

## NANYANG JUNIOR COLLEGE JC 2 PRELIMINARY EXAMINATION Higher 1

CANDIDATE NAME

CLASS

#### TUTOR'S NAME

CHEMISTRY Paper 2 Structured Questions

Candidates answer on the Question Paper

Additional Materials: Data Booklet

#### **READ THESE INSTRUCTIONS FIRST**

Write your name and class in the spaces provided at the top of this page. Write in dark blue or black pen. You may use a soft 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.

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.

For Examiner's Use		
1	/9	
2	/8	
3	/9	
4	/10	
5	/15	
6	/9	
7/8	/20	
Total	/80	

9 September 2024 2 hours

8873/02

#### 2

#### Section A

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

- 1 This question is about the chemistry of sodium and oxygen.
- (a) (i) Define the term *first ionisation energy*.

The first ionisation energy of an element is the amount of energy required to remove one mole of electrons from one mole of gaseous atoms to form one mole of singly-charged gaseous cations. [1]

 $X(g) \rightarrow X^+(g) + e \qquad \Delta H = 1 \text{ st I.E.}$ 

- (ii) Explain the following comparisons of ionisation energies.
  - The first ionisation energy of Na (494 kJ mol<sup>-1</sup>) is very much lower than that of oxygen (1310 kJ mol<sup>-1</sup>).
  - The second ionisation energy of Na (4560 kJ mol<sup>-1</sup>) is very much higher than its first ionisation energy (494 kJ mol<sup>-1</sup>).

### 1<sup>st</sup> I.E. of Na is lower than that of O

- As Na has more protons than O, nuclear charge is higher in Na.
- As Na has one more electron shell than O, shielding effect increases significantly in Na.
- The outermost electron is further away from the nucleus in Na.

The net attraction between the nucleus and outermost electron decreases in Na and less energy is required to remove the outermost electron.
4 points [2], 2 points [1]

2<sup>nd</sup> I.E. of Na is higher than its 1<sup>st</sup> I.E.

A lot more energy is needed to remove a negatively charged electron from a positively charged Na<sup>+</sup> ion **due to stronger electrostatic attraction**. [1] OR

There are **less electrons than protons** in Na<sup>+</sup>. The repulsion/**shielding effect among the remaining electrons decreases** and they are also more strongly attracted to the **constant positive nuclear charge**. Hence more energy is required to overcome the stronger attraction to remove the outermost electron. [1] OR

For 2<sup>nd</sup> IE, the electron to be removed from Na<sup>+</sup> is from the **inner 2p subshell** which is **closer to the nucleus** hence experiences **less shielding and stronger net attraction** to the constant nuclear charge. [1]

- (b) When sodium is burned in oxygen, both sodium oxide Na<sub>2</sub>O and sodium peroxide Na<sub>2</sub>O<sub>2</sub> are produced. The two products are strongly basic and form sodium hydroxide when reacted with water. Hydrogen peroxide is also formed in the reaction of sodium peroxide with water.
  - (i) Explain, in terms of electronegativity, why Na<sub>2</sub>O and Na<sub>2</sub>O<sub>2</sub> are strongly basic.

Due to the <u>large electronegativity difference between Na and O</u>, <u>ionic bonds</u> (or ionic oxides) are formed in Na<sub>2</sub>O and Na<sub>2</sub>O<sub>2</sub>. [1]

(ii) Draw a dot-and-cross diagram and label the **two** different types of bonding present in sodium peroxide, Na<sub>2</sub>O<sub>2</sub>.

covalent bond 2 [Na]<sup>+</sup>[;;;;;;;;;]<sup>2-</sup> ionic bond

# D&C [1] Labels of bond [1] ECF

(iii) Explain why the melting point of Na<sub>2</sub>O (1132 °C) is very much higher than that of Na<sub>2</sub>O<sub>2</sub> (460 °C).

• Both Na<sub>2</sub>O and Na<sub>2</sub>O<sub>2</sub> have giant ionic structures consisting of strong ionic bonds between ions.

• The ionic charge of  $O^{2-}$  is the same as  $O_2^{2-}$ .

• The <u>ionic radius of  $O^{2-}$  is smaller than  $O_2^{2-}$ </u>, hence the interionic distance between Na<sup>+</sup> and  $O^{2-}$  is smaller than the interionic distance between Na<sup>+</sup> and  $O_2^{2-}$ .

• Thus according to  $|LE| \propto \frac{|z^+z^-|}{r_+ + r_-}$ , |L.E.| is larger for Na<sub>2</sub>O hence the ionic

bonds between Na<sup>2+</sup> and O<sup>2-</sup> are <u>stronger</u>

• and <u>requires more energy to break</u> giving rise to a stronger melting point.
4-5 points [2], 2-3 points [1] ECF

2 For many compounds the enthalpy change of formation cannot be calculated directly. An indirect method based on enthalpy changes of combustion can be used.

The enthalpy change of combustion can be found by a calorimetry experiment in which the heat energy given off during combustion is used to heat a known mass of water and the temperature change recorded.

(a) (i) Define the term standard enthalpy change of combustion.

Standard enthalpy change of combustion is energy change when one mole of a substance is completely burnt in excess oxygen under standard conditions. [1]

(ii) Write the equation for the standard enthalpy change of combustion of ethanol,  $C_2H_5OH$ .

 $C_2H_5OH(I) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(I)$  [1] State symbols are required

- (b) In an experiment to determine the enthalpy change of combustion of ethanol, 0.288 g of ethanol was burned and the heat given off raised the temperature of 100 g of water by 16.3 °C.
  - (i) Calculate the standard enthalpy change of combustion of ethanol.

Assume that the process is only 80% efficient, the specific heat capacity of water is 4.2 J  $g^{-1}\ K^{-1}.$ 

n(ethanol) =  $\frac{0.288}{12.0 \times 2 + 16.0 + 6.0} = 0.006261 \text{ mol [1]}$ 

Heat given off =  $(100 \times 4.2 \times 16.3) \times \frac{100}{80} = 8557.5 \text{ J}$  [1]  $\Delta H_c^{\Theta}$  (ethanol) =  $-\frac{8557.5}{0.006261} = -1366822 \text{ J mol}^{-1} = -1370 \text{ kJ mol}^{-1}$  [1]

(ii) Other than heat loss to surroundings, suggest a reason why the value for the standard enthalpy change of combustion of ethanol determined by a simple laboratory calorimetry experiment is likely to be lower than the true value.

Any reason below for [1]: Incomplete combustion of ethanol will result in lower heat given off by ethanol.

Ethanol is volatile and some of it may have evaporated. / The wick is burned. / Ethanol may have impurities. This will result in the measured mass of ethanol being combusted being larger than the true value.

(c) Some relevant standard enthalpy change of combustion values,  $\Delta H_c^{\Theta}$ , are given in Table 2.1.

Table	2.1
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substance	∆ <i>H</i> c <sup>⊖</sup> / kJ mol <sup>-1</sup>
C(s)	-393.5
H <sub>2</sub> (g)	-285.8
C <sub>3</sub> H <sub>7</sub> OH(I)	-2021.0

Using the data in Table 2.1, calculate the standard enthalpy change of formation of C<sub>3</sub>H<sub>7</sub>OH(I),  $\Delta H_f^{\Theta}$ .

 $\begin{array}{c} \Delta H_{\!f}^{\Theta} \\ 3C(s) + 4H_2(g) + \frac{1}{2}O_2(g) \rightarrow C_3H_7OH(I) \end{array}$ 

 $\Delta H_{rxn^{\Theta}} = \Sigma n \Delta H_c^{\Theta} (rxts) - \Sigma m \Delta H_c^{\Theta} (pdts)$ = [3(-393.5) + 4(-285.8)] - [(-2021.0)] = -302.7 kJ mol<sup>-1</sup> (3 sf)

[1] correct application of formula[1] correct final answer (ECF from (e)(i))

**3** When ethanoic acid reacts with ethanol to form ethyl ethanoate and water, the following equilibrium is established.

 $CH_3CO_2H(I) + C_2H_5OH(I) \rightleftharpoons CH_3CO_2C_2H_5(I) + H_2O(I) \qquad \Delta H < 0$ 

A student mixed 1.20 g (0.0200 mol) of ethanoic acid in a conical flask with 0.92 g of ethanol (0.0200 mol) and 1.80 g (0.100 mol) of water. He then carefully added 0.49 g of concentrated sulfuric acid,  $H_2SO_4$ . The flask was sealed with a bung and placed in a thermostatic water bath set at 25 °C for 5 days.

After 5 days, the student titrated the entire contents of the conical flask with 1.00 mol dm<sup>-3</sup> aqueous NaOH, from a burette, adding phenolphthalein indicator to the flask. The indicator turned pink when 23.30 cm<sup>3</sup> of NaOH had been added.

(a) State the role of concentrated sulfuric acid.

Catalyst to speed up the reaction Dehydrating agent to remove water produced. any one for [1]

(b) Calculate the number of moles of NaOH used in the titration.

n(NaOH) used in the titraion = 1.00 x 23.30/1000 = 0.0233 mol [1]

(c) Calculate the number of moles of NaOH that react with the H<sub>2</sub>SO<sub>4</sub>.

 $n(H_2SO_4) = \frac{0.49}{2.0 + 32.1 + 16.0 \times 4} = 0.004995 \text{ mol}$ 

 $2NaOH + H_2SO_4 \rightarrow Na_2SO_4 + 2H_2O$ 

n(NaOH) that reacted with H<sub>2</sub>SO<sub>4</sub> = 2 x  $n(H_2SO_4)$  present = 2 x 0.004995 = 0.00999 mol [1]

(d) Hence, calculate the number of moles of ethanoic acid present at equilibrium. NaOH + CH<sub>3</sub>COOH  $\rightarrow$  CH<sub>3</sub>COO<sup>-</sup>Na<sup>+</sup> + H<sub>2</sub>O

 $n(CH_3COOH)$  at equilibrium = n(NaOH) reacted with  $CH_3COOH = 0.0233 - 0.009990 = 0.0133$  mol [1] (e) Use the information given and the results of the calculations you have carried out to complete the table below.

If you were unable to obtain a value in **(d)**, please use the value of 0.00500 mol. This is **not** the correct answer.

	CH <sub>3</sub> CO <sub>2</sub> H(I)	C <sub>2</sub> H <sub>5</sub> OH(I)	$CH_3CO_2C_2H_5(I)$	H <sub>2</sub> O(I)
initial amount / mol	0.0200	0.0200	0	0.10
change in amount / mol	-0.00670	-0.00670	+0.00670	+0.00670
equilibrium amount / mol	0.0133 from (d)	0.0133	0.00670	0.1067

## [1] Correct values in the table

(f) Write an expression for the equilibrium constant,  $K_c$ , for this reaction. Use your answers in the table above to calculate the value of  $K_c$ . State the units, if any are appropriate.

Let the volume of the reaction mixture be V dm<sup>3</sup>.

$$K_{c} = \frac{[CH_{3}CO_{2}C_{2}H_{5}][H_{2}O]}{[CH_{3}COOH][C_{2}H_{5}OH]} = \frac{(\frac{0.0067}{V})(\frac{0.1067}{V})}{(\frac{0.0133}{V})(\frac{0.0133}{V})} = 4.04 \text{ (no units)}$$

[2]: correct  $K_c$  expression and correct answer (with no units)

(g) Explain what would happen to the total volume of NaOH added if the thermostatic water bath is set at 30 °C.

By Le Chatelier's Principle, the system reacts in a way to <u>reduce the added heat</u>. The <u>backward endothermic reaction is favoured</u> and <u>position of equilibrium shifts to the</u> <u>left.</u> [1]

[CH<sub>3</sub>CO<sub>2</sub>H] increases and the total volume of NaOH added will increase. [1]

- 4(a) The Periodic Table usually shows hydrogen on its own and not a member of a group.
  - (i) Suggest why the element hydrogen could be placed at the top of Group 1.

Hydrogen atom has <u>one valence electron</u> and it has a <u>smaller number of</u> <u>protons than lithium</u> [1].

- (ii) Suggest why the element hydrogen is **not** placed at the top of Group 1, in terms of
  - its structure
  - one physical property related to its structure

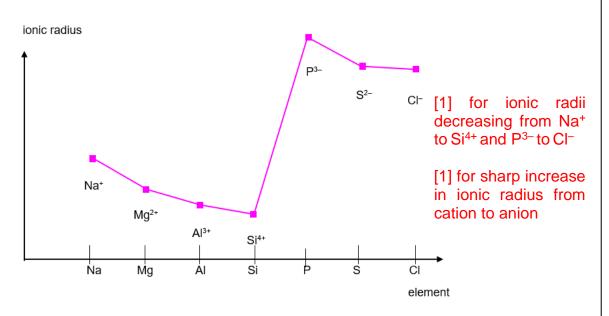
Hydrogen has a <u>simple molecular structure</u> with weak instantaneous dipole – induced dipole interaction between the molecules, while Group I elements have a <u>giant metallic structure</u> with strong metallic bonds between the metallic cations and sea of delocalised valence electrons. [1] (Difference in structure of hydrogen and Group I elements)

The <u>sea of delocalised valence electrons</u> in Group I elements act as <u>mobile</u> <u>charge carriers</u> to <u>conduct electricity</u>, while <u>hydrogen does not contain mobile</u> <u>charged carriers /valence electrons are localised in covalent bonds. Hence</u> <u>does not conduct electricity</u>.

or

Group I elements have higher boiling points as more energy is required to overcome the strong metallic bonds between the metallic cations and sea of delocalised valence electrons. Hydrogen has a lower boiling point as less energy is required to overcome the weak instantaneous dipole – induced dipole interaction between the molecules. [1] (Difference in Physical property for hydrogen and Group I elements)

(b) On the following axes, sketch the variation of the ionic radius across Period 3 of the Periodic Table for the elements Na to Cl.



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(c) Describe the reactions, if any, of the chlorides NaCl, AlCl<sub>3</sub> and PCl<sub>5</sub> with water. Write equations for all the reactions that occur and suggest the pH of the resulting solutions. Relate the reactivity of these chlorides to their structure and bonding.

(•) <u>NaCl has a giant ionic lattice structure</u> where the Na<sup>+</sup> and Cl<sup>-□</sup> ions are held together by (•) <u>strong ionic bonds</u>. Hence the ions are able to form ion – dipole interactions with water, thus NaCl undergoes (•) <u>hydration</u> to form a neutral solution of hydrated ions (•) (pH = 7)

(•) NaCl(s) + aq  $\rightarrow$  Na<sup>+</sup>(aq) + Cl<sup>-</sup>(aq)

(•) <u>AICI<sub>3</sub> has a slight</u> ionic character, allowing it to undergo (•) <u>hydration</u>.

(•)  $AICI_3(s) + 6H_2O(I) \rightarrow [AI(H_2O)_6]^{3+}(aq) + 3CI^{-}(aq)$ 

(•)  $[Al(H_2O)_6]^{3+}$  then undergoes further <u>hydrolysis</u> to give  $[Al(H_2O)_5OH]^{2+}$ (•)  $[Al(H_2O)_6]^{3+}(aq) + H_2O(I) \prod [Al(H_2O)_5OH]^{2+}(aq) + H_3O^+(aq)$ 

(•)  $AI^{3+}$  in  $[AI(H_2O)_6]^{3+}$  has a small size and high charge, thus has a high charge density and is highly polarising. Thus, it is able to polarise the O-H bond in H<sub>2</sub>O, causing H<sup>+</sup> to be released to give an acidic solution (•) (pH  $\approx 2-3$ )

(•) <u>Both AlCl<sub>3</sub> and PCl<sub>5</sub> have simple molecular structure</u> with (•) weak instantaneous dipole – induced dipole interactions between the molecules respectively.

(•) PCI<sub>5</sub> undergoes <u>hydrolysis</u> to give a highly acidic solution (•) (pH  $\approx$  1– 2) and white fumes of HCI gas.

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(•)  $PCI_5(s) + 4H_2O(I) \rightarrow H_3PO_4(aq) + 5HCI(g)$ 

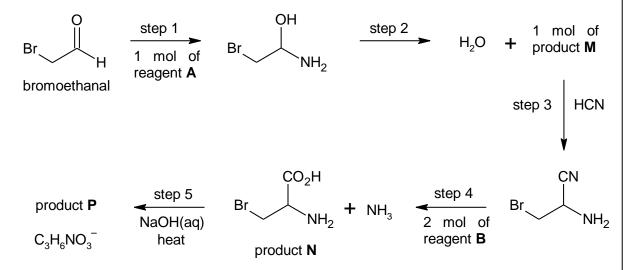
[5] 16-17(•); [4] 10-15(•); [3] 7-9(•); [2] 4-6(•); [1] 3(•)

For Examiner's

- 5 Compound **R** is a common molecule found in muscle cells. It has the molecular formula C<sub>3</sub>H<sub>7</sub>NO<sub>3</sub>.
- (a) Suggest three functional groups that could **all** be present in **R** based on the formula.

amine, carboxylic acid, alcohol, alkene, amide, ester, carbonyl [2] (only one with one unsaturated bond. one nitrogen compound)

(b) Compound **P**, C<sub>3</sub>H<sub>6</sub>NO<sub>3</sub><sup>-</sup>, can be converted to **R** by adding one mol of HCI(aq) in an acid-base reaction. The synthesis route for compound **P** is shown below.



(i) Bromoethanal can be formed from ethanal. State the reagent and conditions to carry out this conversion.

Br<sub>2</sub>, uv light [1]

Product M contains a C=N double bond.
 Suggest the types of reactions for steps 1 and 2.

Step 1: addition step 2: elimination [1] for both

(iii) Draw the displayed structure of **M**.



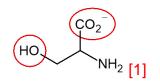
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(iv) Suggest the identities of reagents A and B.

reagent **A**:  $NH_3$  [1] reagent **B**:  $H_2O$  [1] For Examiner's Use (v) State the IUPAC name for product **N**.

2-amino-3-bromopropanoic acid [1]

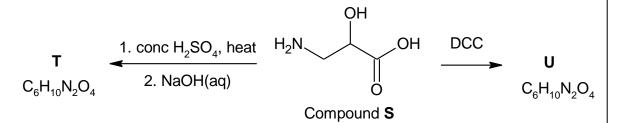
(vi) There are two reactions that occur simultaneously in step 5.
 For each reaction, state the functional group that has reacted, and the type of reaction undergone.
 Draw the structure of product P.



<u>carboxylic acid</u> undergoes <u>acid-base reaction</u> to form carboxylate ion [1]

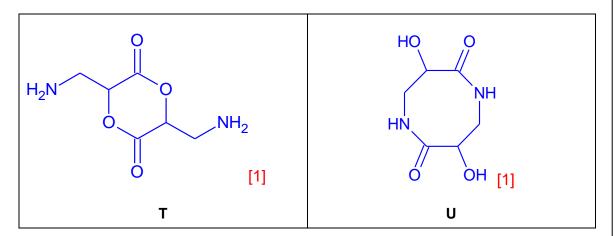
bromoalkene/alkyl halide undergoes hydrolysis/substitution to form alcohol [1]

(c) An isomer of compound **R**, compound **S**, can undergo condensation to form two different products, **T** and **U**, with the same molecular formula.



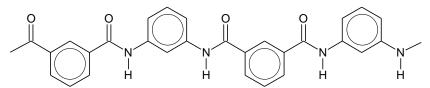
Both **T** and **U** are cyclic compounds.

Suggest the structures of **T** and **U**. Hence, state the type of isomerism they show.



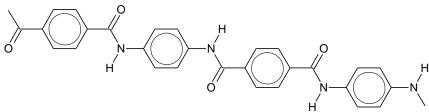
functional group isomerism (constitutional isomerism) [1]

6 Aramid fibres, are a class of heat-resistant and strong synthetic fibres. There are two main types of aramid fibres. Meta-aramid fibres were produced by the DuPont company in the early 1960s under the trade name Nomex<sup>®</sup>. Nomex<sup>®</sup> fibres can be spun and woven, similarly to normal cotton fibres, hence are used in the manufacture of apparel. Unlike cotton fibres, Nomex<sup>®</sup> showed excellent resistance to heat, as it neither melts nor ignites in normal levels of oxygen, hence found extensive use in the production of protective clothing.



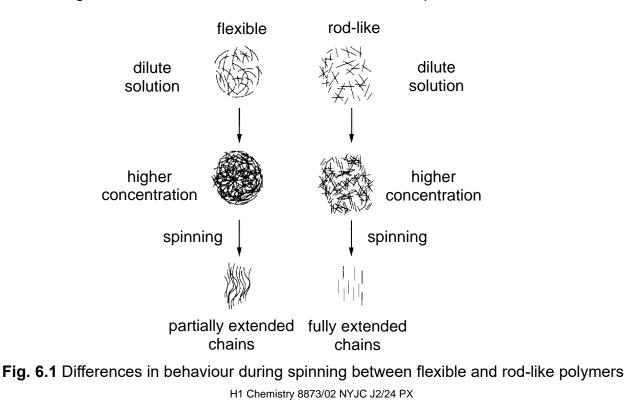
a section of a Nomex<sup>®</sup> polymer chain in meta-aramid fibres

In 1965, scientists at DuPont discovered a new method of producing an almost perfect polymer chain which they named Kevlar<sup>®.</sup> Using para-aramid fibres, the simple repetitiveness in the molecular structure allows the formation of rigid rod-like molecules.



a section of a Kevlar<sup>®</sup> polymer chain in para-aramid fibres

Polymer fibres are formed in a process called spinning. Under high pressure, polymer chains are pushed through tiny openings to form solid fibres. In high concentrations, rod-like polymer chains can align in highly ordered arrangements. This imparts extremely high tensile strength and thermal stability. Kevlar<sup>®</sup> has five times the tensile strength of steel and is well-known for its use in bullet-proof vest.

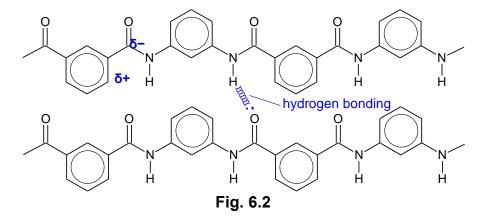


For Examiner's Use (a) Suggest one difference and one similarity in the monomers of a meta-aramid polymer and a para-aramid polymer.

difference: The monomers of a meta-aramid polymer are 1,3-substituted diacids (benzene-1,**3**-dicarboxylic acid) and 1,3-substituted diamines (benzene-1,**3**-diamine) while the monomers of a para-aramid polymer are 1,4-substituted diacids (benzene-1,**4**-dicarboxylic acid) and 1,4-substituted diamines (benzene-1,**4**-diamine). [1]

similarity: Both polymers are formed from two different types of monomers / undergo condensation polymerisation / form polyamides. [1]

(b) (i) Fig. 6.2 shows two adjacent chains of meta-aramid polymer.



[1] for drawing and labelling of hydrogen bond

On **Fig. 6.2**, draw and label the intermolecular forces of attraction that enables meta-aramid polymers to display high thermal stability. [1]

(ii) The diagram below shows two adjacent chains of para-aramid polymer.

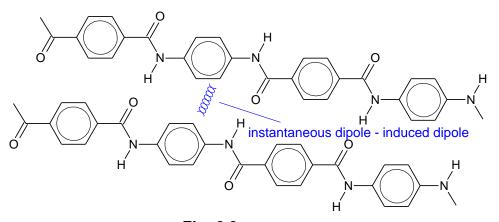
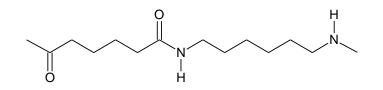


Fig. 6.3

[1] for drawing and labelling of instantaneous dipole-induced dipole

On **Fig. 6.3**, draw and label the **additional** intermolecular forces of attraction not present or only weakly present in **Fig. 6.2**. [1]

(iii) Nylon-6,6 polymers have "flexible" chains whereas para-aramid polymers have chains described as "rod-like". Explain why.



a section of a nylon-6,6 polymer

Para-aramid polymers have chains described as "rod-like" because paraaramids have bulky benzene ring with overlapping p orbitals, resulting in restricted rotation about C–C bonds / –CONH and carbon atoms in benzene are sp<sup>2</sup> hybridised and planar resulting in overlap of p orbitals and hence restricted rotation about C–N and C–C bonds. [1]

Nylon-6,6 polymers have "flexible" chains because Nylon-6,6 have flexible alkyl chains with sp<sup>3</sup> hybridised carbon that can rotate and bend around the C-C single bonds. [1]

(iv) Suggest and explain why Kevlar<sup>®</sup> polymer have higher tensile strength than Nomex<sup>®</sup> polymer.

Regularly arranged rod-like p-aramid molecules can <u>form extensive</u> instantaneous dipole – induced dipole interactions that aggregates and intermolecular hydrogen bonding as they can pack very closely together. [1]

- (c) Nomex<sup>®</sup> polymers are used in fire-retardant garments. Upon heating, Nomex<sup>®</sup> fibres undergo a charring process, creating a carbonaceous layer similar to graphene sheets that can absorb heat and prevents further heat from entering the garment. Small gaseous molecules are evolved in the charring process.
  - (i) Suggest and explain how the carbonaceous layer can absorb large amounts of heat.

Strong C–C bonds in carbonaceous layer need to absorb large amounts of energy to break. [1]

(ii) Suggest the identity of two molecules formed during the charring process that are hazardous.

NO<sub>x</sub>, CO [1]

For Examiner's

# 15 Section B

Answer one question from this section in the spaces provided.

7(a) Alcohol X reacts with acidified potassium dichromate(VI), K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> to form propanone.

The relevant half-equation for dichromate ion in the above reaction is as follows.

 $Cr_2O_7^{2-}$ + 14H<sup>+</sup> + 6e<sup>-</sup>  $\rightarrow$  2Cr<sup>3+</sup> + 7H<sub>2</sub>O

(i) Explain, in terms of the change in oxidation number of chromium, the role of potassium dichromate(VI) in the reaction with alcohol **X**.

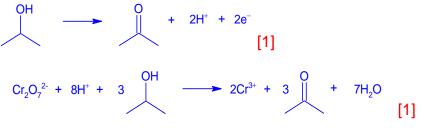
Oxidation number of <u>Cr decreases from +6 in K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> to +3 in Cr<sup>3+</sup></u>. <u>Cr in K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> is reduced</u>, hence it is acting as an <u>oxidising agent</u> in the reaction with X. both role and explanation [1]

(ii) Draw the skeletal formula of alcohol X.



Correct structure [1] Skeletal formula [1]

(iii) Write the half-equation for the oxidation reaction of alcohol **X** to propanone. Hence, construct an ionic equation for the reaction between dichromate(VI) ions and alcohol **X** in acidic solution.



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A 10.0 cm<sup>3</sup> sample of alcohol **X** was mixed with dilute sulfuric acid and made up to a volume of 250 cm<sup>3</sup> in a volumetric flask.

A 25.0 cm<sup>3</sup> portion of this diluted solution was pipetted into a conical flask and heated. A few drops of N-phenylanthranilic acid indicator was added to the flask. 0.0100 mol dm<sup>-3</sup> aqueous potassium dichromate(VI) was run from the burette into the conical flask until a distinct colour change was observed. The titration was repeated to obtain two consistent results (i.e. at least two titres that are within 0.10 cm<sup>3</sup> of each other).

The results are shown in Table 7.1.

	1	2	3
initial burette reading / cm <sup>3</sup>	0.00	21.40	0.00
final burette reading / cm <sup>3</sup>	21.40	43.35	21.50
titre / cm <sup>3</sup>	21.40	21.95	21.50

Table 7 1

(iv) Complete Table 7.1 and use the consistent results to obtain the average volume of aqueous potassium dichromate(VI). Show clearly how you obtained this volume.

[1] for completing table

Average volume of  $K_2Cr_2O_7 = (21.40 + 21.50)/2 = 21.45 \text{ cm}^3$  [1]

(v) Use your answers in (iii) and (iv), calculate the concentration of alcohol X in the sample.

 $n(Cr_2O_7^{2-}) = 0.0100 \times (21.45/1000) = 2.145 \times 10^{-4} \text{ mol}$ 

n(X) in 25.0 cm<sup>3</sup> = 2.145 x 10<sup>-4</sup> x 3 = 6.435 x 10<sup>-4</sup> mol allow ecf [1]

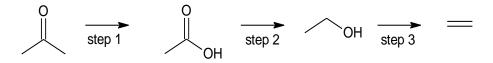
n(X) in 250 cm<sup>3</sup> = n(X) in 10.0 cm<sup>3</sup> = 6.435 x 10<sup>-4</sup> x (250/25.0) = 6.435 x 10<sup>-3</sup> mol

[X] in 10.0 cm<sup>3</sup> sample =  $6.435 \times 10^{-3} / (10.0/1000) = 0.644$  mol dm<sup>-3</sup> [1]

(b) Poly(ethene) is a polymer made by heating ethene molecules with a small amount of benzoyl peroxide (RO-OR) initiator.

reaction (1) 
$$(n+2)H_2C = CH_2 \xrightarrow{\text{RO-OR}} RO - CH_2 - CH_2 + CH_2 - CH$$

Ethene can be manufactured from propanone in a series of steps.



(i) Explain what is meant by the term *polymer*.

Polymers are macromolecules built up from monomers, with average molar mass of at least 1000 or at least 100 repeat units. [1]

(ii) State the types of reactions which occur in reaction (1) and step 2.

reaction (1): Addition polymerisation[1] step 2: Reduction[1]

(iii) Suggest reagents and conditions needed for step 3.

Excess concentrated H<sub>2</sub>SO<sub>4</sub>, 170 °C or Al<sub>2</sub>O<sub>3</sub>, 350 °C [1]

(iv) Calculate the enthalpy change for the reaction in reaction (1) if the value of n is 10. Use relevant information from the *Data Booklet*. Show your working.

 $\Delta H = BE(bonds broken) - BE(bonds formed)$ = 12BE(C=C) + BE(O-O) - 2BE(C-O) - (12+11)BE(C-C) = (12 x 610) + 150 - (2 x 360) - (23 x 360) = -1300 kJ mol<sup>-1</sup> [1] for quoting correct BE values [1] for final answer (c) Using a different catalyst and pressure, ethene can be polymerised to produce two types of polyethene – low-density polyethene (LDPE) and high-density polyethene (HDPE).

Table 7.2 shows the estimated melting points of polyethene.

polymer	melting point / °C
low density poly(ethene), LDPE	108
high density poly(ethene), HDPE	135

Table 7.2

Explain the differences in melting point of these polymers in terms of their structures and intermolecular forces between the chains. You may draw simplified diagrams of LDPE and HDPE to explain the difference in their melting points. Structural formulae of these polymers are **not** required.

In LDPE, the polymer chains are <u>highly branched</u>. The polymer chains <u>cannot be packed</u> <u>together closely and regularly</u>. This arrangement results in <u>empty spaces between</u> <u>polymer chains</u> and a smaller surface area of contact between adjacent chains. The <u>instantaneous dipole – induced dipole forces of attraction between polymer chains is</u> <u>weaker</u>. [1] explanation

In HDPE, the polymer chains have <u>minimal or no branching</u>. The polymer chains can be <u>packed closely together</u>, giving a <u>more regular structure</u>. The regular arrangement results in <u>less empty spaces</u> and a greater surface area of contact between adjacent chains. The <u>instantaneous dipole – induced dipole forces of attraction between polymer chains is</u> <u>stronger</u>. [1] explanation

Hence, more energy is needed to overcome the id-id forces of attraction between polymer chains in HDPE.

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[1] diagram

(d) An oil spill occurred in June 2024 after a digger collided with a stationary bunker vessel, causing oil from the vessel's damaged cargo tank to spill into the sea water. The clean-up effort, which has impacted parts of Singapore's shores, has teams of workers employed to remove oil-covered sand from the beach using sorbent pads and shovels.

There are various types of materials used in sorbent pads, including poly(propene), which can be made into sheets to absorb oil.

(i) Explain why propene, the monomer of poly(propene), is unable to exist as cis and trans isomers.

Cis-trans isomers cannot exist in propene as the carbon atoms on one end of the double bond contain <u>two H atoms</u>. [1]

(ii) Suggest the forces of attraction that exist between poly(propene) in sorbent pads and oil molecules.

Instantaneous dipole-induced dipole forces of attraction between poly(propene) and non-polar oil molecles. [1]

**8(a)** Hypophosphorous acid,  $H_3PO_2$  is an inorganic acid.

1.77 g of hypophosphorous acid was dissolved in water and made up to 250 cm<sup>3</sup> of aqueous solution. 25.0 cm<sup>3</sup> of the diluted solution required 26.75 cm<sup>3</sup> of 0.100 mol dm<sup>-3</sup> sodium hydroxide for neutralisation.

(i) The basicity of an acid is defined as the number of hydrogen ions which can be given out by one molecule of that acid. HCl, H<sub>2</sub>SO<sub>4</sub> and H<sub>3</sub>PO<sub>4</sub> are examples of monobasic, dibasic and tribasic acids respectively.

Determine the mole ratio of hypophosphorous acid and sodium hydroxide, hence deduce the basicity of the acid.

n(H<sub>3</sub>PO<sub>2</sub>) in 250 cm<sup>3</sup> =  $\frac{1.77}{66.0}$  = 0.02681 mol [1]

n(H<sub>3</sub>PO<sub>2</sub>) in 25.0 cm<sup>3</sup> diluted solution =  $0.02681 \times \frac{25.0}{250} = 0.002681$  mol [1]

mole ratio of acid : base =  $\frac{n(H_3PO_2)}{n(NaOH)} = \frac{0.002681}{0.100 \times \frac{26.75}{1000}} = \frac{0.002681}{0.002675} = 1.002 = 1$ 

H<sub>3</sub>PO<sub>2</sub> is monobasic / monoprotic. [1] for mole ratio and basicity

(ii) The diluted solution of hypophosphorous acid is found to have a pH of 2.9.

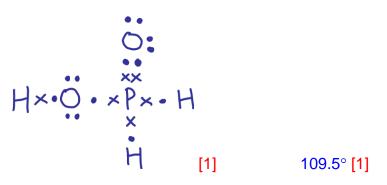
Determine by calculation whether hypophosphorous acid is a weak or strong acid.

[H<sub>3</sub>PO<sub>2</sub>] in diluted solution =  $\frac{0.002681}{\frac{25.0}{1000}}$  = 0.1072 = 0.107 mol dm<sup>-3</sup>

 $[H^+] = 10^{-2.9} = 0.001258 = 0.00126 \text{ mol dm}^{-3}$ [1] for  $[H_3PO_2]$  and  $[H^+]$ 

Since  $[H_3PO_2] > [H^+]$ ,  $[H_3PO_2]$  is partially ionised and a weak acid. [1]

(iii) Using your answer in (a)(i), draw a 'dot-and-cross' diagram to show the bonding in hypophosphorous acid. State the O-P-O bond angle.



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(b) The conjugate base of hypophosphorous acid is  $H_2PO_2^{-}$ .

 $H_2PO_2^-$  is a strong reducing agent. It can be used to reduce metal cations without the need for electrolysis.

Under alkaline conditions, H<sub>2</sub>PO<sub>2</sub><sup>-</sup> reduces Ni<sup>2+</sup> to Ni and is itself oxidised to HPO<sub>3</sub><sup>2-</sup>.

(i) Write a half-equation for the oxidation of  $H_2PO_2^-$  to  $HPO_3^{2-}$ , under alkaline conditions.

 $H_2PO_2^- + 3OH^- \rightarrow HPO_3^{2-} + 2H_2O + 2e^-$ [1]

(ii) Using your answer to (b)(i), construct a balanced equation for the reaction between  $H_2PO_2^-$  and  $Ni^{2+}$ .

 $H_2PO_2^- + Ni^{2+} + 3OH^- \rightarrow HPO_3^{2-} + Ni + 2H_2O$  [1]

(iii) The high conductivity of nickel is a consequence of its electronic configuration. Complete the electronic configuration of a nickel atom, Ni.

Ni  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^8 4s^2$  [1]

(iv) Using your answer to (b)(iii), state the number of unpaired electrons of a nickel atom, Ni in its ground state.

2 unpaired electrons [1]

(c)  $H_2PO_2^{-}(aq)$  reacts with  $OH^{-}(aq)$ .

$$H_2PO_2^{-}(aq) + OH^{-}(aq) \rightarrow HPO_3^{2-}(aq) + H_2(g)$$

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Table 8.1 shows the results of a series of experiments used to investigate the rate of this reaction.

experiment	[H₂PO₂⁻(aq)] / mol dm <sup>-3</sup>	[OH⁻(aq)] / mol dm <sup>-3</sup>	volume of H <sub>2</sub> produced in 60 s / cm <sup>3</sup>
1	0.40	2.00	6.4
2	0.80	2.00	12.8
3	1.20	1.00	4.8

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(i) Use of the Data Booklet is relevant to this question.

6.4

The volume of H<sub>2</sub> was measured under room conditions.

Use the molar volume of gas,  $V_m$  to calculate the rate of reaction for experiment 1 in mol dm<sup>-3</sup> s<sup>-1</sup>.

rate of reaction =  $\frac{24000}{60}$  = 4.444 × 10<sup>-6</sup> = 4.44 × 10<sup>-6</sup> mol dm<sup>-3</sup> s<sup>-1</sup> [1]

(ii) Use data from Table 8.1 to determine the order of reaction with respect to  $H_2PO_2^-$  and  $OH^-$  respectively and hence deduce the rate equation for this reaction.

Comparing experiment 1 and 2:

As  $[H_2PO_2^-]$  doubles from 0.40 to 0.80 mol dm<sup>-3</sup>,

V(H<sub>2</sub>) produced in 60 s doubles from 6.4 to 12.8 cm<sup>3</sup> / rate of reaction doubles from  $4.44 \times 10^{-6}$  to  $8.88 \times 10^{-6}$  mol dm<sup>-3</sup> s<sup>-1</sup>. Rate is directly proportional to [H<sub>2</sub>PO<sub>2</sub><sup>-</sup>].  $\therefore$  first order with respect to H<sub>2</sub>PO<sub>2</sub><sup>-</sup> [1]

Comparing experiment 1 and 3:

Method 1

Let the order of reaction with respect to OH<sup>-</sup> be x

Expt 1:	$4.444 \times 10^{-6} = k(0.40)(2.00)^{\times}$	(1)
Expt 3:	$3.333 \times 10^{-6} = k(1.20)(1.00)^{x}$	(2)

Divide (1) by (2), so as to eliminate k:

$$\frac{4.444 \times 10^{-6}}{3.333 \times 10^{-6}} = \frac{k}{k} \times \frac{0.40}{1.20} \times \left(\frac{2.00}{1.00}\right)^{x}$$
$$2^{x} = 4$$
$$x = 2$$

Therefore, order of reaction is 2 with respect to OH<sup>-</sup>[1]

### Method 2

Comparing experiment 1 and 3:

As reaction is first order w.r.t.  $[H_2PO_2^-]$ , when  $[H_2PO_2^-]$  increases by 3 times from 0.40 to 1.20 mol dm<sup>-3</sup>, V(H<sub>2</sub>) produced in 60 s should increase by 3 times from 6.4 to 19.2 cm<sup>3</sup>. When  $[OH^-]$  decreases by 2 times from 2.00 to 1.00 mol dm<sup>-3</sup>, V(H<sub>2</sub>) produced in 60 s decreases by 4 times from 19.2 to 4.8 cm<sup>3</sup>  $\therefore$  second order wrt OH<sup>-</sup> [1]

rate =  $k[H_2PO_2^-][OH^-]^2[1]$ 

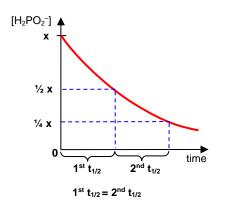
(iii) Use your answer to (c)(ii) and the data from experiment 1 to calculate a value for the rate constant, *k* and state its units.

rate =  $k [H_2 PO_2^-] [OH^-]^2$ 

 $4.444 \times 10^{-6} = k (0.40) (2.00)^2$ 

 $k = 2.78 \times 10^{-6}$  [1] mol<sup>-2</sup> dm<sup>6</sup> s<sup>-1</sup> [1]

(iv) Sketch a graph of [H<sub>2</sub>PO<sub>2</sub><sup>-</sup>] against time for this reaction when [OH<sup>-</sup>] is in large excess.



[1] for curve shape and constant half-life

For Examiner's Use (v) A student suggests that the reaction between H<sub>2</sub>PO<sub>2</sub>-(aq) and OH-(aq) might happen more quickly in the presence of a heterogeneous catalyst.

Outline the mode of action of a heterogeneous catalyst.

1. <u>Reactants diffuse towards catalyst surface and become chemically</u> adsorbed on neighbouring active sites. [1]

2. <u>The formation of these bonds cause the covalent bonds within the reactants</u> to weaken, hence lowering the activation energy of the reaction. The adsorbed reactants are also held in the right orientation for reaction to occur, hence increasing the frequency of effective "collisions". [1]

3. Eventually, the molecules dissociate, forming highly reactive intermediates which then combine to form the products. <u>After reaction, the products break</u> <u>free (desorb) from the surface and diffuse away from the surface.</u> [1]