| | NANYANG JUNIOR COLLEGE JC 2 PRELIMINARY EXAM Higher 1 | | | | | | |
|---|---|--------------------|--|--|--|--|--|
| CANDIDATE NAME | | | | | | | |
| CLASS | TUTOR'S NAME | | | | | | |
| CHEMISTRY Paper 2 Candidates answer Section A on the Question Paper. Additional Materials: Answer Paper Data Booklet | | | | | | | |
| READ THESE INSTRUCTIONS FIRST Write your name and class on all the work you hand in. Write in dark blue or black pen on both sides of the paper. | | | | | | | |
| | off pencil for any diagrams, graphs or rough working. s, paper clips, highlighters, glue or correction fluid. | | | | | | |
| Section A Answer all question | ons. | For Examiner's Use | | | | | |
| Section B Answer two ques | tions on separate answer paper. | A 1 | | | | | |
| At the end of the | A2 | | | | | | |
| | arks is given in brackets [] at the end of each question or part | А3 | | | | | |
| | | | | | | | |
| | | B1 | | | | | |
| | | B2 | | | | | |
| | | В3 | | | | | |

Total

Section A

Answer all questions in this section in the spaces provided.

For examiner's use only

1(a) A sample of carbon containing different isotopes was artificially enriched. The relative isotopic masses and its relative abundances determined in a mass spectrometer are given in the table below.

| Relative isotopic mass | Relative abundance | |
|------------------------|--------------------|--|
| ¹² C | 85.0 % | |
| ¹³ C | 10.0 % | |
| ¹⁴ C | 5.0 % | |

Calculate the relative atomic mass of carbon in the sample to 1 decimal place.

[1]

$$A_r = 12 \times 0.850 + 13 \times 0.100 + 14 \times 0.050 = 12.2$$

[1]

(b) A 0.100 mol of a hydrocarbon **W** was burnt completely to produce 26.4 g of carbon dioxide gas and 10.8 g of water.

The same mass of $\bf W$ when burnt under a container with 300 g of water at 30 $^{\circ}$ C was found to bring the water to boil. The process was known to be only 70% efficient.

The specific heat capacity of water is 4.2 J g⁻¹ K⁻¹.

(i) Determine the molecular formula of the hydrocarbon W.

[2]

$$C_xH_y + (x + \frac{1}{4}y)O_2 \rightarrow xCO_2 + \frac{1}{2}y (H_2O)$$

Amt of CO_2 formed = 26.4 / 44.0 = 0.600 mol

Amt of
$$H_2O$$
 formed = 10.8 / 18.0 = 0.600 mol

[1]

| | C_xH_y | CO ₂ | H ₂ O |
|--------------|----------|-----------------|------------------|
| n | 0.100 | 0.600 | 0.600 |
| Lowest ratio | 1 | 6 | 6 |
| Mol ratio | 1 | Х | ½ y |

∴ Comparing coefficient x = 6

$$6 = \frac{1}{2} \text{ y} \Rightarrow \text{y} = 12$$
 [1]

Molecular formula **T** is C₆H₁₂

(ii) Calculate the enthalpy change of combustion of W.

[2]

Heat lost from combustion = heat gained by water

[1]

[1]

$$\Delta H_c = \frac{\text{m c } \Delta T}{\text{n}} = -\frac{300 \times 4.2 \times (100-30)}{0.100} \div \frac{70}{100}$$
$$= -1260 \ 000 \ \text{J mol}^{-1} = -1260 \ \text{kJ mol}^{-1}$$

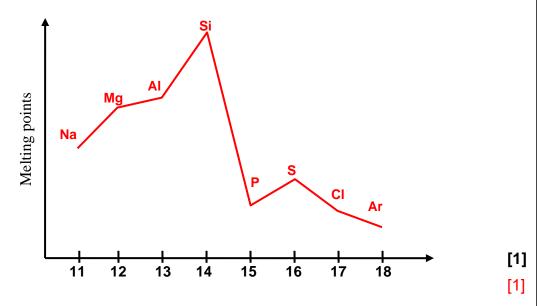
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(c) Arranging the following in order of increasing boiling points. Explain your choice in terms of structure and bonding.

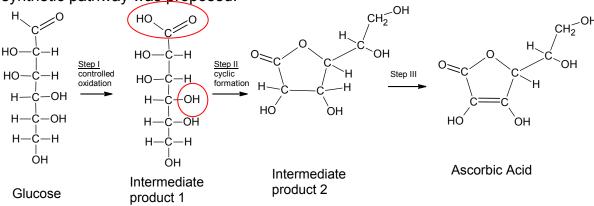
H₂O, NH₃, NaCl, CH₄ [5] H₂O, NH₃, CH₄ and C₆H₁₄ have simple molecular structure consisting of [1] molecules held together by weak forces. CH₄ consists of simple non–polar molecules held together by weak van [1] der waals forces. NH₃ and H₂O molecules are held together by stronger hydrogen bonds [1] thus have higher boiling points than C₆H₁₄. H₂O has higher boiling points than NH₃ because it has 2 hydrogen-lone pair units per molecule thus has more hydrogen bonds per molecule. [1] NaCl has giant ionic structure consisting of Na⁺ and Cl⁻ ions held together by strong electrostatic forces of attraction thus has highest boiling point. [1]

[Total: 10 marks]

2 (a) (i) Complete the graph below for the melting points of elements in period 3.



- (ii) Explain the shape of your graph in terms of bonding and structure. [5]
 - Na, Mg and Al have giant metallic structures with strong [1] electrostatic attraction between the cations and the sea of delocalized electrons.
 - The metallic bonds increases as more electrons are added to the [1] sea of delocalized electrons.
 - Si has a giant molecular structure consisting of Si atoms held [1] together by very strong covalent bonds.
 - P, S, Cl and Ar have simple molecular structure consisting of [1] molecules or atoms held by weak van der Waals' forces.
 - The melting points are in the order of S₈> P₄ > Cl₂ > Ar as van der Waals' forces are proportional to the number of electrons in the [1] molecules / atoms.
- **(b)** The building block for ascorbic acid is the glucose molecule. The following synthetic pathway was proposed:



For examiner's use only

(i) State the type of reaction found in **step II** and hence <u>circle</u> the functional group(s) present in the <u>intermediate product 1</u> that is/are involved in the reaction.

Condensation [1]; both circles correct [2]

(ii) State the type of reaction present in **Step III**.

[1]

[2]

[3]

Elimination

(c) Aspirin, also known as acetylsalicylic acid is often used as an analgesic (pain-remover) to relieve minor aches and pains. It is readily absorbed from the intestines since it diffuses rapidly into the tissues.

The molecule is hydrolysed by acids in the stomach.

(i) Draw the structural formulae of the hydrolysis products.

$$H_3C-C$$
OH
 CO_2H
OH
 CO_2H
 CO_2H

Aspirin can be synthesised from 2-methylphenol via the following steps:

2-methylphenol Aspirin

(ii) Draw the structural formula of the intermediate A. [1]

(d) The enthalpy of combustion of Compound A, CH₂=CHCO₂H, can be determined either by direct measurement of the heat evolved using a bomb calorimeter or by indirect method using Hess Law.

The energy cycle involving Compound **A** is given below.

$$CH_{2}CHCO_{2}H(I) + H_{2}(aq) \xrightarrow{\Delta H_{c}} 3CO_{2}(g) + 2H_{2}O(I) + H_{2}(g)$$

$$\Delta H_{1} = +1/2 O_{2} \Delta H_{3} = -286 \text{ kJ mol}^{-1}$$

$$CH_{3}CH_{2}CO_{2}H(I) \xrightarrow{+7/2 O_{2}} 3CO_{2}(g) + 3H_{2}O(I)$$

$$\Delta H_{2} = -1450 \text{ kJ mol}^{-1}$$

- (i) Name the enthalpy change represented by ΔH_2 [1]
 - ΔH_2 : Enthalpy of combustion of propanoic acid [1]
- (ii) State the type of reaction for ΔH_1 . [1]

Reduction reaction [1]

(iii) Using Hess' Law, calculate the enthalpy change of combustion of compound A. [1]

$$\Delta H_c + (-286) = -380 + (-1450)$$

 $\Delta H_c = -1544 \text{ kJ mol}^{-1}$ [1]

[Total: 16 marks]

- **3(a)** Hydrogen peroxide, H_2O_2 , is a strong oxidizing agent and is used as an antiseptic. However, it is not stable at room temperature and will undergo decomposition reaction.
 - (i) Draw the dot and cross diagram of H_2O_2 . [1]



[1]

(ii) State, with reason, the shape about the oxygen atom.

[2]

[1]

[1+1]

(iii) State the oxidation number of O in the reactants and products.

O in $H_2O_2 : -1$

uncatalysed reaction.

- O in $H_2O = -2$
- O in $O_2 = 0$ [1]
- (iv) Hence write two balanced half and overall equations for the decomposition of H_2O_2 .

[2]

[1]

[1]

[4]

$$H_2O_2 + 2H^+ + 2e \rightarrow 2H_2O$$

$$H_2O_2$$

No of

molecules

No of molecules with energy ≥ Ea

No of molecules with energy ≥ Ea_c (catalysed)

(b) The rate of H₂O₂ decomposition can be catalysed by adding small amounts of MnO₂. Using an appropriate diagram, explain in molecular terms, how the presence of MnO₂ catalyst increases the rate of decomposition of H₂O₂.



Ea_c E_a
Catalysed rxn uncatalysed rxn

- Catalysed rxn uncatalysed rxn

 The presence of a catalyst, lowers the activation energy compared to the [1]
 - to the [1]
- More molecules will possess energy greater than or equal to this lowered activation energy,
- hence frequency of activated collisions will increase.

[1]

[1]

(c) An experiment in the laboratory found that iodide ions are oxidized by hydrogen peroxide according to the equation below:

$$H_2O_2$$
 (aq) + $2H^+$ (aq) + $2I^-$ (aq) $\rightarrow I_2$ (aq) + $2H_2O$ (I)

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Assuming the rate of the above reaction is zero order with respect to $[H^+]$, determine the order of reaction with respect to $[H_2O_2]$ and $[I^-]$ based on the experimental results shown below. Hence determine the value for the rate constant of the reaction, stating the units.

| Expt | [H ₂ O ₂] / mol dm ⁻³ | [l ⁻] / mol dm ⁻³ | Initial rate / mol dm ⁻³ s ⁻¹ |
|------|---|--|---|
| 1 | 0.01 | 0.02 | 0.8 x 10 ⁻⁴ |
| 2 | 0.01 | 0.03 | 1.2 x 10 ⁻⁴ |
| 3 | 0.03 | 0.04 | 4.8 x 10 ⁻⁴ |

[4]

Rate = $k[H_2O_2]^m [I^-]^n$

Using Expt 1 and 2

$$\frac{1.2 \times 10^{-4}}{0.8 \times 10^{-4}} = \frac{k (0.01)^m (0.03)^n}{k (0.01)^m (0.02)^n}$$

$$1.5 = (1.5)^n \Rightarrow n = 1$$
[1]

Using expt 1 and 3

$$\frac{4.8 \times 10^{-4}}{0.8 \times 10^{-4}} = \frac{k (0.03)^{m} (0.04)^{1}}{k (0.01)^{m} (0.02)^{1}}$$

$$6 = 2(3)^{m} \Rightarrow m = 1$$
[1]

Rate = $k[H_2O_2][I^-]$

Substituting values from expt 2

1.2 x
$$10^{-4}$$
 = k(0.01) (0.03) \Rightarrow k = 0.4 mol⁻¹ dm³ s⁻¹ [1+1]

[Total: 14 marks]

Section B

Answer **two** of the following three questions. Answer these questions on separate answer paper.

1(a) (i) Aluminium(III) oxide and phosphorous(V) chloride differ in their behaviour with water.

Write balanced equations (if any) for each of the behaviour. [2]

$$AI_2O_3 + H_2O \rightarrow No reaction$$
 [1]

$$PCI_5 + 4 H_2O \rightarrow H_3PO_4 + 5 HCI$$
 [1]

- (ii) Explain these differences in terms of the different structures and types of [2] chemical bonding in the compounds.
 - Al₂O₃ very strong ionic bonds, high lattice energy no reaction with [1] water
 - PCI_5 simple molecular structure, molecule undergoes hydrolysis to [1] form an acidic solution
- **(b)** In each of the following reactions, describe the way in which the oxide of the named element is reacting and discuss whether its behaviour is what you would expect from the position of the element in the Periodic Table:
 - (i) Silicon: MgO + SiO₂ \rightarrow MgSiO₃
 - (ii) Beryllium: 2 NaOH + BeO \rightarrow Na₂BeO₂ + H₂O [4]
- (i) [1] SiO₂ acted as an **acidic oxide** as it formed a salt with the basic oxide MgO.
 - [1] It is acting **as expected** of a **Group 4** member as **non-metal oxides** are expected to be acidic.
- [1] BeO acted as an **acidic oxide** as it formed a salt with the basic hydroxide / alkali NaOH.
 - [1] It is **not acting as expected** of a **Group 2** member as **metal oxides** are expected to be basic.

[Additional info for students: in actual fact, due to high charge density of Be^{2^+} ion, BeO shows a high degree of covalency, and is amphoteric like Al_2O_3). Hence, BeO also shows acidic properties and would react with alkali NaOH to give a salt, Na_2BeO_2 and water.]

(c) Ascorbic acid, also known as vitamin C is required for the synthesis of collagen in humans. A vitamin C deficient diet leads to a disease called scurvy. Ascorbic acid is known to be water soluble and is commonly used as food additives.

Ascorbic Acid

- (i) Name the four functional groups present in the ascorbic acid compound. [2]
 [1/2 each] .Ester, secondary alcohol, primary alcohol, alkene
- (ii) Explain in terms of structure and bonding, why Ascorbic Acid is water soluble. [2]
 - [1] The molecule has **many OH** (or alcohol or hydroxy) groups
 - [1] that allows it to form (intermolecular) **hydrogen bonds with water** molecules

making it soluble in water.

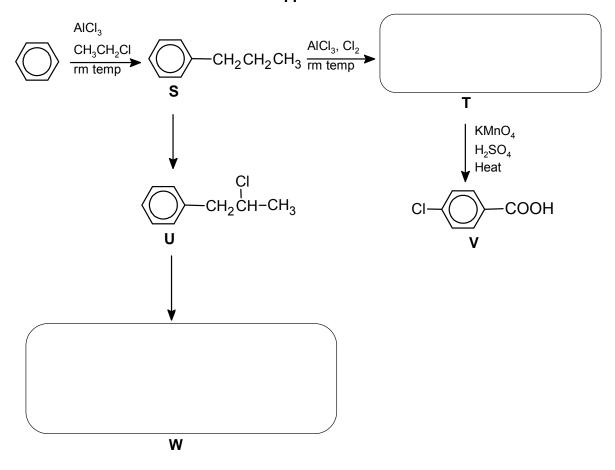
(ii) The ascorbic acid molecule was reacted with acidified potassium dichromate (VI) followed by 2,4-dinitrophenylhydrazine. Draw the structural formula of the product formed. [2]

$$\begin{array}{c|c}
O & O & O \\
O & C & O \\
O & C & N-N \\
HO & OH & NO_2
\end{array}$$

- [1] For changing primary alcohol to carboxylic acid
- [1] For reacting resultant ketone with 2,4-DNPH.

(minus [1] for any other mistakes until 0)

(d) Benzene is used as the starting reagent for the production of many aromatic compounds shown below.



(i) Give the corresponding structural formula for **T**. [1]

$$CI \longrightarrow CH_2CH_2\cdot CH_3$$
 [1]

- (ii) Suggest the reagents and conditions needed to convert **S** to **U**. [1]
 - [1] Cl₂, UV light / heat
- (iii) U can react with a suitable reagent to give W, C₉H₁₀, which exists as a pair of geometric isomers.

Name the reaction for the formation of **W** and hence suggest the reagents and condition needed to form **W**. [2]

- [1] Elimination reaction
- [1] Ethanolic sodium hydroxide, heat
- (iv) Draw the pair of geometric isomers of W. [2]

$$C=C$$
 CH_3
 $C=C$
 CH_3
 $C=C$
 CH_3

- [1] cis and trans arrangements
- [1] correct groups

[Total: 20 marks]

2(a) The reaction between 2-hydroxypropanonic acid and ethanol occurs as follows:

 $CH_3CH(OH)CO_2H$ (aq) + CH_3CH_2OH (aq) — $CH_3CH(OH)CO_2CH_2CH_3$ (aq) + H_2O (aq)

The above reaction was carried out by heating 500 cm^3 of 0.10 mol dm^{-3} 2–hydroxypropanonic acid with 500 cm^3 of 0.10 mol dm^{-3} of ethanol for some time in the presence of acid catalyst. When the reaction vessel was subsequently cooled rapidly in ice bath, it was found that 1.67×10^{-2} mol of acid and ethanol was left in the reaction vessel.

- (i) Explain the purpose of cooling the reaction vessel rapidly. [1]
 - It is to stop the reversible reaction form taking place (to prevent the position of equilibrium from shifting) so that the amounts of reactants / products can be determined. [1]
- (ii) Write an expression for the equilibrium constant, K_c, for the above equilibrium. [1]

$$K_{c} = \frac{[CH_{3}CH(OH)CO_{2}CH_{2}CH_{3}]}{[CH_{3}CH(OH)CO_{2}H][CH_{3}CH_{2}OH]}$$
[1]

(iii) Calculate the concentration of the ester present at equilibrium and hence determine the value of K_c, stating its units. [3]

Since total volume is 1 dm³,

amt of ester formed in 1 dm³ = amt of acid (or alcohol) reacted

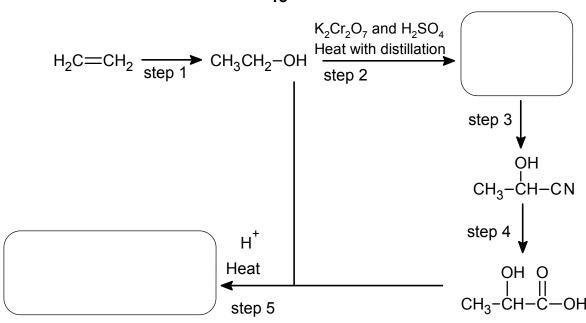
$$= \left(\frac{500}{1000} \times 0.10\right) - \left(1.67 \times 10^{-2}\right) = 0.0333 \text{ mol}$$
 [1]

$$K_c = \frac{0.0333}{(0.0167)(0.0167)} = 3.98 \text{ mol}^{-1} \text{ dm}^3$$
 [2]

(iv) State and explain, in terms of La Chatelier's Principle, the effect on the position of equilibrium if a small amount of ester was added to the reaction before it was rapidly cooled. [1]

According to Le Chatelier's Principle, the position of equilibrium would shift left to remove some of the added ester. [1]

(b) The synthesis of the ester can be done by using ethene as the starting reagent shown below.



- (i) State the reagents and conditions for Steps 1 and 3. [4]
 - Step 1: Steam, conc. H₃PO₄, 60 atm, 300 °C [2]
 - Step 3: HCN, trace NaCN or NaOH, 10–20 °C [2]
- (ii) Draw the structure of the products of Step 2 and 5. [2]

(iii) Name the type of reaction taking place in Step 4.

Acid hydrolysis [1]

[1]

- **(c)** Suggest a simple chemical test to distinguish the following pairs of compounds. Your answers should include the reagents and conditions for each test and the observations you would expect to see for each compound.
 - (i) $CH_3CHCICH_3$ and CH_3CHICH_3 [3]

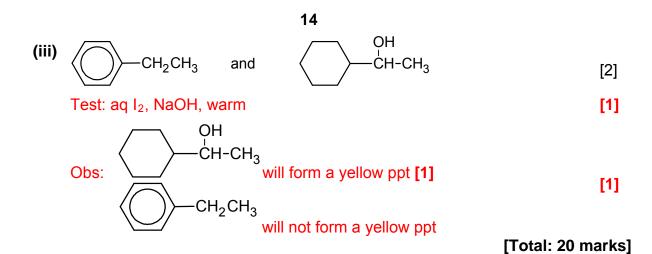
Test: Add ethanolic AgNO₃ to each sample and heat

OR Add NaOH and heat, followed by dil HNO3 and AgNO₃ [1]

Observation: White ppt formed for CH₃CHClCH₃ [1] while yellow ppt formed for CH₃CHICH₃ [1]

(ii) $CH_3C(OH)CICH_2CH_3$ and $CH_3COCH(OH)CI$ [2]

Test: Heat [1] both samples with KMnO₄ and H₂SO₄ [1]
Observation: With CH₃COCH(OH)Cl, purple KMnO₄ will decolourise [1]
With CH₃C(OH)ClCH₂CH₃, KMnO₄ will remain purple



- **3(a)** Ethanoic acid is an organic compound and is able to function like mineral acid by providing H⁺ (aq) ions in solution. The numerical value for the acid dissociation constant, K_a, of ethanoic acid is 1.74 x 10⁻⁵.
 - (i) Given the pH of ethanoic acid is 2.88 determine the concentration of the H⁺ ions present in solution. [1]

$$[H^{+}] = 10^{-2.88} = 1.32 \text{ x } 1.0^{-3} \text{ mol dm}^{-3}$$

(ii) State with reason whether ethanoic acid is a weak or strong acid. [1]

Since [ethanoic acid] >>> [H⁺] ethanoic acid

- ⇒ dissociation of acid is incomplete thus ethanoic acid is a weak acid. [1]
- (iii) Write a balanced equation to show how ethanoic acid functions as an acid in aqueous solution and hence write the expression for the acid dissociation constant, K_a. [2]

$$CH_3COOH + H_2O - CH_3COO^- + H_3O^+$$
 [1]

$$K_a = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]}$$
 [1]

(iv) Based on your answers from (a)(i) - (iii), determine the initial concentration of ethanoic acid. [1]

$$1.74 \times 10^{-5} = \frac{(1.32 \times 10^{-3}) (1.32 \times 10^{-3})}{[CH_3COOH]}$$

$$[CH_3COOH] = 0.100 \text{ mol dm}^{-3}$$
[1]

- (b) When 20 cm³ of 0.050 mol dm⁻³ sodium hydroxide was added into a bottle containing 40 cm³ of 0.050 mol dm⁻³ ethanoic acid and some universal indicator. The colour of the resulting solution changed from red to orange. When 5 cm³ of 0.050 mol dm⁻³ of sodium hydroxide or hydrochloric acid was added, the colour of the solution remained orange.
 - (i) Deduce the species present in the solution after sodium hydroxide was added into the bottle. Hence, state the type of solution formed.. [2]
 - Sodium ethanoate, ethanoic acid and water. A buffer solution is formed. [2]
 - (ii) By means of suitable equations, explain how the species present in the resulting solution is able to cause the colour of the solution to remain orange upon adding small volumes of sodium hydroxide or hydrochloric acid.

 [4]

$$CH_3COO^-Na^+ + H^+ \rightarrow CH_3COOH$$
 [1]

The <u>large reservoir of CH_3COO^2 ions</u> removes the added H^+ to <u>form the</u> [1] <u>molecular acid</u> thus maintaining the pH of the solution constant and the colour of solution remains orange.

 CH_3COOH + $OH^- \rightarrow CH_3COO^-Na^+$ [1]

The <u>large reservoir of CH₃COOH molecules</u> remove the added OH⁻ to [1] <u>form neutral water</u>, thus maintaining the pH of the solution constant and the colour of solution remains orange.

(c) An organic compound E, C₄H₈, can exists as a pair of geometrical isomers.

E undergoes reduction to give butane, C₄H₁₀.

Oxidation of 1 mole of E using potassium manganate (IIV) solution produces 2 moles of F, $C_2H_4O_2$.

However, changing the oxidation conditions produces \mathbf{G} , $C_4H_{10}O_2$.

E reacts with aqueous bromine to give **H**, C₄H₉OBr, which gives a positive test when warmed with alkaline aqueous iodine.

(i) State the reagents and conditions needed for the reduction of E to form [2] butane.

H₂ [1]

Ni catalyst, heat **OR** Pt or Pd catalyst at rm temp [1]

(ii) Draw the structure of the 2 isomers of E. [2]

$$H_3C$$
 CH_3 H_3C H $C=C$ $C=C$ CH_3 CH_3 [2]

(iii) Give the structural formula of **F**. [1]

(iv) Name the functional group present in G and hence suggest the conditions needed to produce **G**. [2]

2º alcohol [1]

Cold acidic / alkaline dil KMnO₄ [1]

(v) Write a balanced equation when **H** reacts with alkaline agueous iodine. [2]

$$CH_3CHBrCH(OH)CH_3 + 4I_2 + 6NaOH \rightarrow$$

[Balanced Eqn: 1m]

[Correct cpd: 1m]

[Total: 20 marks]