4.8 mol.

(i) Write an expression for the equilibrium constant, K_c for the reaction, stating its units. [2]

$K_c = [N_2O_3]^2 / [N_2O_4][NO]^2$

Units: mol^{-1} dm^3

(b) (ii) Determine the equilibrium concentration of the gases and hence the value of K_c. [3]

	N_2O_4 (g)	+ 2 NO(g) $\rightleftharpoons$	2 N_2O_3 (g)
Initial amt / mol	4	9	0
Change amt / mol	-2.4	- 4.8	+ 4.8
Eqm amt / mol	1.6	4.2	4.8

Eqm Conc / mol dm^{-3}	0.533	1.4	1.6

$K_c = (1.6)^2 / \{(0.533)(1.4)^2\}$

$= 2.45\ mol^{-1}\ dm^3$

(iii) Define the term *dynamic equilibrium*. [1]

Dynamic equilibrium is when **rate of forward reaction equals rate of backward reaction** and that there is **no further change in concentrations of reactants and products**.

(iv) Suggest and explain the temperature and pressure conditions which could help to increase the yield of N_2O_3. [4]

By Le Chatelier's Principle (LCP), a **low temperature** condition will shift **position of equilibrium to the right** and increase yield as the system will want to **increase temperature through releasing heat**

by favouring the exothermic reaction.

By LCP, a **high pressure** condition will shift **position of equilibrium to the right** and increase yield as the system will want to **reduce pressure by forming lesser gaseous particles**

(v) The actual industrial temperature and pressure conditions were as followed:

Temperature: 500 ºC

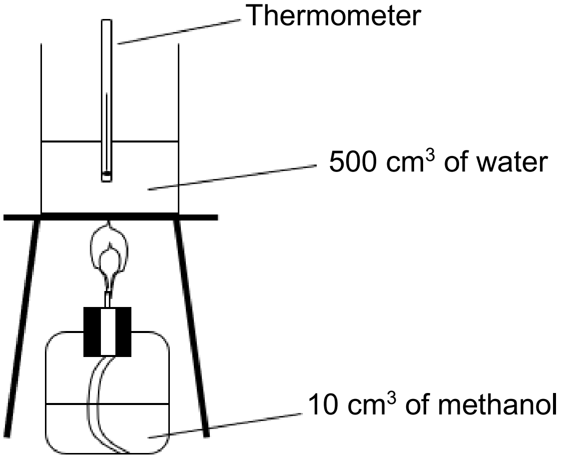
Pressure: 150 atm

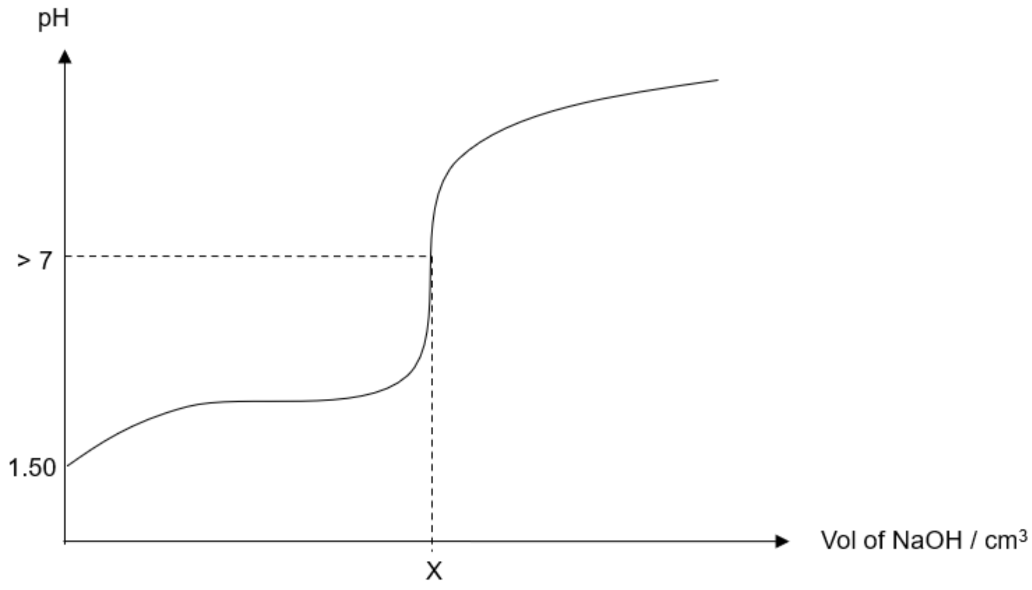
Explain why these conditions were applied instead of what was suggested in **(b)(iv)**. [2]

Too low a temperature will result in the **reaction rate to be very slow**. Hence, a moderately high temperature of 500 ºC is applied to **achieve optimum rate and yield** .

Too high a pressure will result in **high cost to maintain the equipment needed to withstand the pressure**. Hence, a moderately high pressure of 150 atm was applied.

[Total: 20 marks]

6	In this current environmental landscape, it is important to search for alternative energy sources. Methanol and methane have been investigated to serve as alternative sources of fuels for motor cars.			
	(a)	**(i)**	Write an equation to represent the standard enthalpy change of combustion of methanol.	[1]
			$CH_3OH\ (l) + 3/2\ O_2\ (g) \rightarrow CO_2\ (g) + 2\ H_2O\ (l)$	
		(ii)	Using relevant data from the *Data Booklet*, calculate another value for the standard enthalpy change of combustion of methanol.	[2]
			$\Delta H_c = \{3(410) + 360 + 460 + 3/2(496)\} - \{2(805) + 4(460)\}$ $= -656\ kJ\ mol^{-1}$	
		(iii)	Use of *Data Booklet* is relevant to this question. The standard enthalpy change of combustion of methanol can be determined in the laboratory using the apparatus shown in the diagram below.  The temperature of water rose from 25 °C to 90 °C when all the methanol was completely burnt. The density of methanol is 0.792 g cm^{-3} and the standard enthalpy change of combustion of methanol is –715 kJ mol^{-1}. Calculate the percentage efficiency of this heating process.	[4]
			Amt of methanol burnt = (10 X 0.792) / [12.0 + 4(1.0) + 16.0] = 0.2475 mol $q_{100\%}$ = 0.2475 X 715 000 = 176962.5 J actual q = 4.18 X 500 X (90 – 25) = 135850 J	

			% efficiency = (135850 / 176962.5) X 100 = 76.8 %	
		(iv)	Suggest why there was a discrepancy between your answer in **(a) (ii)** and that quoted in **(a) (ii)**.	[1]
			Bond energy values are **average values** / The **conversion of methanol to gaseous state was not considered** in the calculation in (iii).	
	(b)	Methanoic acid, commonly known as formic acid, is used as a food preservative. It can be formed from oxidising methanol.		
		(i)	Write a balanced equation for the formation of methanoic acid from methanol. You can use [O] to represent the oxidising agent.	[1]
			$CH_3OH + 2\,[O] \rightarrow HCOOH + H_2O$	
		(ii)	Using methanoic acid as an example, explain what is meant by a acid – conjugate base pair.	[1]
			An acid – conjugate base pair **differ from each other by a H^+**. **$HCOO^-$** is the strong **conjugate base** of HCOOH, a weak **acid**.	
	(c)	25.0 cm^3 of 0.100 mol dm^{-3} methanoic acid, HCOOH, was titrated with 0.100 mol dm^{-3} NaOH. The titration curve is shown below. 		

		(i)	Justify, with relevant calculations, that methanoic acid is a weak acid.	[2]
			$[H^+] = 10^{-1.50} = 0.0316$ mol dm^{-3} Since **$[H^+] < [HCOOH]$**, methanoic acid is a weak acid. OR Assuming methanoic acid is a strong acid, Expected pH = -lg (0.100) = 1 Since actual pH > expected pH, actual $[H^+]$ lesser than expected, thus methanoic acid is a weak acid.	
		(ii)	Write a balanced chemical equation for the reaction between methanoic acid and sodium hydroxide.	[1]
			$HCOOH + NaOH \rightarrow HCOO^-Na^+ + H_2O$	
		(iii)	Determine the value of X.	[1]
			Amt of HCOOH = (25/1000) X 0.100 = 0.0025 mol = Amt of NaOH X = Vol of NaOH = (0.0025 / 0.100) X 1000 = 25.0 cm^3	
		(iv)	Explain, with the aid of a chemical equation to explain why pH is greater than 7 when X cm^3 of NaOH was added.	[2]
			$HCOO^- + H_2O \rightleftharpoons HCOOH + OH^-$ $HCOO^-$, a strong **conjugate base**, will hydrolyse in water to **release OH^-**, causing the resultant solution at equivalence point to be basic, hence pH>7.	
		(v)	Suggest a suitable indicator for this titration and explain your choice.	[2]
			Phenolphthalein / Thymolphthalein. The **region of rapid pH change** of the titration/ **vertical region** of the titration curve coincides with **working range** of the indicator.	
		(vi)	It was found that a buffer mixture was obtained when $\frac{X}{2}$ cm^3 of NaOH was added. Write equations to show how the mixture resisted changes in pH when small amounts of H^+ and OH^- was added to a separate solution of this buffer mixture.	[2]
			Add H^+ , $H^+ + HCOO^- \rightarrow HCOOH$	

			Add OH^-, $OH^- + HCOOH \rightarrow HCOO^- + H_2O$	
			[Total: 20 marks]	

END OF PAPER