Class Adm No

Candidate Name: _____

H

millennia institute

2022 Preliminary Exams
Pre-University 3

H2 CHEMISTRY **9729/02**

Paper 2 Structured Questions **14 Sep 2022**

2 hours

Candidates answer on the Question paper.

Additional materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Do not turn over this question paper until you are told to do so

Write your name, class and admission number on all the work 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.

Answer **all** questions.

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

A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.

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

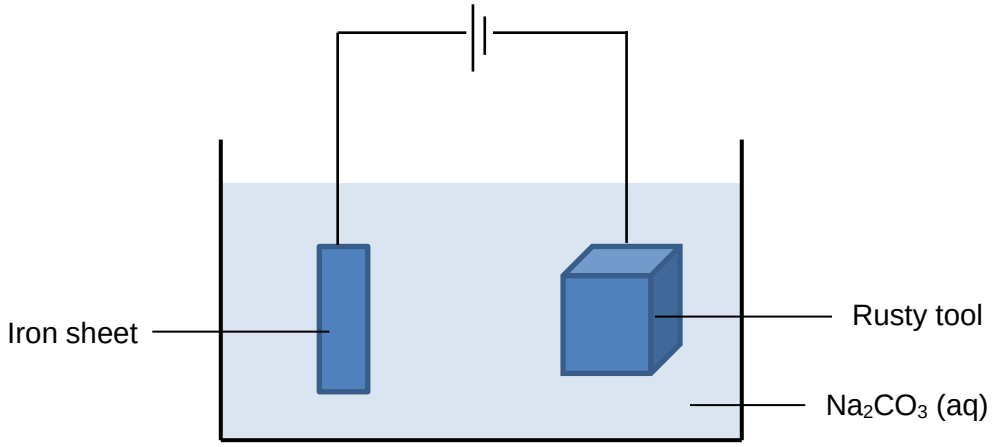
Question	1	2	3	4	5	Total
Marks	/20	/13	/24	/9	/9	/75

Answer all questions in the spaces provided.

1 Many household tools are made from stainless steel as it is highly resistant to corrosion and rust. Stainless steel contains iron, chromium, manganese, nickel, molybdenum, silicon and carbon which interacts with oxygen from water and air to form oxides. Of these elements, chromium has the highest resistance to corrosion.

Despite the high resistance, rusting still occurs in a humid environment. A 'Do-it-Yourself' (DIY) kit has been launched in the market to remove rust from household tools and the set-up is shown in **Figure 1.1**.

Figure 1.1



(a) **(i)** State if the iron sheet is the anode or the cathode. [1]

anode

(ii) *Use of Data Booklet is relevant to this question.*

State and explain the observations found at the iron sheet electrode. [2]

The iron sheet will becomes smaller. (;)

$Fe \rightarrow Fe^{2+} + 2e$ $\quad E^{\circ} = -0.44$ V

$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ $\quad E^{\circ} = +1.23$ V (;)

Since $E^{\circ}_{Fe2+/Fe}$ is more negative than $E^{\circ}_{(O2/H2O)}$), Fe is preferentially oxidized to Fe^{2+}. (;)

(iii) Suggest why carbonate ions from Na_2CO_3 electrolyte cannot be oxidised at the anode. [1]

Carbon in carbonate is at the maximum oxidation state of +4 or the electrode potential involving carbonate ion is very positive.

(iv) A consumer saw the DIY kit and decided to purchase it and try out on his rusted dumbbell. He prepared the set up as shown in **Figure 1.1** with a 20 A power source and switched it on for 6 hours.

Determine the change in mass of the iron sheet. [2]

Q = It = 20 x 6 x 60 x 60 = 432000 C

Amount of electrons = 432000 / 96500 = 4.477 mol (;)

Amount of Fe = 4.477 / 2 = 2.238 mol

Mass of Fe = 2.238 x 55.8 = 125 g (;)

(b) Fe_2O_3 is the main constituent of the rust found on household items. The standard electrode potentials involving the iron containing species can be found in **Table 1.1**.

Table 1.1

Half-equations	E^{θ}/ V
$3Fe_2O_3 + H_2O + 2e \rightleftharpoons 2OH^- + 2Fe_3O_4$	–0.62
$Fe_2O_3 + 3H_2O + 6e \rightleftharpoons 2Fe + 6OH^-$	–0.88
$Fe_3O_4 + 4H_2O + 8e \rightleftharpoons 3Fe + 8OH^-$	–0.91

A layer was coated around the rusty tool after using the DIY kit.

With reference to the standard electrode potentials given in **Table 1.1**, explain fully whether the layer coated is iron. [2]

Using data from the question,

$$3Fe_2O_3 + H_2O + 2e \rightleftharpoons 2OH^- + 2Fe_3O_4 \qquad E^{\theta} = –0.62V$$

$$Fe_2O_3 + 3H_2O + 6e \rightleftharpoons 2Fe + 6OH^- \qquad E^{\theta} = –0.88V$$

The layer is Fe_3O_4. Since $E^{\circ}_{Fe2O3/Fe3O4}$ is more positive/less negative than $E^{\circ}_{Fe2O3/Fe}$, Fe_2O_3 will be reduced to Fe_3O_4 and not to Fe. (;)

$$Fe_3O_4 + 4H_2O + 8e \rightleftharpoons 3Fe + 8OH^- \qquad E^{\theta} = –0.91V$$

It is not possible to regenerate pure iron as the reduction potential $E^{\circ}_{Fe3O4/Fe}$ is the least positive/most negative, thus Fe_3O_4 will not be further reduced. (;)

Hence, the layer coated is Fe_3O_4.

(c) The metal alloy that made up the main components of stainless steel are transition metals.

(i) Define *transition metal*. [1]

A transition element is a **d-block element** which forms **at least one simple ion**, in compounds, with a **partially filled d-subshell**.

(ii) State a physical property of transition metals which makes them a suitable material used for household tools compared to main group metals. [1]

They have high densities

(iii) Iron(III) ions catalyse the reaction between I^- ions and $S_2O_8^{2-}$ ions through homogeneous catalysis.

Explain the term *homogeneous catalyst*. [1]

The catalyst is in the same phase as the reactants and it speeds up the rate of reaction by lowering the activation energy without itself being chemically changed at the end of the reaction. .

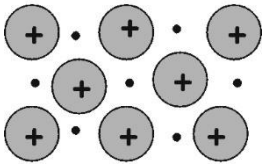
(iv) By considering relevant $E^{\ominus}$ values from the Data Booklet, and using balanced equations, determine whether chromium(III) ions are suitable catalyst for the reaction between I^- ions and $S_2O_8^{2-}$ ions. [2]

No it is not suitable as the E_{cell} for one of the step is less than zero, making the reaction non-spontaneous. (;)

$2Cr^{3+} + 2I^- \rightarrow I_2 + 2Cr^{2+}$ $E_{cell} = -0.41 - (+0.54) = -0.95$ V(;)

$2Cr^{2+} + S_2O_8^{2-} \rightarrow 2Cr^{3+} + 2SO_4^{2-}$ $E_{cell} = +2.01 - (-0.41) = +2.42$ V

(v) Describe the structure and bonding in the element chromium. Draw a diagram to illustrate your answer. [2]



(;)

Cr has giant metallic structure held by strong electrostatic forces of attraction between (positive) chromium ions and 'sea' of delocalised electrons. (;)

(d) Chromium(III) oxide has the same acid-base behaviour as aluminium oxide.

(i) State the type of oxide chromium(III) oxide exists as in terms of its acid-base behaviour. [1]

Amphoteric oxide

(ii) By quoting relevant data from the *Data Booklet*, explain why chromium(III) oxide and aluminium oxide have the same acid-base behaviour. [2]

Cr^{3+} has an ionic radius of 0.062 nm while Al^{3+} has an ionic radius of 0.050 nm (;) while both have the charge of +3. As the charge density of the cations are similar(;), they have similar degree of covalent character, hence behave similarly.

(iii) *Use of Data Booklet is relevant to this question.*

Describe the observations when dilute NaOH is slowly added to the solution containing chromium(III) ions until in excess. [2]

Grey-green precipitate is formed which dissolves in excess to give a dark green solution.

[Total: 20]

2 **(a)** An aqueous solution of chlorine dioxide undergoes disproportionation in sodium hydroxide to form chlorate(V) ion, ClO_3^-, and hypochlorite ion, ClO^-. The reaction is catalysed by OBr^- ion.

$$4ClO_2(aq) + 4OH^-(aq) \xrightarrow{OBr^-} 3ClO_3^-(aq) + ClO^-(aq) + 2H_2O(l)$$

To study the kinetics of this reaction at 25 °C, initial rates were measured using various concentrations of ClO_2, OH^- and OBr^-.

experiment	$[ClO_2]$/ mol dm^{-3}	$[OH^-]$/ mol dm^{-3}	$[OBr^-]$ / mol dm^{-3}	initial rate/ mol dm^{-3} s^{-1}
1	0.02	0.05	0.01	2.30×10^{-3}
2	0.10	0.02	0.03	6.90×10^{-2}
3	0.02	0.10	0.01	4.60×10^{-3}
4	0.04	0.02	0.03	1.10×10^{-2}

(i) Explain, in terms of oxidation numbers, why this reaction is a disproportionation reaction. [2]

The oxidation number of Cl in ClO_2 increases from +4 to +5 in ClO_3^- and decreases from +4 to +1 in ClO^-.(;) Since ClO_2 is oxidised and reduced at the same time(;), it is a disproportionation reaction.

(ii) Determine the orders of reaction with respect to ClO_2, OH^- and OBr^-. [3]

Comparing experiment 1 and 3, when $[OH^-]$ increases by 2 times, keeping $[ClO_2]$ and $[OBr^-]$ constant, initial rate is increased by 2 times, order of reaction w.r.t OH^- is 1.

Comparing experiment 2 and 4, when $[ClO_2]$ increase by 2.5 times, keeping $[OH^-]$ and $[OBr^-]$ constant, initial rate is increased by 6.27 times, order of reaction w.r.t. ClO_2 is 2.

Let the rate equation be: rate = $k[ClO_2]^2[OH^-][OBr^-]^x$

Using Expt 1 and 4

$$\frac{2.30\times10^{-3}}{1.10\times10^{-2}} = \frac{k(0.02)^2(0.05)(0.01)^x}{k(0.04)^2(0.02)(0.03)^x}$$

$$0.3345 = (\frac{0.01}{0.03})^x$$

x = 1

order of reaction w.r.t. OBr^- is 1.

(iii) Hence, write the rate equation for the reaction. [1]

Rate = $k[ClO_2]^2[OH^-][OBr^-]$

(iv) Calculate the rate constant, *k*, of the reaction and state its units. [2]

Using Expt 1,

$2.3 \times 10^{-3} = k(0.02)^2 (0.05)(0.01)$

$k = 11500$ (;) $mol^{-3}\ dm^9\ s^{-1}$ (;)

(v) Determine the initial pH of an aqueous solution of the reaction mixture if the concentration of chlorine dioxide is 0.200 mol dm^{-3} and the concentration of OBr^- is 0.1 mol dm^{-3}, given that the initial rate of reaction is 1.45 mol $dm^{-3}\ s^{-1}$. [2]

$1.45 = 11500\ [0.200]^2[0.1][OH^-]$

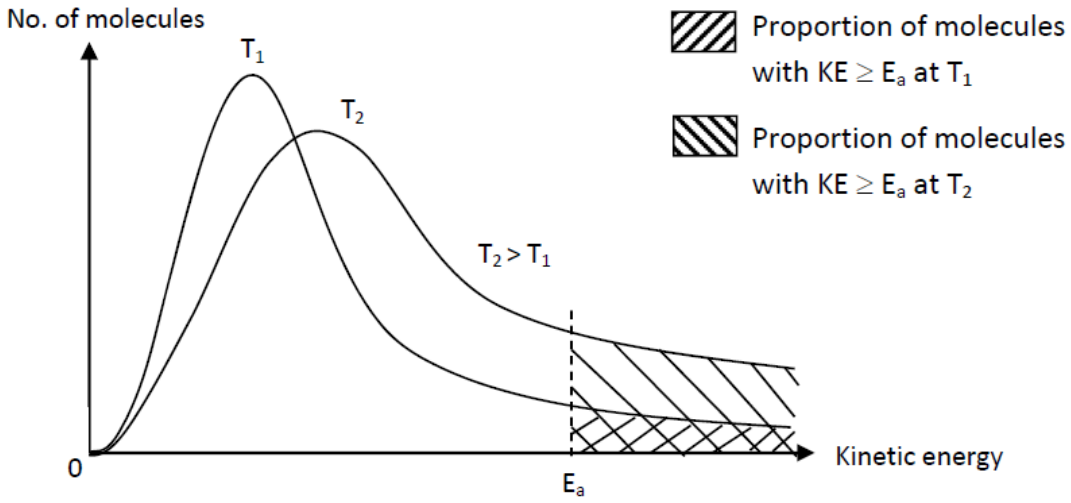
$[OH^-] = 0.03152$ mol dm^{-3} (;)

$pOH = -\log [OH^-]$

$= 1.50$

pH = 14 – 1.50 =12.5 (;)

(b) With an appropriate sketch of the Maxwell-Boltzmann distribution, explain how a rise in temperature affects the rate of reaction. [3]



(;)

At higher temperatures, molecules gain kinetic energy. (;) The fraction of molecules with kinetic energy greater than or equal to activation energy increases. Thus, frequency of effective collision increases, rate increases. (;)

[Total: 13]

3 Alpha hydroxy acids (AHA) have a general formula of RCH(OH)COOH. They are a group of plant and animal-derived acids used in a variety of skincare products and are known to tackle hyperpigmentation and signs of skin aging.

(a) **(i)** Explain why AHAs are generally water-soluble. [2]

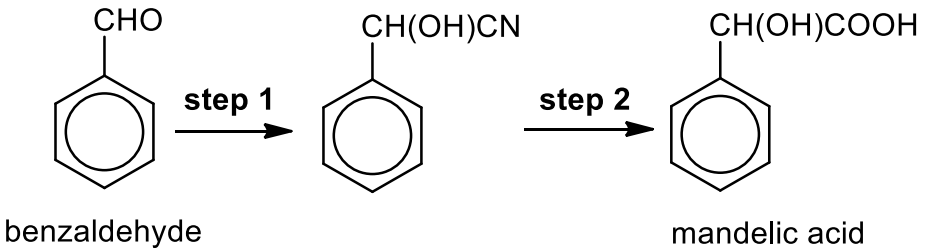
Energy given out from the formation of hydrogen bonding between AHA and water is sufficient to overcome the hydrogen bonding between AHA and between water molecules.

(ii) Glycolic acid, $CH_2(OH)COOH$, lactic acid, $CH_3CH(OH)COOH$, and mandelic acid, $C_6H_5CH(OH)COOH$, are examples of AHA.

Suggest, with reasoning, which of the three AHAs is the most soluble in water. [1]

Glycolic acid as it is the most polar with the smallest hydrocarbon chain.

(b) Mandelic acid can be synthesised in the laboratory from benzaldehyde by the following reactions.



(i) State the reagent and conditions used in **step 1**. [1]

HCN, trace amount of NaCN, cold

(ii) State the type of reaction that occurs in **step 1** and **2**. [2]

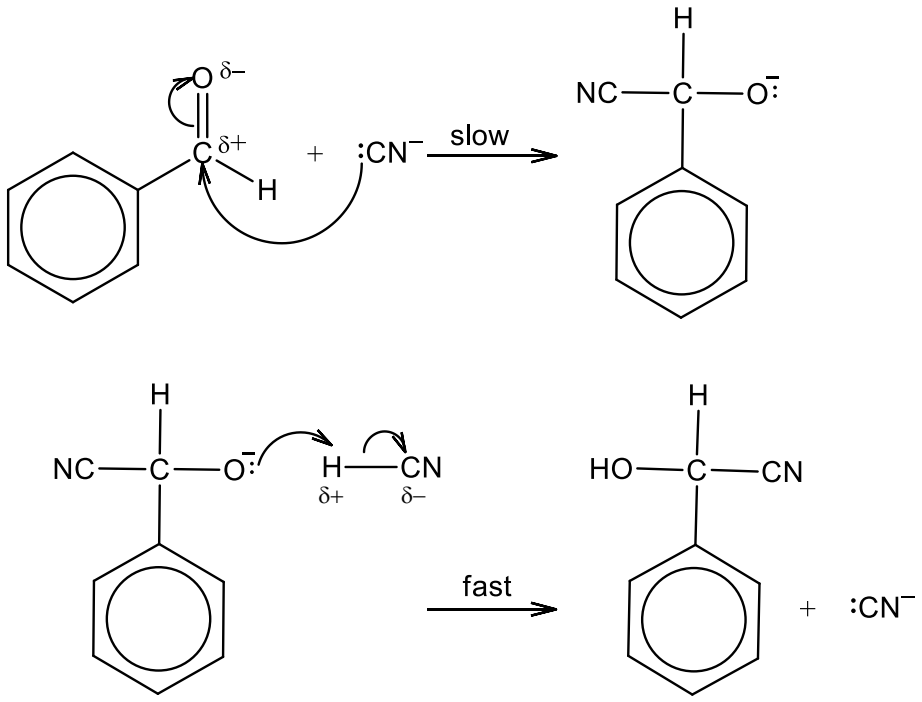
Step 1: Nucleophilic addition

Step 2: acidic hydrolysis

(iii) Describe the mechanism of the reaction in **step 1**. Show clearly all charges and the intermediate formed and use curly arrows to indicate the movement of electron pairs. [3]

$HCN \rightleftharpoons H^+ + CN^-$

$NaCN \rightarrow Na^+ + CN^-$



(iv) Predict, with reasoning, whether the product of **step 1** is able to rotate plane-polarised light. [3]

There is a trigonal planar arrangement about the carbonyl carbon (;). The CN^- nucleophile can attack from either side of the plane with equal probability. This results in an equimolar mixture of both enantiomers/ racemic mixture (;) being formed which does not rotate the plane of polarised light. (;)

(v) A scientist carrying out the synthesis of mandelic acid would like to check if all the reactants in **step 1** have been used up.

Devise a suitable chemical test which can help him verify if all the reactants in **step 1** have been used up and include observations in your answer. [2]

Add Tollens' reagent and warm to a small sample of the reaction mixture. (;)

No silver mirror precipitate will be formed if all the reactants have been used up. (;)

(c) Glycolic acid is produced by plants during photorespiration and is recycled by conversion to glycine, H_2NCH_2COOH, within the cytoplasm. The same conversion can be done in the laboratory.

Devise a two-step synthetic route that converts glycolic acid to glycine in a laboratory.

Include the reagents and conditions and the structure of the intermediate product. [3]

$HOCH_2COOH \rightarrow ClCH_2COOH \rightarrow H_2NCH_2COOH$

Step 1: HCl(g) / NaCl, conc H_2SO_4, heat

Step 2: excess concentrated ethanolic NH_3, heat in sealed tube

(d) A polypeptide made up of 10 amino acid residues is partially hydrolysed to give four smaller fragments. The four fragments are:

ala-gly-ser-gln

lys-trp-arg-pro

gln-his-lys

asp-ala-gly.

Deduce the sequence of the peptide chain. [1]

asp-ala-gly

ala-gly-ser-gln

gln-his-lys

lys-trp-arg-pro

asp-ala-gly-ser-gln- his-lys-trp-arg-pro

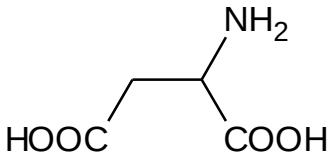
(e) Amino acids can be neutral, positively or negatively charged, depending on the pH of the solution.

Amino acid exists as zwitterions at the isoelectric point.

(i) Define *zwitterion*. [1]

Zwitterion is a dipolar ion formed by the intramolecular migration of the proton (H+), from the carboxyl group to the amino group. There is no net charge and is electrically neutral.

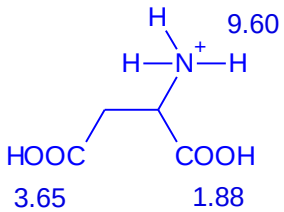
(ii) Aspartic acid is an α-amino acid which has the R group $-CH_2COOH$.



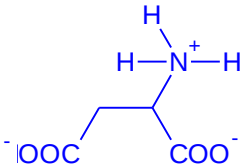
Aspartic acid (asp)

When fully protonated, the pK_a values of the acidic groups are 1.88, 3.65 and 9.60.

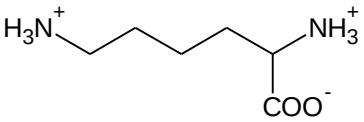
Draw the fully protonated aspartic acid and assign the pK_a values. [2]



(iii) Hence, draw the major species of aspartic acid at pH 5. [1]



(iv) Aspartic acid was accidentally mixed with lysine at pH 5.



lysine at pH 5

Electrophoresis is a technique to separate the amino acids in an electric field. The sample was loaded onto an electrophoresis tank buffered at pH 5.0 and an electric field was applied.

On **Figure 3.1**, draw and label the relative positions of lysine and aspartic acid after the electrophoresis.

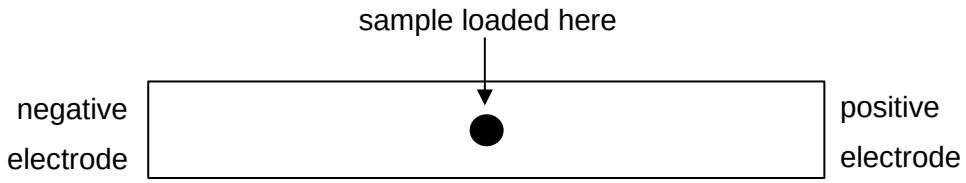
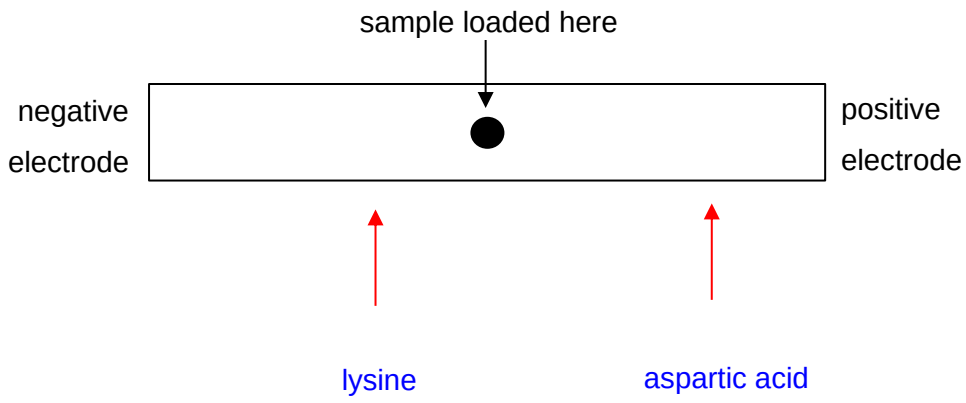


Figure 3.1

[2]



[Total: 24]

4 **(a)** Methane, CH_4 is the second major greenhouse gas after CO_2, exerting a significant influence on the climate and the chemistry of the atmosphere.

Biological methods have also been developed to produce methane from organic acids using bacteria. An example of this reaction where methane is produced from butanoic acid is shown below.

___ $CH_3CH_2CH_2COOH(l)$ + ___ $H_2O(l)$ → ___ $CH_4(g)$ + ___ $CO_2(g)$ ΔH_r

(i) Calculate the average oxidation state of C in each of the following carbon-containing compound.

C in $CH_3CH_2CH_2COOH$: ……..

C in CH_4: ……

C in CO_2: …… [1]

C in $CH_3CH_2CH_2COOH$: -1

C in CH_4: -4

C in CO_2: +4

(ii) Hence, or otherwise, balance the equation by filling in the stoichiometric coefficient in the above equation where methane is produced from butanoic acid in **(a)**. [1]

$2CH_3CH_2CH_2COOH + 2H_2O \rightarrow 5CH_4 + 3CO_2$

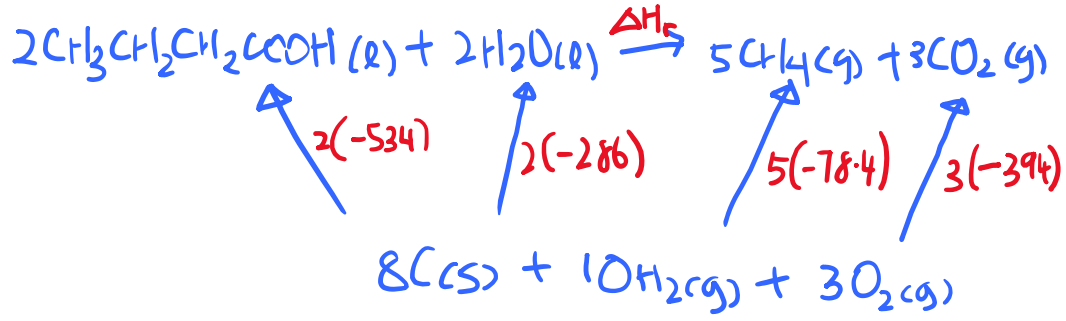
(iii) Using the thermochemical data shown in **Table 4.1**, draw a fully-labelled energy cycle to calculate the standard enthalpy change of reaction, ΔH_r in **(a)**.

Table 4.1

Standard enthalpy change of formation of liquid butanoic acid	–534 kJ mol^{-1}
Standard enthalpy change of combustion of carbon	–394 kJ mol^{-1}
Standard enthalpy change of combustion of hydrogen	–286 kJ mol^{-1}
Standard enthalpy change of formation of methane	–78.4 kJ mol^{-1}

[3]

ΔH_{rxn} = - 2(-534) - 2(-286) + 5(-78.4) + 3(-394) = + 66.0 kJ mol^{-1}



1m for balanced energy cycle

1m for correct substitution of values

1m for final answer

(iv) Hence, predict the sign of ΔS for the reaction in **(a)** and explain the spontaneity of the reaction at high temperatures. [2]

- ΔH is positive
- ΔS is positive as the number of gaseous particles increases. [1]
- $-T\Delta S$ is negative
- Since $\Delta G = \Delta H - T\Delta S$

⇨ ΔG will only be negative when T is large and the reaction is spontaneous at high temperatures. [1]

(b) Trouton's rule states that the entropy change of vapourisation for liquids such as benzene and hexane at their boiling points is almost the same value at around +85 to +88 J K^{-1} mol^{-1}.

However, the entropy change of vapourisation for butanoic acid is +130 J K^{-1} mol^{-1}.

Compare and explain the difference in the entropy change of vapourisation for butanoic acid and benzene. [2]

ΔS^{o}_{vap}(butanoic acid) is more positive than +85 J mol^{-1} K^{-1}(;), as hydrogen bonds between butanoic acid molecules in the liquid state reduces its entropy due to the relatively strong intermolecular forces of attraction between the molecules which results in less ways to arrange the molecules. In the gaseous state, the molecules are further apart and would be much more disordered with less significant intermolecular forces of attraction between the molecules. (;)

[Total: 9]

5 Compounds **P**, **Q**, **R** and **S** are oxides or chlorides of Period 3 elements.

Table 5.1 shows some properties of the compounds.

Table 5.1

Compounds	Melting point	Solubility in water	pH of solution
P	High	Yes	13
Q	Low	Yes	2
R	High	Yes	6.5
S	High	No	

(a) Based on the information from **Table 5.1**, deduce the identities of compounds **P** and **R** and write the equations to justify the pH of the respective solutions. [2]

P: Na_2O

$Na_2O + H_2O \rightarrow 2NaOH$

R: $MgCl_2$

$MgCl_2 + 6H_2O \rightarrow [Mg(H_2O)_6]^{2+} + 2Cl^-$

$[Mg(H_2O)_6]^{2+} + H_2O \rightleftharpoons [Mg(H_2O)_5(OH)]^+ + H_3O^+$

(b) **S** is only soluble in hot concentrated sodium hydroxide.

Identify compound **S** and write the equation for the reaction with hot concentrated sodium hydroxide. [2]

S is SiO_2 (as it has a high melting point, insoluble in water and only reacts with hot concentrated NaOH.)

Reaction of **S** with hot NaOH:

$SiO_2 (s) + 2OH^- (aq) \rightarrow SiO_3^{2-} (aq) + H_2O (l)$

(c) When water is added to 0.0500 mol of **Q**, the resulting solution requires 0.250 mol of silver nitrate for complete reaction.

Identify compound **Q** and write the equations to show:

- its reaction with water
- the reaction between the resulting solution and silver nitrate [3]

Q is PCl_5

$PCl_5(s) + 4H_2O(l) \rightarrow H_3PO_4(aq) + 5HCl(aq)$

$HCl(aq) + AgNO_3(aq) \rightarrow AgCl(s) + HNO_3(aq)$

(d) The melting point of compound **P** is 1132 ^oC while that of potassium carbonate is 891 ^oC.

Explain the difference in the melting points in terms of structure and bonding. [2]

Na_2O and K_2CO_3 have giant ionic structures held by strong electrostatic forces of attraction between oppositely charged ions.

$|L.E.| \propto \left|\frac{q^+q^-}{r^+ + r^-}\right|$ Since the charge of cation and anions are the same for both compounds **while K^+ is larger in size than Na^+ and CO_3^{2-} is larger than O^{2-}**, the magnitude of lattice energy for K_2CO_3 is smaller than Na_2O. Less energy is required to overcome the weaker ionic bonds in K_2CO_3. K_2CO_3 has a lower melting point.

[Total: 9]

END OF PAPER 2