



ST ANDREW'S JUNIOR COLLEGE  
 JC2 PRELIMINARY EXAMINATIONS  
 HIGHER 2

CANDIDATE  
 NAME

STUDENT WORKED SOLUTIONS

CLASS

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CHEMISTRY

9729/01

Paper 1 Multiple Choice

15 September 2022

Additional Materials: Multiple Choice Answer Sheet

1 hour

Data Booklet

**READ THESE INSTRUCTIONS FIRST**

Write in soft pencil.

Do not use staples, paper clips, glue or correction fluid.

Write your name and class on the Answer Sheet in the spaces provided.

There are **thirty** questions on this paper. Answer **all** questions. For each question there are four possible answers **A, B, C** and **D**.

Choose the **one** you consider correct and record your choice in **soft pencil** on the separate Answer Sheet.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer.

Any rough working should be done in this booklet.

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

This document consists of **19** printed pages (including this cover page) and **1** blank page.

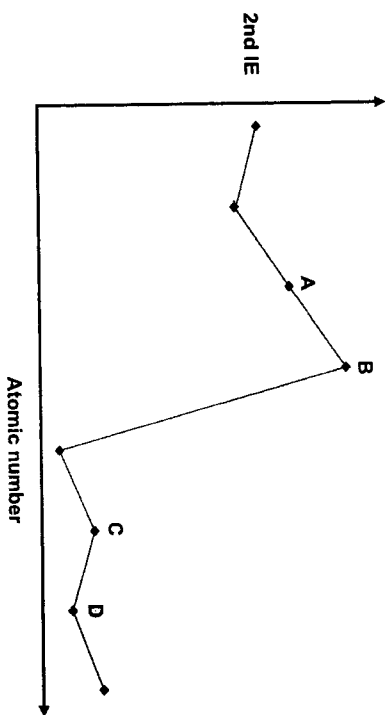
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1	2	3	4	5	6	7	8	9	10
C	D	C	A	B	A	A	C	B	C
11	12	13	14	15	16	17	18	19	20
C	B	D	C	C	D	D	A	D	C
21	22	23	24	25	26	27	28	29	30
C	B	D	B	A	B	B	C	B	D

1	Use of the Data Booklet is relevant to this question. Which statements about chromium and its compounds are correct?
1	The valence electronic configuration of Cr contains both an unpaired s electron and an unpaired p electron.
2	One of the 3d orbitals in chromium atom has only 2 lobes.
3	There are 58 electrons and 60 neutrons in the $^{52}\text{Cr}^{16}\text{O}_4^{2-}$ ion.
A	1, 2, and 3
B	1 and 2
C	2 and 3
D	1 only
	1. The electronic configuration of Cr is $[\text{Ar}]3d^54s^1$ . Cr contains both an unpaired s electron and an unpaired d electron (not p electron). 2. Only the $3d_{z^2}$ d orbital has 2 lobes. 3. No of electrons = $24 + (4 \times 8) + 2 = 58$ No of neutrons = $(52 - 24) + 4(16 - 8) = 60$ Answer: C

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2 The following graph shows the second ionisation energy of eight consecutive elements in Period 2 and 3.



Which of the options A, B, C or D is silicon?

B must be group 14 as the second electron is removed from the inner shell hence resulting in a large energy gap. Hence, D is group 14 and belongs to silicon.

Answer: D

3 Which option is correct?

Molecule	Planar	Polarity	Diagram
A Xenon difluoride	Yes	Polar	
B Chlorine(I) oxide	No	Non-polar	
C Methanal	Yes	Polar	
D Dichloromethane	No	Non-polar	

Molecule	Planar	Polarity	Diagram
* A Xenon difluoride	Linear (Yes)	Non-polar	
* B Chlorine(I) oxide	Bent (Yes)	Polar	
✓ C Methanal	Trigonal Planar (Yes)	Polar	

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* D	Dichloromethane	Tetrahedral (No)	polar	
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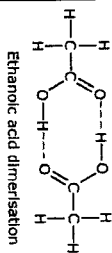
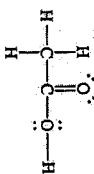
Answer: C

4 Which statements about ethanoic acid are correct?

- 1 molecule of ethanoic acid has 4 lone pairs of electrons.
- 2 Gaseous ethanoic acid forms a dimer comprising of two hydrogen bonds within a ring of 8 atoms.
- 3 The C-C bond in ethanoic acid is formed from a  $sp^3$ - $sp^2$  orbital overlap.

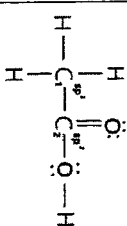
- A 1 and 2  
B 1 and 2  
C 2 and 3  
D 1 only

1. Ethanoic acid has 4 lone pairs of electrons as shown above.



Ethanoic acid dimerisation

2. The dimer of ethanoic as shown above. There is illustration of 2 hydrogen bonds and 8 atoms are within the hydrogen bond structure.



3.  $C_1-C_2$  forms a  $sp^3$ - $sp^2$  orbital overlap as shown above.

Answer: A

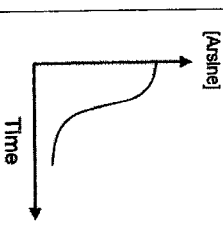
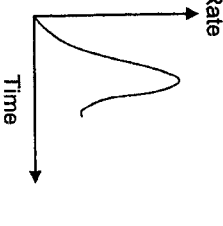
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5	Which description of Dalton's law is correct?
A	Equal volumes of gases at the same temperature and pressure contain equal numbers of molecules.
B	The total pressure of a mixture of gases is equal to the sum of the partial pressures of those gases.
C	The partial pressure of a gas in mixture is given by the product of its mole fraction and the total pressure.
D	The partial pressure of a gas in a mixture is given by the product of its percent by mass and the total pressure.
Answer: B	
<b>Dalton's Law of Partial Pressure:</b>	
At constant temperature, for gases which do not react chemically, the total pressure of a mixture of gases in a given volume is equal to the sum of the partial pressures of the constituent gases.	
<div style="border: 1px solid black; padding: 5px; display: inline-block;"> <math display="block">p_T = p_A + p_B + p_C + \dots</math> </div>	

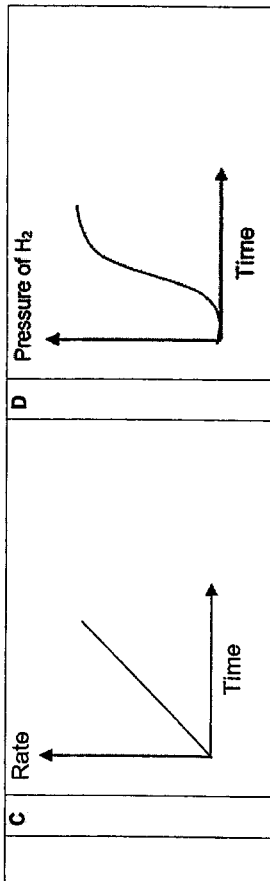
6	Which graph shows the correct trends when the physical property of each of the elements Na, Al, Si and S is plotted against its atomic radius?
A	
B	
C	
D	
<p>Atomic radius decreases across the period. Thus, Atomic radius increases in the following order: <math>S &lt; Al &lt; Na</math>. Thus options A and B in terms of atomic radius is accurate.</p> <p>Melting point depends on the structure and bonding of the elements. <math>Si &gt; Al &gt; Na &gt; S</math>. Si is a giant covalent molecule, Al and Na are giant metallic lattice but Al has more delocalised electrons hence a higher melting point. S is a simple covalent molecule hence the lowest boiling point.</p> <p>Electronegativity depends on the ability of the nucleus to attract the bonding pair of electrons. The trend is <math>S &gt; Si &gt; Al &gt; Na</math>.</p> <p>Answer: A</p>	

7	Which property describes the trend for the hydrogen halides as stated below?  $\text{HCl} > \text{HBr} > \text{HI}$
A	thermal stability
B	boiling point
C	ease of oxidation
D	acidity
	Option A is correct as down the group, the bond length of H-X increases, bond strength decreases and bond energy decreases. Hence thermal stability decreases down the group.
	Option B is wrong as down the group, the size of electron cloud of H-X compound increases, it is more easily polarised, hence the strength of instantaneous dipole-induced dipole (d-d) interactions between molecules increases, more energy is needed to overcome the d-d interactions, resulting in higher boiling point.
	Option C is wrong as the ease of oxidation of the compounds, $\text{X}^-$ increase down the group. Down the group, $E^\ominus(\text{X}_2/\text{X}^-)$ becomes less positive, $\text{X}^-$ is more readily oxidized to $\text{X}_2$ . Reducing power of $\text{X}^-$ increases down the group.
	Option D is wrong as acid strength increases down the group, i.e. $\text{HCl} < \text{HBr} < \text{HI}$ . Down the group, size of halogen atom increases, -X bond length increases, H-X bond strength decreases less energy required to break H-X bond. H-X dissociates to give $\text{H}^+$ more easily.
	Answer A
8	Use of the Data Booklet is relevant to this question. Which contains the largest number of molecules?
A	810 $\text{cm}^3$ of sulfur dioxide gas (measured at r.t.p.)
B	1.56 g of methyl methanoate
C	5.25 $\text{cm}^3$ of ethanol where the density of ethanol is 0.785 $\text{g cm}^{-3}$
D	1.70 $\times 10^{22}$ molecules of hydrogen peroxide.
	Amount of $\text{SO}_2 = 810 / 24000 = 0.03375$ mol Amount of methyl methanoate = 1.56 / 60 = 0.0260 mol Mass of ethanol = 5.25 $\times$ 0.785 = 3.964 g Amount of ethanol = 3.964 / 46 = 0.0862 mol

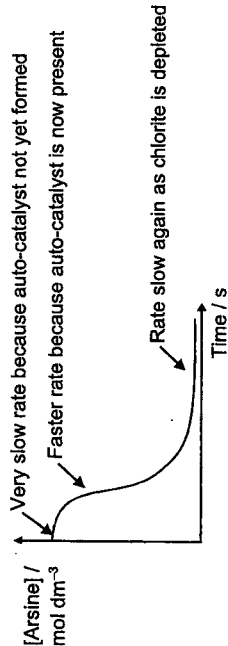
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	Amount of hydrogen peroxide = $1.70 \times 10^{22} / 6.02 \times 10^{23} = 0.0282$ mol Since option C has the largest amount, the number of molecules will also be the largest. Answer: C
9	Silane, $\text{SiH}_4$ , exists as a gas at standard temperature and pressure. Hess' Law can be used to calculate the average Si-H bond energy in gaseous $\text{SiH}_4$ . Which information is needed to perform the calculation?
A	$\Delta H^\ominus_{\text{formation}}(\text{SiH}_4)$ only
B	$\Delta H^\ominus_{\text{atomisation}}(\text{Si})$ , $\Delta H^\ominus_{\text{atomisation}}(\text{H})$ , $\Delta H^\ominus_{\text{formation}}(\text{SiH}_4)$
C	$\Delta H^\ominus_{\text{combustion}}(\text{Si})$ , $\Delta H^\ominus_{\text{combustion}}(\text{H}_2)$ , $\Delta H^\ominus_{\text{combustion}}(\text{SiH}_4)$
D	$\Delta H^\ominus_{\text{combustion}}(\text{Si})$ , $\Delta H^\ominus_{\text{combustion}}(\text{H}_2)$ , $\Delta H^\ominus_{\text{formation}}(\text{SiH}_4)$
	$\begin{array}{c} \text{H} \\   \\ \text{H}-\text{Si}-\text{H}(\text{g}) \\   \\ \text{H} \\ \text{silane} \end{array} \xrightarrow{4 \times \text{BE Si-H}} \text{Si}(\text{g}) + 4\text{H}(\text{g})$ $\begin{array}{c} \text{H} \\   \\ \text{H}-\text{Si}-\text{H}(\text{g}) \\   \\ \text{H} \\ \text{silane} \end{array} \xrightarrow{\Delta H^\ominus_{\text{a}} \text{Si}} \text{Si}(\text{s}) + 2\text{H}_2(\text{g})$ $\begin{array}{c} \text{H} \\   \\ \text{H}-\text{Si}-\text{H}(\text{g}) \\   \\ \text{H} \\ \text{silane} \end{array} \xrightarrow{4 \times \Delta H^\ominus_{\text{a}}(\text{H})} 4\text{H}(\text{g})$
	Answer: B
10	The decomposition of Arsine, $\text{AsH}_3$ , is catalysed by Arsenic, As, and can be represented by the following equation. $\text{AsH}_3 \rightarrow \text{As} + \frac{3}{2} \text{H}_2$ Which graph does not describe the above reaction?
A	[Arsine] 
B	Rate 

TURN OVER



Options A and D accurately describes an autocatalytic graph where the reaction or Arsine and the production of hydrogen shows the following feature. The [Arsine] is as shown below.

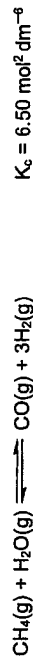


Option B shows the correct shape for an autocatalytic graph. The rate increase significantly when the product is formed as the product catalyses the reaction. The rate starts to fall when the reactants are used up.

Option C is incorrect as the rate-time graph is increasing throughout which is not typical of an autocatalytic reaction.

Answer: C

**11** Steam reforming process is the most common method used for the industrial production of hydrogen.



What is the number of moles of steam used to react with 0.60 mol of methane, to form 0.90 mol of hydrogen in a 1 dm<sup>3</sup> vessel?

<b>A</b>	0.304 mol	<b>C</b>	0.412 mol
<b>B</b>	0.112 mol	<b>D</b>	0.346 mol

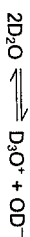
  

Mol	CH <sub>4</sub>	H <sub>2</sub> O	CO	3H <sub>2</sub>
Initial	0.60	x	0	0
Change	-y	-y	+y	+3y
Eqm	0.60 - y	x - y	y	3y
	= 0.30	x - 0.30	0.30	0.90

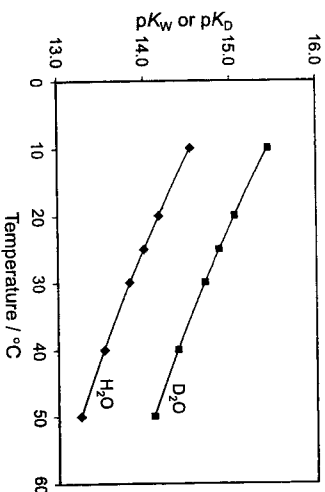
$3y = 0.90$   
 $y = 0.30$   
 $K_c = \frac{(0.30)(0.90)^3}{(0.30)(x-0.30)} = 6.5$   
 $0.0336 = 0.3x - 0.09$   
 $0.1236 = 0.3x$   
 $x = 0.412$   
 Answer: C

12 Deuterium oxide, otherwise known as 'heavy water', consists of an oxygen atom bonded to two atoms of the hydrogen isotope, deuterium ( ${}^2\text{D}$ ).

Like water, deuterium oxide can undergo autoionisation. For  $\text{D}_2\text{O}$ , we can use the term  $K_0$  instead of  $K_w$ .



The following graph show how the values of  $K_w$  of  $\text{H}_2\text{O}$  and  $K_0$  of  $\text{D}_2\text{O}$  vary with temperature.



Which deduction is correct?

A The enthalpy changes of autoionisation for both  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  are negative.

B The extent of ionisation is smaller for  $\text{D}_2\text{O}$ .

C  $[\text{OH}^-]$  and  $[\text{OD}^-]$  decrease with increasing temperature.

D O–D bond is weaker than O–H bond.

Option A: The enthalpy change of ionisation for both is endothermic. As T increases,  $pK_w / pK_0$  decreases (or  $K_w / K_0$  increases). Hence ionisation increases. When T increases, endothermic reaction is favoured to reduce T.

Option B: Greater  $pK_w, pK_0$  values imply smaller  $K_w, K_0$  values, and hence, smaller degree of ionisation. The  $pK_0$  curve is higher than the  $pK_w$  curve. Therefore, it has the smaller the degree of ionisation.

Option C: When T increases, ionisation increases (see Option A) hence both  $[\text{OH}^-]$  in  $\text{H}_2\text{O}$  and  $[\text{OD}^-]$  in  $\text{D}_2\text{O}$  increases.

TURN OVER

Option D: O–D is stronger than O–H bond since the ionisation of  $\text{D}_2\text{O}$  is weaker than  $\text{H}_2\text{O}$ .  
Answer: B

13 The numerical values of the solubility product of calcium hydroxide and calcium carbonate are  $6.5 \times 10^{-6}$  and  $8.0 \times 10^{-7}$  respectively at 25 °C.

Which statements are correct?

1 A precipitate is formed when equal volumes of 0.001 mol  $\text{dm}^{-3}$  calcium nitrate and a solution of pH 12.5 are mixed.

2 The solubility of calcium hydroxide in a solution of pH 12.5 is higher than the solubility of calcium carbonate in water.

3 The solubility product of calcium carbonate and calcium hydroxide decrease in a solution containing calcium nitrate.

A 1, 2, and 3

B 1 and 2

C 2 and 3

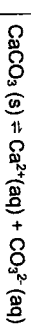
D 2 and 1

$[\text{OH}^-] = 0.0316 \text{ mol dm}^{-3}$

$\text{IP} = (0.0316 / 2)^2 \times (0.001/2) = 2.5 \times 10^{-7} \text{ mol}^3 \text{dm}^{-9}$

Since  $\text{IP} < K_{sp}$ , ppt is not formed.

Option 1 is incorrect.

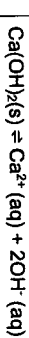


s s s



$8.0 \times 10^{-7} = (\text{s})(\text{s})$

$\text{s} = 8.9 \times 10^{-4} \text{ mol dm}^{-3}$



s s 2s



$6.5 \times 10^{-6} = (\text{s})(2\text{s})^2$

$\text{s} = 0.0118 \text{ mol dm}^{-3}$

The solubility of calcium hydroxide in pH = 12.5 is calculated as follows.

$[\text{OH}^-] = 0.0316 \text{ mol dm}^{-3}$

TURN OVER

$$K_{sp} = [Ca^{2+}][OH^-]^2$$

$$6.5 \times 10^{-6} = (s) (2s+0.0316)^2$$

$$6.5 \times 10^{-6} = (s) (0.0316)^2$$

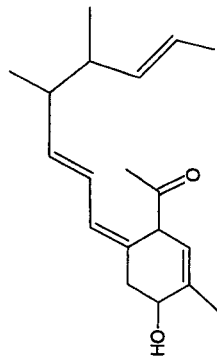
$$s = 6.51 \times 10^{-8} \text{ mol dm}^{-3}$$

**Option 2 is correct**

$K_{sp}$  is only affected by temperature. Hence **option 3 is incorrect**.

Answer: D

14 How many stereoisomers does the following molecule have?

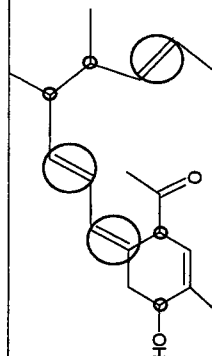


A 16

B 64

C 128

D 256



Stereoisomers include cis-trans isomers (for C=C) and enantiomers (chiral carbons).

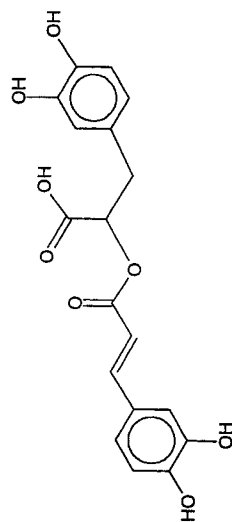
As seen in the diagram above, there are 4 chiral centres (smaller circles) and 3 C=C that can exhibit cis-trans isomerism. The C=C in the cyclic ring do not exhibit cis-trans isomerism as they are restricted by the cyclic structure.

Hence, the total number of stereoisomers =  $2^{(4+3)} = 2^7 = 128$

Ans: C

[TURN OVER

15 Rosmarinic acid can be found in herbs such as rosemary, sage and thyme. It has the following structure.



Which functional groups will remain in the product after rosmarinic acid reacts with excess hydrogen gas in the presence of platinum?

1 Alkene

2 Carboxylic acid

3 Ester

4 Phenol

A 1 and 2

B 3 and 4

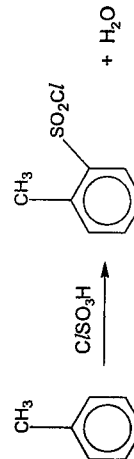
C 2, 3 and 4

D 4 only

Of the 4 functional groups present, hydrogen gas in the presence of a platinum catalyst will only react with alkene, which will not be present in the product. The other 3 will remain.

Ans: C

16 Methylbenzene can undergo the following reaction.



Which statement about the mechanism of this reaction is correct?

[TURN OVER

A	The hybridisation states of the carbon atoms in benzene do not change during the reaction.
B	The $\pi$ electron cloud of benzene will attack the O atom in $C/ISO_3H$ .
C	The mechanism of this reaction is electrophilic addition.
D	The bond broken in $C/ISO_3H$ is the S-O bond.
This type of reaction undergone is electrophilic substitution as the $\pi$ electrons in benzene is restored. Hence Option C is wrong.	
As seen in the reaction, the bond formed between the benzene ring and $C/ISO_3H$ is S. Hence the $\pi$ electron attacks the S atom in $C/ISO_3H$ and not the O atom. Hence, option B is wrong. The intermediate formed during this reaction involves one of the carbon having 4 bonds. Hence, the hybridisation of this carbon changed from $sp^2$ to $sp^3$ and back to $sp^2$ when the $\pi$ electrons in benzene are restored. Hence Option A is wrong.	
$C/ISO_3H$ will lose the OH as seen from the product formed. Hence the bond broken has to involve S and O. Option D is correct.	
Ans: D	
17	1-bromo-2,2-dimethylpropane, $(CH_3)_3CCH_2Br$ , can be obtained from 2,2-dimethylpropane, $(CH_3)_4C$ , via free radical substitution with excess bromine. The yield however is low. What is the main reason for this?
A	Different mono-substituted products are formed.
B	The Br-Br bond requires a lot of energy to break.
C	$(CH_3)_3CCH_2Br$ is very unstable.
D	The bromine radical is regenerated during the formation of $(CH_3)_3CCH_2Br$ .
All the H in 2,2-dimethylpropane are equivalent. Hence there is only 1 mono-brominated product formed and no other isomers, making statement A wrong. Since the reaction is carried out with excess bromine and bromine radical is regenerated during the mechanism, this will result in a lot of bromine radicals, leading to a mixture of products being formed. Ans: D	
18	Molecule M is a halogenoalkane. It is reacted with various reagents to give the following results. <ul style="list-style-type: none"><li>M is first heated with <math>NaOH(aq)</math>. After it has cooled, <math>HNO_3</math> is added followed by <math>AgNO_3</math>. A precipitate appears and is only soluble in concentrated <math>NH_3</math>.</li></ul>

TURN OVER

<ul style="list-style-type: none"> <li>M reacts with ethanolic KCN when heated. The product reacted with <math>LiAlH_4</math> in dry ether to yield a product that has the molecular formula <math>C_5H_9N</math>.</li> </ul>	
Which conclusion can be drawn from these results?	
A	<del>There are 4 possible isomers for molecule M.</del>
B	When treated with ethanolic $AgNO_3$ , the precipitate for molecule M will appear slower than 1-chlorobutane.
C	Molecule M contains 5 carbon atoms.
D	Molecule M is a tertiary halogenoalkane.
From the first reaction, molecule M is a bromoalkane. Hence, when reacted with ethanolic $AgNO_3$ , its ppt will appear faster than 1-chlorobutane. Hence option B is wrong. From the second reaction, it's a carbon extension reaction. Since the product after extension has 5 carbon atoms, molecule M can only contain 4 carbon atoms. Hence option C is wrong. Molecule M would have a molecular formula of $C_4H_9X$ (where X = halogen). It can be a primary, secondary or tertiary halogenoalkane and there is not enough information about molecule M to conclude. Option D is wrong. The possible isomers for molecule M are $CH_2XCH_2CH_2CH_3$ , $CH_3CH(X)CH_2CH_3$ , $CH_2XCH(CH_3)CH_3$ and $(CH_3)_3CX$ Ans: A	
19	Which statement about $S_N1$ nucleophilic substitution mechanism is correct?
A	The rate of the reaction is dependent on the concentration of the nucleophile.
B	If the product formed is chiral, it will be able to rotate the plane of polarised light.
C	Transition states are formed but not intermediates.
D	<del>The reaction takes place on a halogenoalkane.</del>
<p><math>S_N1</math> nucleophilic substitution reactions takes places in 2 steps. The first step is the rate determining step which involved the halogen leaving to produce a carbocation intermediate. Thus, the rate equation for such reaction is only <math>k[RX]</math> as the nucleophile is only involved in the 2<sup>nd</sup> step which is fast. Rate of such reactions is thus independent of the nucleophile. Hence statement A and C is wrong.</p> <p>The intermediate formed from the first step is planar. This allows the nucleophile to attack from both the top and the bottom of the plane in equal proportion, giving rise to a racemic mixture. Hence, even if the product is chiral, it would not rotate the plane of polarised light. Statement B is thus wrong.</p>	

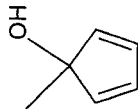
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As mentioned earlier, the first step involved the halogen leaving first to make space for the nucleophile to attack. This would mean that this reaction favors tertiary halogenoalkanes as there are many bulky groups around the halogen, blocking the attack of the nucleophile.

Ans: D

Compound **E** has the following structure.



Which statements are correct about the organic product formed after compound **E** has reacted with hot acidified  $\text{KMnO}_4$ ?

- 1 It contains 6 carbon atoms.
- 2 It can react with 3 moles of  $\text{PCl}_5$ .
- 3 It gives a yellow ppt with alkaline aqueous iodine.
- 4 It can react with 2 moles of aqueous  $\text{NaOH}$ .

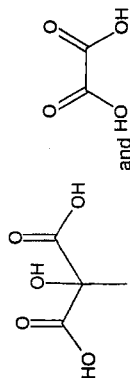
**A** 1 and 2

**B** 1 and 3

**C** 2 and 4

**D** 3 and 4

After compound **E** undergoes a reaction with hot acidified  $\text{KMnO}_4$ , the  $\text{C}=\text{C}$  are broken. This will result in


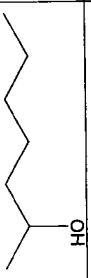
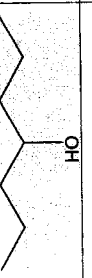
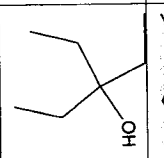


The latter product will continue to be oxidised to give  $\text{CO}_2$  and  $\text{H}_2\text{O}$  and hence not considered the organic product.

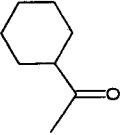
The former organic product

- contains only 4 carbon atoms (statement 1 is incorrect)
- can react with 3 moles of  $\text{PCl}_5$  due to 3 OH groups (statement 2 is correct)
- does not give a positive test with iodoform due to the lack of methyl alcohol and methyl ketone (statement 3 is incorrect)
- reacts with 2 moles of  $\text{NaOH}(\text{aq})$  due to 2  $\text{COOH}$  groups (statement 4 is correct)

Ans: C

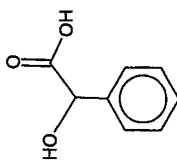
<p>21 Alcohol Q undergoes the following reactions.</p> <ul style="list-style-type: none"> <li>• With concentrated <math>H_2SO_4</math> at <math>170^\circ C</math>, only one product is formed.</li> <li>• With hot acidified <math>K_2Cr_2O_7</math>, a green solution is formed that does not produce effervescence with <math>Na_2CO_3</math>.</li> </ul> <p>What could be the identity of Q?</p>	<p><b>A</b> </p> <p><b>B</b> </p> <p><b>C</b> </p> <p><b>D</b> </p>
<p>Since alcohol Q undergoes elimination with concentrated <math>H_2SO_4</math> to give only 1 product, option B is wrong as the elimination can form a C=C to the left and right of the -OH group, which gives 2 products. Option A can only eliminate to the left of the OH group thus forming 1 product, while option C and D are symmetrical hence only 1 product is formed no matter where the elimination takes place.</p> <p>Then when alcohol Q undergoes oxidation, orange <math>K_2Cr_2O_7</math> turns green implies the alcohol can be oxidised, making option D wrong as it is a tertiary alcohol. Then when <math>Na_2CO_3</math> is added to the resultant solution, no effervescence is observed implies no acid is formed, making option A wrong as it will form an acid after oxidation.</p> <p>Ans: C</p>	

[TURN OVER

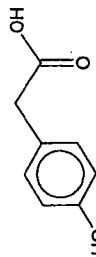
<p>22 Compound L has the following structure.</p>  <p>Which statement about compound L is <b>Incorrect</b>?</p>	<p><b>A</b> It can undergo a condensation reaction.</p> <p><b>B</b> <del>It can undergo hydrolysis reaction.</del></p> <p><b>C</b> It can undergo reduction reaction.</p> <p><b>D</b> It can be attacked by a nucleophile.</p> <p>The ketone group present in the molecule can undergo a condensation reaction with 2,4-DNP and hence Option A is true.</p> <p>The ketone group can also undergo a reduction reaction to form a secondary alcohol and hence Option C is true</p> <p>The C of ketone can also be attacked a nucleophile due to it being electron deficient as it is attached to an electronegative O. Hence, Option D is also true.</p> <p>Ketones cannot undergo hydrolysis.</p> <p>Ans: B</p>

[TURN OVER

23 Mandelic acid and 4-hydroxyphenylacetic acid are isomers. They have the following structures.



Mandelic acid



4-hydroxyphenylacetic acid

Given that the  $pK_a$  value of the carboxylic acid in mandelic acid is 3.75, which option about 4-hydroxyphenylacetic acid is correct?

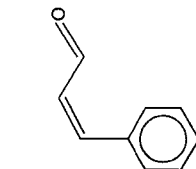
	$pK_a$ of the carboxylic acid in 4-hydroxyphenylacetic acid	Reason
A	3.25	Lone pair of electrons on O of the phenol in 4-hydroxyphenylacetic acid can delocalise into the benzene ring
B	3.25	The alcohol group of mandelic acid is an electron withdrawing group
C	4.05	Lone pair of electrons on O of the phenol in 4-hydroxyphenylacetic acid can delocalise into the benzene ring
D	4.05	The alcohol group of mandelic acid is an electron withdrawing group

The alcohol OH group in mandelic acid is nearer the carboxylic acid group. Hence, due to the electronegativity of O, it is an electron withdrawing group and hence able to better stabilise the carboxylate ion of the conjugate base of mandelic acid, making mandelic acid a stronger acid than 4-hydroxyphenylacetic acid. Hence, 4-hydroxyphenylacetic acid is less acidic than mandelic acid, resulting in it having a lower  $K_a$  but higher  $pK_a$  value when compared to mandelic acid.

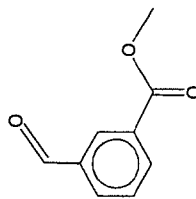
Ans: D

[TURN OVER

24 Compounds X and Y have the following structures.



Compound X



Compound Y

Which reagents can be used to distinguish them?

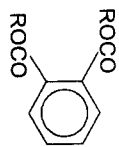
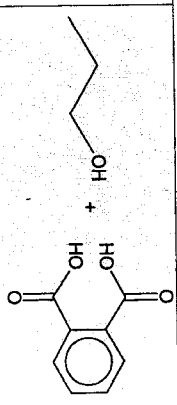
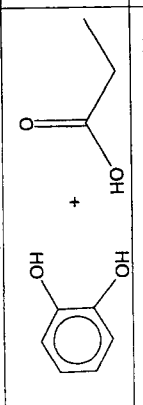
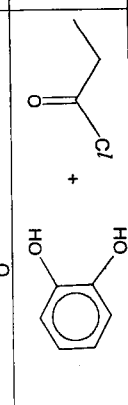
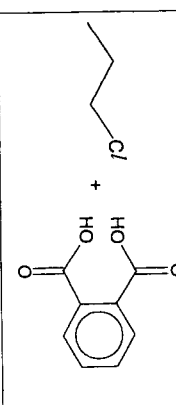
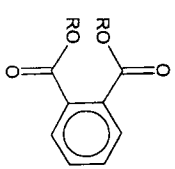
- 1  $Br_2(aq)$   
 2 Fehling's solution and warm  
 3 Tollens' reagent and warm  
 A 1 only  
 B 1 and 2  
 C 2 and 3  
 D 1, 2 and 3

$Br_2(aq)$  can be used as Compound X has the  $C=C$  but Compound Y does not have any functional group that will react with  $Br_2(aq)$ . Option 1 is possible.

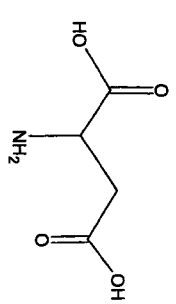
Fehling's solution can also be used as Compound X has an aliphatic aldehyde but Compound Y has a benzaldehyde which does not react with Fehling's solution. Option 2 is possible  
 Tollens' reagent will react with the aldehyde groups in both the compounds and hence it cannot be used. Option 3 is not possible.

Ans: B

[TURN OVER

25	Phthalate esters are mainly used in plasticisers to increase their flexibility, transparency and durability. They have the following structure.	
A	Which pair of compounds can react to form a phthalate ester?	
B		
C		
D		
	Based on the structure given in the question, the structure of phthalate esters are as follows	 <p>This implies that the acid group is attached to the benzene ring and hence come of benzene-1,4-dioic acid. This means Option B and C are wrong. Option D will not yield an ester hence its also wrong.</p>

TURN OVER

Ans: A											
26	Which option correctly shows the product and observation of the resultant solution when aqueous propanoic acid is added dropwise to aqueous propylamine until the reaction is complete?										
	<table border="1"> <thead> <tr> <th data-bbox="1220 1205 1260 1512">Product formed</th> <th data-bbox="1220 1512 1260 2092">Observations</th> </tr> </thead> <tbody> <tr> <td data-bbox="1189 1205 1220 1512">A <math>\text{CH}_3\text{CH}_2\text{CONHCH}_2\text{CH}_2\text{CH}_3</math></td> <td data-bbox="1189 1512 1220 2092">One homogenous solution</td> </tr> <tr> <td data-bbox="1157 1205 1189 1512">B <del><math>\text{CH}_3\text{CH}_2\text{CONHCH}_2\text{CH}_2\text{CH}_3</math></del></td> <td data-bbox="1157 1512 1189 2092"><del>One homogenous solution</del></td> </tr> <tr> <td data-bbox="1125 1205 1157 1512">C <math>\text{CH}_3\text{CH}_2\text{CONHCH}_2\text{CH}_2\text{CH}_3</math></td> <td data-bbox="1125 1512 1157 2092">Two distinct layers</td> </tr> <tr> <td data-bbox="1093 1205 1125 1512">D <math>(\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_3)^+(\text{CH}_3\text{CH}_2\text{COO})^-</math></td> <td data-bbox="1093 1512 1125 2092">Two distinct layers</td> </tr> </tbody> </table>	Product formed	Observations	A $\text{CH}_3\text{CH}_2\text{CONHCH}_2\text{CH}_2\text{CH}_3$	One homogenous solution	B <del><math>\text{CH}_3\text{CH}_2\text{CONHCH}_2\text{CH}_2\text{CH}_3</math></del>	<del>One homogenous solution</del>	C $\text{CH}_3\text{CH}_2\text{CONHCH}_2\text{CH}_2\text{CH}_3$	Two distinct layers	D $(\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_3)^+(\text{CH}_3\text{CH}_2\text{COO})^-$	Two distinct layers
Product formed	Observations										
A $\text{CH}_3\text{CH}_2\text{CONHCH}_2\text{CH}_2\text{CH}_3$	One homogenous solution										
B <del><math>\text{CH}_3\text{CH}_2\text{CONHCH}_2\text{CH}_2\text{CH}_3</math></del>	<del>One homogenous solution</del>										
C $\text{CH}_3\text{CH}_2\text{CONHCH}_2\text{CH}_2\text{CH}_3$	Two distinct layers										
D $(\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_3)^+(\text{CH}_3\text{CH}_2\text{COO})^-$	Two distinct layers										
27	<p>The reaction between propanoic acid and propylamine is an acid-base reaction that will result in a salt form and not an amide. Hence Option A and C are wrong. Since a salt is form, the salt will readily dissolve in water as it is able to form ion-dipole interaction with water, allowing it to dissolve readily to give a homogenous solution. Ans: B</p>										
27	<p>Aspartic acid is used in the biosynthesis of proteins and has the following structure.</p>  <p>Aspartic acid has <math>\text{pK}_a</math> values of 2.0, 3.7 and 9.7. At what pH will the major species in the solution be the zwitterion of aspartic acid?</p> <table border="1"> <tbody> <tr> <td data-bbox="414 1205 446 1344">A</td> <td data-bbox="414 1344 446 1512">1.5</td> </tr> <tr> <td data-bbox="383 1205 414 1344">B</td> <td data-bbox="383 1344 414 1512">3.7</td> </tr> <tr> <td data-bbox="351 1205 383 1344">C</td> <td data-bbox="351 1344 383 1512">7.0</td> </tr> <tr> <td data-bbox="319 1205 351 1344">D</td> <td data-bbox="319 1344 351 1512">10.3</td> </tr> </tbody> </table> <p>The <math>\text{pK}_a</math> values assigned to aspartic acid are as follows.</p>	A	1.5	B	3.7	C	7.0	D	10.3		
A	1.5										
B	3.7										
C	7.0										
D	10.3										

TURN OVER

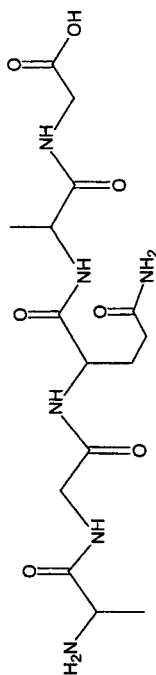
- The  $\alpha$  carboxylic group is 2.0 as it's the most acidic due to it being nearer the N of the  $\alpha$  amino group which is electronegative and helps to stabilise the conjugate base ion more than the side chain carboxylic group.
- The side chain carboxylic group is hence assigned the  $pK_a$  of 3.7
- The  $\alpha$  amino group is thus assigned the  $pK_a$  of 9.7

The zwitterion of aspartic acid is when one of the carboxylic groups and the  $\alpha$  amino group are protonated to produce a species that is electrically neutral. This would mean the  $\alpha$  carboxylic group would be in the basic form and pH has to be above its  $pK_a$  which is 2.1. This also means the  $\alpha$  amino group would be in the acidic form and pH has to be below its  $pK_a$  which is 9.7. This would mean Options A and D are incorrect.

As for option C, at pH 7.0, the side chain carboxylic group will be protonated (i.e. COOH) as the pH is above its  $pK_a$  which is 3.7. This would not result in the formation of the zwitterion.

Ans: B

28 A pentapeptide has the following structure.



Which statement about this pentapeptide is incorrect?

- A** When this pentapeptide reacts with aqueous  $H_2SO_4$ , the product will have an overall charge of  $1+$ .
- B** This pentapeptide contains 4 peptide bonds.
- C** This pentapeptide is made up of 4 different types of  $\alpha$ -amino acids.
- D**  $M_r$  of this pentapeptide = (Sum of  $M_r$  of all the  $\alpha$ -amino acids residues) - 72

Since this pentapeptide only has 1 basic group, which is the  $NH_2$  group at the start, it will form  $NH_3^+$  and hence carry an overall charge of  $+1$ . Option 1 is correct.

Since this is a pentapeptide, it is made up of 5  $\alpha$ -amino acid residues and the number of peptide bonds it will form is 4 ( $5 - 1$ ). The bond in the side chain of the 3<sup>rd</sup>  $\alpha$ -amino acid is an amide bond and not a peptide bond as it was not formed by  $\alpha$ -amino acids. Option 2 is correct. Polypeptides are made of up  $\alpha$ -amino acids, which all have the general formula,  $H_2NCH(R)COOH$ . They only differ by the R. For this pentapeptide, the R groups are (from left to right)  $-CH_3$ ,  $-H$ ,  $-CH_2CH_2CONH_2$ ,  $-CH_3$  and  $-H$ . Since the  $-CH_3$  and  $-H$  groups are repeated, it is hence only made up of 3 different  $\alpha$ -amino acids. Option C is wrong.

[TURN OVER

Polypeptides are formed from various  $\alpha$ -amino acid residues. When the  $\alpha$ -amino acids react to form the peptide bonds, water is lost. Since there are 4 peptide bonds formed in this pentapeptide, 4 water molecules are lost. The  $M_r$  of this pentapeptide is hence the sum of the  $M_r$  of all the  $\alpha$ -amino acid residues minus away 4 water molecules which has a collective  $M_r$  of 72. Hence Option D is correct.

Ans: C

29 Use of the Data Booklet is relevant to this question.

Given the following information on the colours of the aqueous vanadium-containing ions, what is likely to be the colour change when excess nickel is added to a solution containing  $VO^{2+}$ ?

Aqueous vanadium-containing ions	Colour
$VO_2^+$	Yellow
$VO^{2+}$	Blue
$V^{3+}$	Green
$V^{2+}$	Purple

**A** Blue to yellow

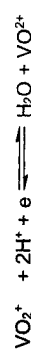
**B** Blue to green

**C** Blue to purple

**D** Yellow to green



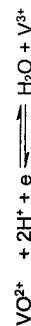
$$E^\ominus = -0.25 \text{ V}$$



$$E^\ominus = +1.00 \text{ V}$$

yellow

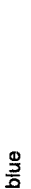
blue



$$E^\ominus = +0.34 \text{ V}$$

blue

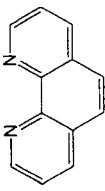
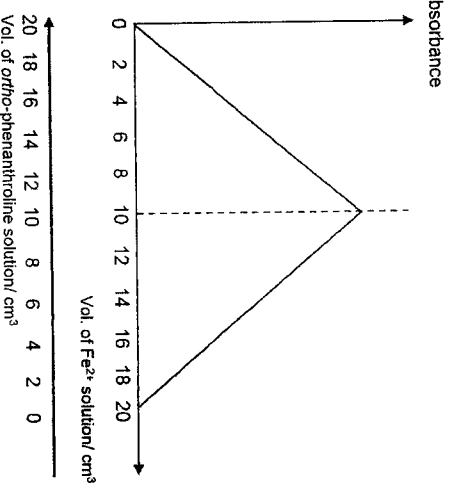
green



$$E^\ominus = -0.26 \text{ V}$$

green

purple

	$E^{\circ}_{\text{cell}} = (+0.34) - (-0.25) = +0.60 \text{ V}$ $E^{\circ}_{\text{cell}} = (-0.26) - (-0.25) = -0.01 \text{ V}$ Colour change will be from blue to green Answer: B
30	<p><math>\text{Fe}^{2+}</math> forms a red complex with <i>ortho</i>-phenanthroline. Various samples containing different volumes of <math>1 \times 10^{-5} \text{ mol dm}^{-3} \text{ Fe}^{2+}</math> and <math>3 \times 10^{-5} \text{ mol dm}^{-3}</math> <i>ortho</i>-phenanthroline were prepared. The structure of <i>ortho</i>-phenanthroline is shown below. Each <i>ortho</i>-phenanthroline molecule is a bidentate ligand.</p> <div style="text-align: center;">  <p><i>ortho</i>-phenanthroline</p> </div> <p>The following graph was obtained when the colour intensity of the samples was measured using a colorimeter.</p> <div style="text-align: center;">  </div> <p>Which statement about the complex ion is correct?</p> <p>A The complex ion absorbs red light.</p>

TURN OVER

B	The overall charge of the complex ion is 4-.
C	The co-ordination number of the complex ion is 3.
D	The geometry of the complex ion is octahedral.

Option A: Since the colour of the complex is red, the complex ion reflects red light and not absorb it.

Option B - D:

$\text{Fe}^{2+}$  : *ortho*-phenanthroline  
 $= 1 \times 10^{-5} : 3 \times 10^{-5}$   
 $= 1 : 3$

Since *ortho*-phenanthroline is a bidentate ligand, there are 6 dative bonds formed (coordination number = 6) around  $\text{Fe}^{2+}$ , resulting in an octahedral geometry. The overall charge of the complex is +2 i.e.  $[\text{Fe}(\text{ortho-phenanthroline})_3]^{2+}$

Answer: D

END OF PAPER

TURN OVER



ST ANDREW'S JUNIOR COLLEGE  
JC2 PRELIMINARY EXAMINATIONS  
HIGHER 2

CANDIDATE  
NAME

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CLASS

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**CHEMISTRY**

**9729/02**

Paper 2 Structured Questions

**31 August 2022**

Candidates answer on the Question Paper.

**2 hours**

Additional Materials: Data Booklet

**READ THESE INSTRUCTIONS FIRST**

Write your name and class on all the work that you hand in.

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.

Answer all questions in the spaces provided on the Question Paper.

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.

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

<b>1</b>	Hydrazine, N <sub>2</sub> H <sub>4</sub> , is a colourless liquid with an ammonia-like odour. It is an important precursor in the pharmaceuticals industry.		
<b>(a)</b>	Hydrazine exists as a liquid while ammonia exists as a gas at room temperature and pressure. State two reasons to explain this difference in physical state.  Both ammonia and hydrazine are polar simple covalent molecules, capable of forming intermolecular hydrogen bonds. Hydrazine has more hydrogen bonding sites and therefore, it is able to form <u>more extensive intermolecular hydrogen bonds</u> . At the same time, it has <u>more electrons / larger electron cloud size</u> and this leads to <u>stronger intermolecular instantaneous dipole-induced dipole interactions</u> . Hence, both of these require more energy to overcome.	[2]	
<b>(b)</b>	The K <sub>b</sub> values of hydrazine, ethylamine, and phenylamine are shown in Table 1.1.	[1]	
<b>(i)</b>	Explain what is meant by the term <i>Bronsted-Lowry base</i> .  A Bronsted-Lowry base refers to a <u>proton acceptor</u> .	[1]	
<b>(ii)</b>	Explain the relative magnitudes of the K <sub>b</sub> values in Table 1.1.  (most basic) <u>ethylamine &gt; hydrazine &gt; phenylamine</u> Unlike hydrazine, ethylamine has an <u>electron donating alkyl/ethyl group</u> which makes the <u>lone pair of electrons on N more available to accept H<sup>+</sup></u> . Phenylamine is weaker base than hydrazine as the <u>lone pair of electrons on N is delocalised into the benzene ring</u> , making it <u>less available to accept H<sup>+</sup></u> .	[2]	
<b>(iii)</b>	The K <sub>b</sub> values of diethylamine and triethylamine are shown in Table 1.2.	[1]	

Table 1.1

base	K <sub>b</sub> / mol dm <sup>-3</sup>
Hydrazine	1.7 × 10 <sup>-6</sup> (for K <sub>b1</sub> )
Ethylamine	4.5 × 10 <sup>-4</sup>
Phenylamine	7.4 × 10 <sup>-10</sup>

For Examiner's Use						Total
	Q1	Q2	Q3	Q4	Q5	
	12	14	14	10	25	75

Table 1.2

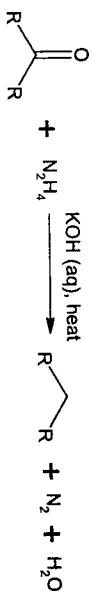
base	$K_b$ / mol dm <sup>-3</sup>
Diethylamine	$6.9 \times 10^{-4}$
Triethylamine	$6.5 \times 10^{-5}$

Suggest why the  $K_b$  value of triethylamine is significantly smaller than the  $K_b$  values of ethylamine and diethylamine.

Triethylamine is a tertiary amine and the presence of (one) more R(alkyl) groups will result in steric hindrance, thus leading to a smaller extent of base dissociation in aqueous / less likely to accept a  $H^+$ .

[1]

(c) The Wolff-Kishner reaction is a valuable synthetic method to convert carbonyl compounds into alkanes. This is done by reacting a carbonyl compound with excess hydrazine in the presence of potassium hydroxide.



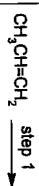
(i) Suggest a simple chemical test to monitor the completion of the Wolff-Kishner reaction.

[2]

Add **2,4-dinitrophenylhydrazine / 2,4-DNPH** to the reaction mixture (and warm)

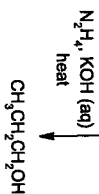
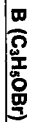
If the reaction was complete, there will be **no orange ppt**.

(ii) Propan-1-ol can be synthesised from propene by the following 3-step route that incorporates the Wolff-Kishner reaction.



A

step 2



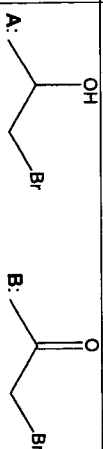
Suggest the structures of intermediate products **A** and **B** and state the reagents and conditions for each step.

[4]

Reagents and conditions

Step 1: .....

Step 2: .....



Reagents and conditions

Step 1: Br<sub>2</sub>/aq

Step 2: K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>/aq or KMnO<sub>4</sub>/aq, H<sub>2</sub>SO<sub>4</sub>/aq, heat

[Total: 12]

[TURN OVER

[TURN OVER



2	Organic matter is known to decay under low oxygen conditions, such as in swamps. The sulfate-reducing bacteria present in the organic matter will reduce the various sulfates into hydrogen sulfide, H <sub>2</sub> S. Some of the hydrogen sulfide will react with Fe <sup>2+</sup> present in swamp to produce insoluble FeS, which is responsible for the brown colour of sludge in the swamp.								
	<b>reaction 1</b>	$\text{H}_2\text{S}(\text{g}) + \text{aq} \rightleftharpoons 2\text{H}^+(\text{aq}) + \text{S}^{2-}(\text{aq})$							
	<b>reaction 2</b>	$\text{Fe}^{2+}(\text{aq}) + \text{S}^{2-}(\text{aq}) \rightleftharpoons \text{FeS}(\text{s})$					$\Delta H^\circ_{\text{ppt}}$		
	<b>(a) (i)</b>	In a saturated solution of hydrogen sulfide, $[\text{H}^+][\text{S}^{2-}]$ is $1.0 \times 10^{-23} \text{ mol}^2 \text{ dm}^{-6}$ . Calculate the maximum concentration of sulfide ions present in the swamp, given that the pH of swamp water is 6.8.							[1]
		$[\text{H}^+] = 10^{-6.8}$	$= 1.5848 \times 10^{-7} \text{ mol dm}^{-3}$	$[\text{S}^{2-}] = \frac{1 \times 10^{-23}}{[1.5848 \times 10^{-7}]^2} = 3.98 \times 10^{-10} \text{ mol dm}^{-3}$					
	<b>(ii)</b>	Hence, calculate the minimum concentration of Fe <sup>2+</sup> in the swamp required for the precipitation of FeS. ( $K_{\text{sp}}$ of FeS = $4.9 \times 10^{-16} \text{ mol}^2 \text{ dm}^{-6}$ )							[1]
		<i>Ecf from (a)(i)</i>	$K_{\text{sp}} = [\text{Fe}^{2+}][\text{S}^{2-}]$	$[\text{Fe}^{2+}] = \frac{4.9 \times 10^{-16}}{3.981 \times 10^{-10}} = 1.23 \times 10^{-6} \text{ mol dm}^{-3}$					
	<b>(iii)</b>	$\Delta G^\circ_{\text{ppt}}$ can be determined by using the following expression, where $R$ is the molar gas constant and $T$ is the temperature measured in K.							[2]
							$\Delta G^\circ_{\text{ppt}} = 2.303RT \lg K_{\text{sp}}$		
							$\Delta G^\circ_{\text{ppt}} = 2.303 \times 8.31 \times 298 \times \lg(4.9 \times 10^{-16})$	$= -98719 \text{ J mol}^{-1}$	

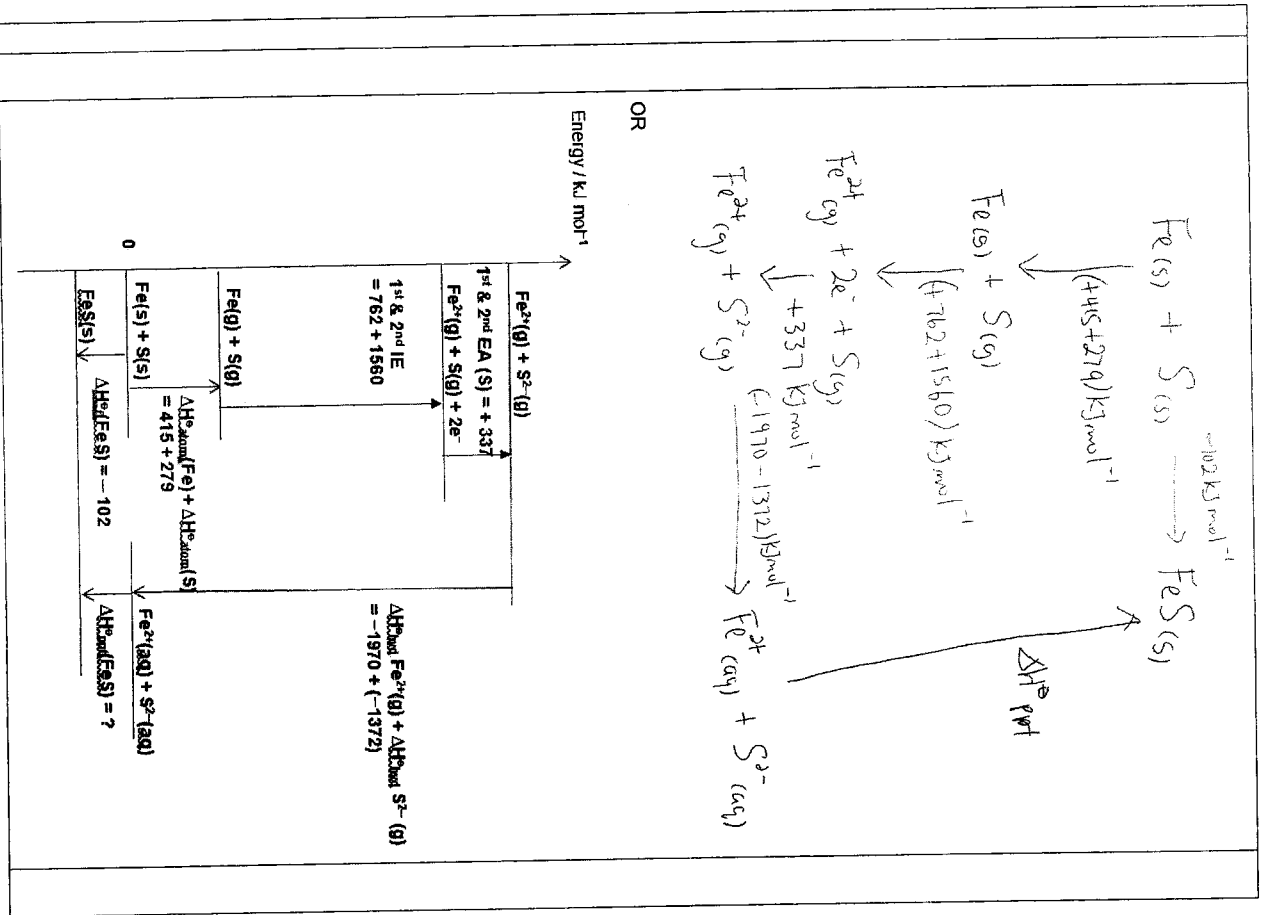
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		$= -98.7 \text{ kJ mol}^{-1}$ (3 sf)							
	<b>(iv)</b>	Predict how the brown colour intensity of sludge will change when pH decreases. Explain your answer.							[2]
		When pH decreases, $[\text{H}^+]$ increases. By Le Chatelier's Principle, position of equilibrium 1 will shift left, reducing $[\text{S}^{2-}]$ . This will in turn cause position of equilibrium 2 to shift left, resulting in less FeS solid and hence, the brown colour intensity will decrease.							
	<b>(b)</b>	Using data from Table 2 below, together with relevant data from the Data Booklet, draw an energy cycle and calculate $\Delta H^\circ_{\text{ppt}}$ for reaction 2.							[4]

Table 2

standard enthalpy change of formation of FeS(s)	-102 kJ mol <sup>-1</sup>
standard enthalpy change of atomisation of Fe(s)	+415 kJ mol <sup>-1</sup>
standard enthalpy change of atomisation of S(s)	+279 kJ mol <sup>-1</sup>
sum of first and second electron affinity of sulfur	+337 kJ mol <sup>-1</sup>
standard enthalpy change of hydration of Fe <sup>2+</sup> (g)	-1970 kJ mol <sup>-1</sup>
standard enthalpy change of hydration of S <sup>2-</sup> (g)	-1372 kJ mol <sup>-1</sup>

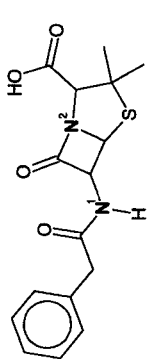
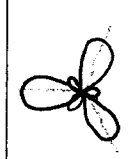
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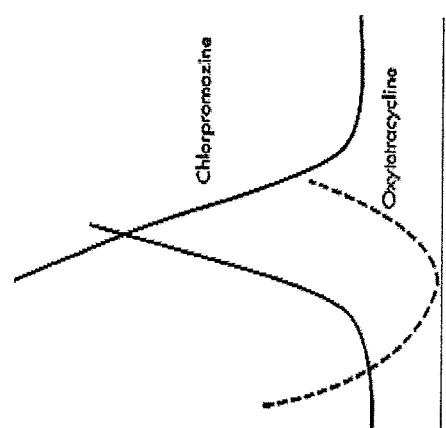


	Applying Hess' Law, -102 = 415 + 279 + 762 + 1560 + 337 - 1970 - 1372 + ΔH° <sub>precip</sub> (FeS) ΔH° <sub>precip</sub> (FeS) = <b>-113 kJ mol⁻¹</b> (3 s.f.)	
(c) (i)	Use your answers in (a)(iii) and (b), calculate the ΔS° <sub>precip</sub> for the formation of FeS precipitate. ecf from (a)(iii) and (b) ΔG° = ΔH° - TΔS° -98.7 = (-113) - 298ΔS° ΔS° = -0.04798 kJ mol⁻¹ K⁻¹ ≈ <b>-0.0480 kJ mol⁻¹ K⁻¹</b> (to 3 sf)	[1]
(ii)	Hence, explain the significance of the sign of ΔS° <sub>precip</sub> in (c)(i). Entropy change is negative because the <u>degree of disorderliness decreases</u> / <u>less disordered</u> owing to a <u>decrease in the number of aqueous particles during precipitation</u> / <u>aqueous species are regularly arranged in crystal lattice structure.</u>	[1]
(d)	Although hydrogen sulfide and water molecules have the same shape, they have slightly different bond angles. State and explain which species has a larger bond angle. In H <sub>2</sub> O, <u>oxygen has a greater electronegativity</u> than sulfur in H <sub>2</sub> S. Hence, the <u>bond pair of electrons are more strongly attracted to oxygen</u> , resulting in <u>greater repulsion between the bond pairs</u> in water. Hence, the <u>H<sub>2</sub>O</u> has a larger bond angle.	[2]
	[Total: 14]	

TURN OVER

TURN OVER

<p>3 Ionisable drugs have acidic, basic or amphoteric properties. An example of an acidic drug is benzylpenicillin G, which is an antibiotic used to treat certain bacterial infection.</p>	
<div style="text-align: center;">  <p>benzylpenicillin G</p> </div>	
<p>(a) Both nitrogen atoms in benzylpenicillin G are sp<sup>2</sup> hybridised.</p>	
<p>(i) Draw the shape of the hybrid orbitals around N<sup>1</sup>.</p>	<div style="text-align: center;">  </div>
<p>(ii) Suggest why sp<sup>2</sup> hybridisation at N<sup>1</sup> and N<sup>2</sup> will make benzylpenicillin G more stable.</p>	<p>p orbitals at N<sup>1</sup> and N<sup>2</sup> can overlap sideways with π electron cloud/bond of C=O. Hence, the <u>lone pair of electrons on N<sup>1</sup> and N<sup>2</sup> can delocalise over N-C-O</u>. This results in resonance stabilisation.</p>
<p>(iii) Suggest a reason why C-N<sup>2</sup> bond is weaker than C-N<sup>1</sup> bond.</p>	<p>There is <u>ring strain</u> in the cyclic amide involving N<sup>2</sup>. OR The <u>bond angle around N<sup>2</sup> (90°) is smaller than the expected (120°)</u>.</p>
<p>(b) The solubility of three different ionisable drugs is shown in Fig. 3.1.</p>	<p style="text-align: center;">solubility</p>

<div style="text-align: center;">  <p>Fig. 3.1</p> </div>	
<p>(i) Explain why the solubility of benzylpenicillin G in aqueous increases from low to high pH.</p>	<p>[2] At low pH, benzylpenicillin G forms hydrogen bonding with water molecules. At higher pH, the -COOH group of benzylpenicillin G is deprotonated to -COO<sup>-</sup>, which can form <u>stronger ion-dipole interactions with water</u>. As more energy is released in the formation of ion-dipole interactions with water, benzylpenicillin G is more soluble at higher pH.</p>
<p>(ii) Classify the following compounds according to the type of ionisable drug (acidic, basic and amphoteric). Chlorpromazine: <u>basic</u> Oxytetracycline: <u>amphoteric</u></p>	<p>[1]</p>
<p>(iii) The pH of blood containing benzylpenicillin G is 7.4. Given that the pK<sub>a</sub> of benzylpenicillin G is 2.76, calculate the concentration of the undissociated benzylpenicillin G. Let benzylpenicillin G be HA. <math>K_a = \frac{[H^+][A^-]}{[HA]}</math> <math>10^{-2.76} = \frac{(10^{-7.4})^2}{[HA]}</math></p>	<p>[2]</p>

	$[H^+] = 9.12 \times 10^{-13} \text{ mol dm}^{-3}$	
(iv)	<p>The Henderson-Hasselbalch equation can be re-expressed to relate the solubility of a drug to the pH of the solution and its <math>pK_a</math>.</p> $pH = pK_a + \log_{10} \left( \frac{S - S_0}{S_0} \right)$ <p>where <math>S</math> is the concentration of the dissolved drug and <math>S_0</math> is the concentration of the undissociated drug.</p> <p>The solubility of the undissociated benzylpenicillin G in blood with pH 7.4 is <math>9 \times 10^{-13} \text{ mol dm}^{-3}</math>. Using the information above and in (b)(ii), calculate the solubility of benzylpenicillin G in blood with pH 7.4. Express your answer in <math>\text{mol dm}^{-3}</math>.</p>	[2]
	$7.4 = 2.76 + \log \left( \frac{S - 9 \times 10^{-13}}{9 \times 10^{-13}} \right)$ $10^{4.64} = \frac{S - 9 \times 10^{-13}}{9 \times 10^{-13}}$ $S = 3.928 \times 10^{-8} \approx \underline{3.93 \times 10^{-8} \text{ mol dm}^{-3}} \text{ (to 3 sf)}$	
(c)	<p>Benzylpenicillin G is administered intravenously as potassium benzylpenicillin G, which is an ionic compound.</p> <p>The drug is prepared in a buffer solution made of citric acid, <math>C_6H_7O_5COOH</math> and potassium citrate, <math>C_6H_7O_5COOK</math> to maintain its solubility and stability.</p>	
(i)	Define the term <i>buffer</i> .	[1]
	A buffer solution is a solution whose <u>pH remains almost unchanged</u> when a <u>small amount of <math>H^+</math> or <math>OH^-</math> is added to it</u> .	
(ii)	Write an equation to show how the citric acid/citrate buffer maintains the pH of the solution when small amounts of alkali are added.	[1]
	<u><math>C_6H_7O_5COOH + OH^- \rightarrow C_6H_7O_5COO^- + H_2O</math></u>	
(iii)	Explain the difference between the ionic radius and atomic radius of potassium.	[2]

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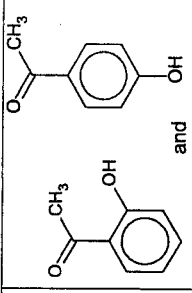
Both $K^-$ and $K$ have the <u>same number of protons</u> and so, <u>nuclear charge is the same / constant</u> . $K^-$ has <u>one less shell of electrons</u> than $K$ . Thus, the valence electrons of $K$ experience lower shielding effect.
The <u>valence electrons in <math>K^+</math> are more strongly attracted</u> and closer to the <u>nucleus</u> . $K^+$ is <u>smaller</u> .
[Total: 14]

[TURN OVER

4 Compound X has the molecular formula  $C_8H_8O_2$ . It contains 2 different functional groups. Data about the reactions of X are given in the table below.

reaction	reagent	observations
1	alkaline aqueous iodine	yellow ppt
2	$Cr_2O_7^{2-}/H^+$ , heat	orange solution
3	$Br_2(aq)$	white solid Y with $M_r = 293.8$

(a) (i)	Based on reaction 1 only, state all the deductions about X.	[1]
	X contains a <u>methyl carbonyl (<math>CH_3C=O</math>)</u> or <u>methyl alcohol (<math>CH_3CH(OH)</math>)</u> .	
(ii)	Which deduction in (a)(i) is confirmed by reaction 2? Explain your answer.	[2]
	<u>Methyl carbonyl</u> X <u>does not get oxidised by <math>Cr_2O_7^{2-}/H^+</math></u> so it cannot contain a methyl alcohol.	
(iii)	Based on your answer in (a)(ii), construct an equation to represent reaction 1. You may use R to represent part of compound X which does not react with alkaline aqueous iodine.	[1]
	$R(C=O)CH_3 + 3I_2 + 4OH^- \rightarrow RCOO^- + CHI_3 + 3I^- + 3H_2O$	
(iv)	State the type of reaction taking place in reaction 3.	[1]
	<u>Electrophilic substitution</u>	
(v)	Deduce the molecular formula of Y. State the identity of the other functional group found in X based on reaction 3.	[3]
	Mr of X = 136. Increase in Mr of $293.8 - 136 = 157.8$ is due to <u>substitution of 2 H for 2 Br</u> . Molecular formula: <u><math>C_8H_6O_2Br_2</math></u> <u>Phenol</u>	
(b)	Based on your answers in (a), draw the structural formulae of the 2 possible isomers of X.	[2]

	[Total: 10]
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5 Wearables, such as smartwatches and fitness trackers, are gaining popularity with new detecting abilities constantly being developed.

In recent years, research has been done to integrate chemical sensors into wearables to detect metabolites in sweat. One such metabolite is lactate, which can be used to determine the fatigue level of muscles in our body. Under conditions of high energy demand, glucose breaks down rapidly into lactate, which accumulates in the muscles. Fig. 5.1 shows the breakdown of glucose to pyruvate, and eventually to lactate ( $M_r = 89.0$ ).

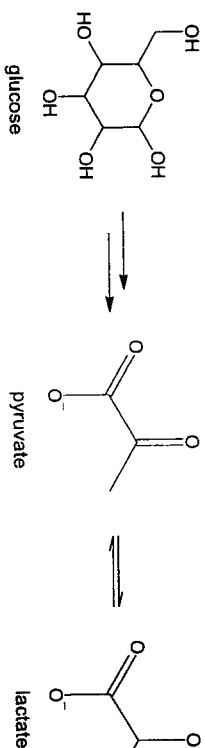


Fig. 5.1

Table 5.1 shows the lactate concentration in sweat before and after intense exercise.

	Table 5.1 Lactate concentration ( $\text{mol dm}^{-3}$ )	
	before exercise	after exercise
sweat	$2.0 \times 10^{-4}$	$6.2 \times 10^{-4}$

Table 5.2 shows the possible lactate concentration ranges that can exist in blood.

Table 5.2	
Lactate concentration ( $\text{mmol dm}^{-3}$ )	Medical condition
0.5 - 1	Normal
2 - 4	Hyperlactaemia
> 4	Acidosis

(a) (i) State the number of chiral centres present in glucose molecule.

5

[1]

TURN OVER

(ii) A normal person loses an average of  $3.5 \text{ dm}^3$  of sweat for every hour of exercise. Using the data in Table 5.1, calculate the mass of lactate lost in sweat after two hours of intense exercise.

$$\text{Volume of sweat lost} = 3.5 \times 2 = 7 \text{ dm}^3$$

$$\text{Amount of lactate lost} = 7 \times [(6.2 \times 10^{-4}) - (2.0 \times 10^{-4})] = 0.00294 \text{ mol}$$

$$\text{Mass of lactate lost} = 0.00294 \times 89.0 = 0.2616 \approx \underline{0.262 \text{ g}} \quad (\text{to 3 sf})$$

[2]

(iii)  $10 \text{ cm}^3$  of blood was drawn from an individual and the mass of lactate was found to be  $0.0027 \text{ g}$ .

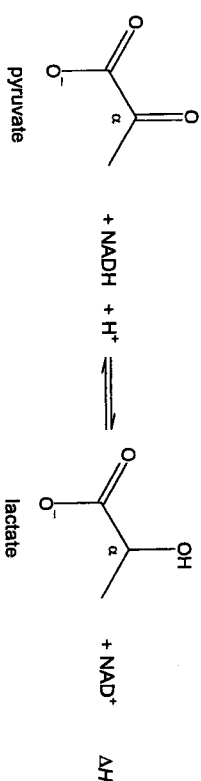
Determine the medical condition of this individual.

[1]

$$\frac{[\text{lactate}]}{[\text{pyruvate}]} = \frac{[(0.0027 / 89)] / 0.01}{0.01} = \underline{0.003033} \text{ mol dm}^{-3} = 3.03 \text{ mmol dm}^{-3}$$

The individual suffers from hyperlactaemia.

The reduction of pyruvate to lactate involves a compound known as reduced nicotinamide adenine dinucleotide (NADH). The reduction is an equilibrium where all species are in aqueous state.



$K_a$  value for this equilibrium at  $298 \text{ K}$  is  $1.46 \times 10^{11}$ .

(b) (i) State the change in oxidation number for carbon  $\alpha$ .

[1]

**+2 to 0 OR Change is -2**

(ii) During an intense exercise, the pH of blood decreases from 7.4 to 7.1. Assuming that  $[\text{NADH}]$  is equal to  $[\text{NAD}^+]$ , calculate the  $[\text{lactate}] / [\text{pyruvate}]$  ratio at pH 7.1.

[2]

$$1.46 \times 10^{11} = \frac{[\text{lactate}]}{[\text{pyruvate}][10^{-7.1}]}$$

$$\frac{[\text{lactate}]}{[\text{pyruvate}]} = 11597 \approx \underline{11600} \quad (\text{to 3 sf})$$

TURN OVER

(iii) Fig. 5.2 shows the graph of  $[\text{lactate}] / [\text{pyruvate}]$  against time. At time  $t_1$ , the temperature of the reaction was increased.

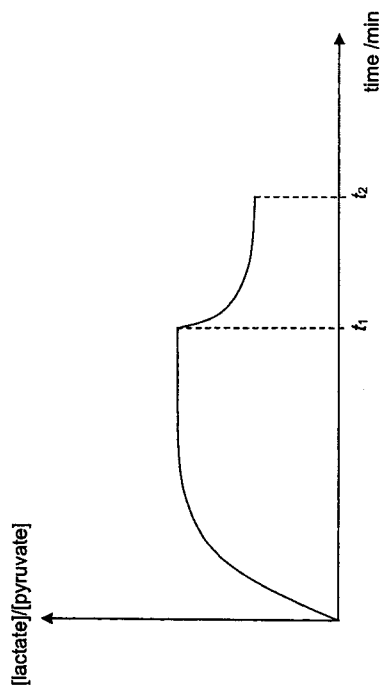


Fig. 5.2

Determine the sign of  $\Delta H$  for this reaction. Explain your answer. [2]

At time  $t_1$ , when temperature is increased, ratio decreased. Hence, the position of equilibrium has shifted left to absorb the excess heat. This meant that the favoured backward reaction is endothermic, the forward reaction is exothermic,  $\Delta H$  is negative.

(iv) On Fig. 5.2, complete the diagram to show the effect on  $[\text{lactate}] / [\text{pyruvate}]$  when  $\text{OH}^-$  was added to the reaction mixture at time  $t_2$ . [1]

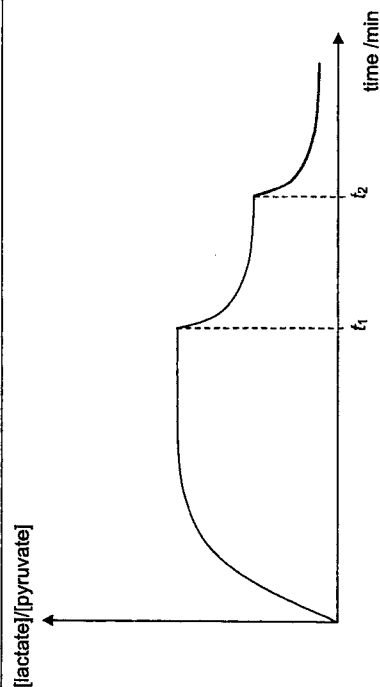


Fig. 5.3 shows the reduction of pyruvate. This reaction happens in the following manner.

- The lone pair of electrons on N of NADH delocalises into a nearby alkene. This causes the  $\pi$  bond to be broken but a new one is subsequently formed.
- A C-H bond of NADH breaks and the two electrons form a  $\sigma$  bond with carbonyl carbon of pyruvate.
- The  $\pi$  bond of C=O breaks and a  $\sigma$  bond is formed with  $\text{H}^+$  as shown.

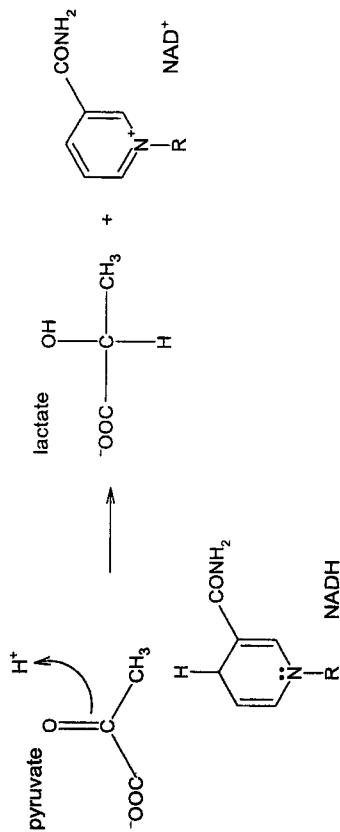
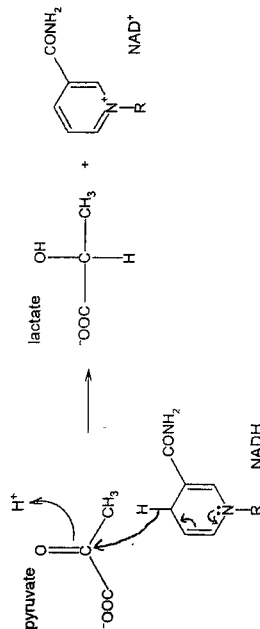
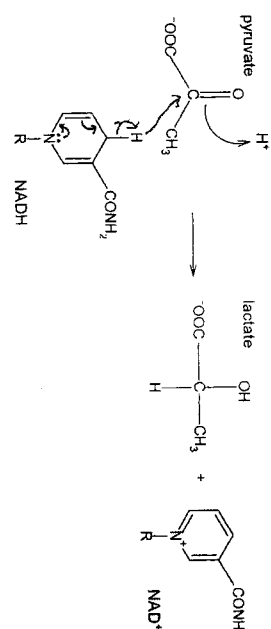
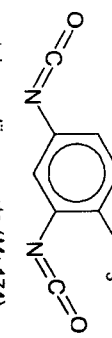


Fig. 5.3

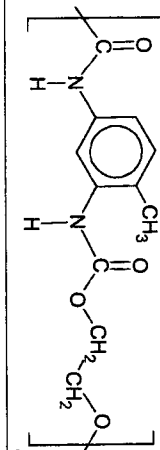
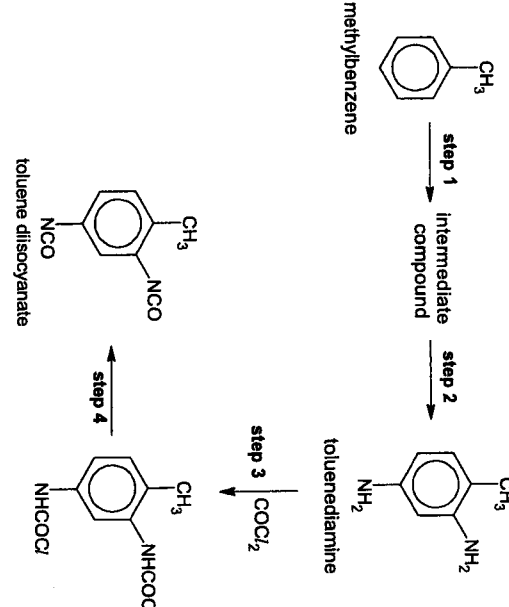
(v) On Fig. 5.3, draw curly arrows to show the movement of electron pairs when NADH reduces pyruvate into lactate. [2]



OR

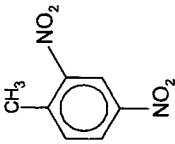
<p>pyruvate</p>  <p>lactate</p> <p>NADH</p> <p>NAD<sup>+</sup></p>	<p>(c) Polyurethane is a polymer used to make the straps of fitness bands and smartwatches as they have good resistance towards salt water and ultra-violet radiation. Hence, unlike cheaper plastic or resin straps, polyurethane straps are more suited for a wide range of sporting activities.</p> <p>The reaction between diisocyanate and diol to form polyurethane is shown in <b>Equation 1</b>.</p> <p><b>Equation 1</b></p> $\text{O}=\text{C}-\text{N}=\text{N}-\text{C}=\text{O} + \text{HO}-\text{R}^2-\text{OH} \longrightarrow \left[ \text{O}=\text{C}-\text{N}(\text{H})-\text{R}^1-\text{N}(\text{H})-\text{C}(\text{O})-\text{O}-\text{R}^2-\text{O} \right]_n$ <p>diisocyanate                      diol                      polyurethane</p> <p><math>n</math> = degree of polymerisation</p>
<p>(i)</p>  <p>toluene diisocyanate (M: 174)</p> <p>Suggest the structure of the polyurethane polymer formed when toluene diisocyanate is reacted with ethane-1,2-diol.</p> <p>[1]</p>	

TURN OVER

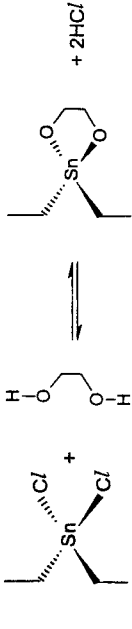
	<p>(ii) The average molar mass of the polyurethane polymer formed in (c)(i) is <math>1.3688 \times 10^4 \text{ g mol}^{-1}</math>. Calculate the degree of polymerisation, <math>n</math>, for this polymer. [1]</p> <p><math>n = 13688 / (174 + 12.0 \times 2 + 6 \times 1.0 + 16.0 \times 2) = 58</math></p> <p>ecf from (c)(i)</p>
<p>(d) Toluene diisocyanate is synthesised from methylbenzene by the following route.</p>  <p>step 1                      step 2</p> <p>intermediate compound</p> <p>step 3                      step 4</p> <p>toluenediamine</p> <p>toluene diisocyanate</p>	<p>(i) Complete the reaction scheme to show how toluenediamine could be synthesised from methylbenzene in two steps. Show the structure of the intermediate product and state the reagents and conditions for each step. [3]</p> <p>Step 1 .....</p> <p>Step 2 .....</p>

TURN OVER



	intermediate compound	
	step 1: conc $\text{H}_2\text{SO}_4$ , conc $\text{HNO}_3$ step 2: Sn, conc $\text{HCl}$ /heat, followed by (excess) $\text{NaOH}$ (aq)	
		
(ii)	Suggest the type of reaction in step 4.	[1]
	<u>Elimination</u>	
(iii)	The reaction between toluenediamine and phosgene gas, $\text{COCl}_2$ , in step 3 is carried out at a temperature of $500^\circ\text{C}$ and 400 kPa. Assuming the process is 100% efficient, calculate the volume of phosgene required to produce 1 kg of toluene diisocyanate.	[2]
	Amount of phosgene required = $(1000 / 174) \times 2 = 11.494 \text{ mol}$ $(400 \times 1000) \text{ V} = 11.494 \times 8.31 \times (500 + 273)$ $\text{V} = 0.1845 \text{ m}^3 \approx \underline{0.185 \text{ m}^3}$ (to 3 sf)	
(iv)	Phosgene gas is known to exhibit non-ideal gas behaviour. State a reason for this observation. There are <b>significant permanent dipole-permanent dipole interactions between phosgene molecules.</b>	[1]
	OR	

[TURN OVER

	The <b>volume / molecular size of each phosgene molecule is significant compared to the total volume occupied by phosgene gas sample.</b>	
(v)	Toluene diisocyanate must be stored in an anhydrous condition. In the presence of water, toluene diisocyanate will react to form toluenediamine and an acidic gas. Suggest the identity of the acidic gas.  <u><math>\text{CO}_2</math></u>	[1]
(e)	The production of polyurethane occurs in the presence of diethyltin dichloride catalyst. Tin atoms are capable of undergoing ligand exchange with ethane-1,2-diol as shown in Fig. 5.4.	
		Fig. 5.4
(i)	Suggest how the presence of a catalyst would affect the magnitudes of the rate constant, $k$ , and activation energy, $E_a$ , of the reaction in Fig. 5.4.  The presence of a catalyst will <b>increase rate constant</b> and <b>decrease activation energy.</b>	[1]
(ii)	Suggest a chemical test to show that ligand exchange has occurred according to Fig. 5.4. Include the expected observations in your answers.  Add <u><math>\text{AgNO}_3(\text{aq})</math></u> followed by $\text{NH}_3(\text{aq})$ . <b>White ppt observed</b> , soluble in $\text{NH}_3(\text{aq})$ to form colourless solution. OR Add <u><math>\text{Na}_2\text{CO}_3(\text{aq})</math></u> . <b>Effervescence observed. Gas formed white ppt in aq <math>\text{Ca}(\text{OH})_2</math>.</b>	[2]
		[Total: 25]

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ST ANDREW'S JUNIOR COLLEGE  
 JC2 PRELIMINARY EXAMINATIONS  
 HIGHER 2

CANDIDATE  
 NAME

CLASS

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**CHEMISTRY**

**9729/03**

Paper 3 Free Response

14 September 2022

Candidates answer on the Question Paper.

2 hours

Additional Materials: Data Booklet

**READ THESE INSTRUCTIONS FIRST**

Write your name and class on all the work that you hand in.

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.

Answer all questions in the spaces provided on the Question Paper.

If additional space is required, you should use the pages at the end of this booklet.

The question number must be clearly shown.

**Section A**

Answer all questions.

**Section B**

Answer one question.

A Data Booklet is provided.

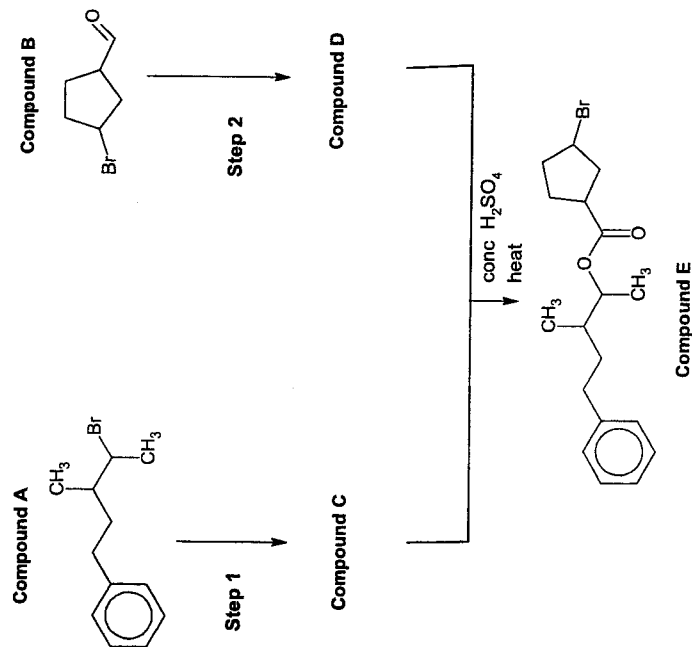
The use of an approved scientific calculator is expected, where appropriate.

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

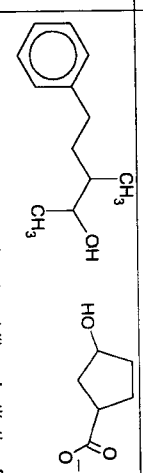
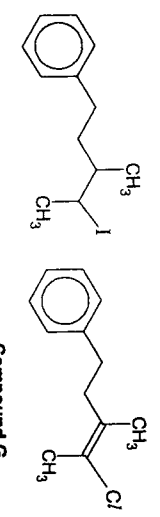
The number of marks is given in brackets [ ] at the end of each question or part question.

This document consists of 26 printed pages (including this cover page).

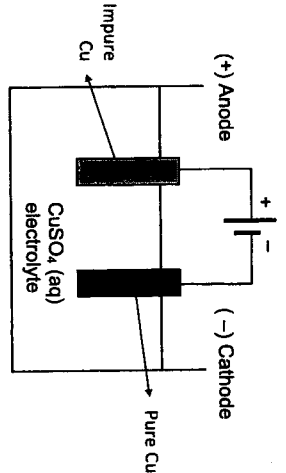
1 (a) The diagram below shows how compound E may be prepared.



(i)	Draw the structural formulae for C and D.	[2]
	Compound C: 	
	Compound D: 	
(ii)	Suggest the reagents and conditions for steps 1 and 2.	[2]
	Step 1: aq NaOH, heat Step 2: aq H <sub>2</sub> SO <sub>4</sub> , aq KMnO <sub>4</sub> , heat	

	or $\text{aq H}_2\text{SO}_4 \text{K}_2\text{Cr}_2\text{O}_7$ , heat	
(iii)	Draw the structures of the products formed when <b>E</b> is reacted with hot aqueous sodium hydroxide.	[2]
	 (nucleophilic substitution for bromoalkane will occur)	
(iv)	State the type of reaction when <b>C</b> and <b>D</b> react to form <b>E</b> . Condensation / nucleophilic (acyl) substitution	[1]
(v)	Equal amounts of <b>A</b> , <b>F</b> and <b>G</b> are added separately to three test-tubes, which each contains equal concentration of ethanolic silver nitrate. The test-tubes are placed in a hot water bath. No precipitate is formed in one of the test-tubes. For the other two test-tubes, precipitates are formed at different rates. Explain these observations.	
	 Compound F                      Compound G	[3]
	Compounds <b>A</b> and <b>F</b> undergo nucleophilic substitution with ethanolic $\text{AgNO}_3$ which releases halide ion to form a ppt with $\text{Ag}^+$ .	
	<b>C-I bond in F is weaker than C-Br bond in A as I is larger atom than Br and has less effective orbital overlap with C. Thus I- is released faster to form ppt, followed by Br-.</b>	
	<b>Lone pair of electrons on the Cl atom delocalise into the <math>\pi</math> bond / C=C, resulting in C-Cl having partial double bond character, hence the bond does not break easily and no ppt is formed for compound G.</b>	

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(b)	Copper is an important metal which can be used to catalyse many organic reactions. It exists naturally as an ore containing calcium and silver impurities. To obtain copper metal, the ore is purified using electrolysis.	
(i)	Draw a labelled diagram for the purification set-up.	[2]
		
(ii)	With reference to relevant data from the <i>Data Booklet</i> , explain what happens to the calcium and silver impurities during the purification.	[3]
	$\text{Ag}^+(\text{aq}) + \text{e}^- \rightleftharpoons \text{Ag}(\text{s}) \quad E^\ominus = +0.80 \text{ V}$ $\text{Ca}^{2+} + 2\text{e}^- \rightleftharpoons \text{Ca} \quad E^\ominus = -2.87 \text{ V}$ $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Cu}(\text{s}) \quad E^\ominus = +0.34 \text{ V}$ <p>When an electric current is applied, <b>copper and calcium at the anode (+), are oxidised</b> to their respective ions. Ca is oxidised because of the <b>negative <math>E^\ominus</math></b>.</p> <p><math>\text{Cu}^{2+}</math> and <math>\text{Ca}^{2+}</math> then migrate to the cathode (-). At the cathode, <b>only <math>\text{Cu}^{2+}</math> ions are reduced</b> to Cu due to its <b>more positive <math>E^\ominus</math></b>. <b><math>\text{Ca}^{2+}</math> remains as ions in the electrolyte</b> as it is not reduce to metal easily.</p> <p><b>Ag will not be oxidised</b> due to its <b>positive <math>E^\ominus</math> value</b> and it falls off the electrode and accumulate at the bottom as <b>anodic sludge (or words to the effect eg. drop to the bottom).</b></p>	
(iii)	A current was passed through the set up in (b)(i) for 50 minutes and the electrodes were then removed, washed, dried and weighed. It was found that the cathode had gained 0.95 g in mass. Calculate the current passing through the cell.	[2]
	Amount of Cu = $0.95 / 63.5 = 0.01496 \text{ mol}$ $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$	

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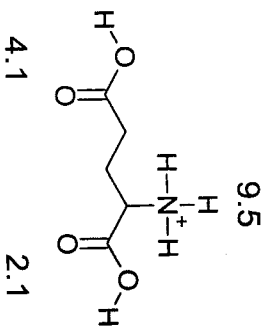
	Amount of $e^- = 2 \times 0.01496 = 0.02992 \text{ mol}$ $Q = It$ $0.02992 \times 96500 = I(50 \times 60)$ $I = 0.962 \text{ A}$	
(c)	Calcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$ , is used as a supplement for people who either do not get enough calcium from their diet or those who suffer from medical conditions like osteoporosis.	
(i)	With the aid of relevant data from the <i>Data Booklet</i> , deduce whether copper(I) phosphate or calcium phosphate will decompose at a lower temperature. Explain your answer. [2]	
	From data booklet, $r. \text{Cu}^{2+} = 0.073 \text{ nm}$ , $r. \text{Ca}^{2+} = 0.099 \text{ nm}$ $\text{Cu}^{2+}$ has higher charge density and therefore, is able to distort / polarise the electron cloud of $\text{PO}_4^{3-}$ to a larger extent. P-O is weakened to a larger extent in $\text{Cu}_3(\text{PO}_4)_2$ and therefore, need less energy to overcome it. $\text{Cu}_3(\text{PO}_4)_2$ will decompose at lower temperature.	
(ii)	50 $\text{cm}^3$ of 0.05 $\text{mol dm}^{-3}$ sodium phosphate solution is mixed with 30 $\text{cm}^3$ of 0.05 $\text{mol dm}^{-3}$ calcium nitrate solution. Determine whether calcium phosphate precipitate is formed. ( $K_{sp}$ of calcium phosphate = $2.07 \times 10^{-33} \text{ mol}^5 \text{ dm}^{-15}$ ) [2]	
	$[\text{PO}_4^{3-}]_{\text{mixture}} = (0.05 \times 0.05) / 0.08 = 0.03125 \text{ mol dm}^{-3}$ $[\text{Ca}^{2+}]_{\text{mixture}} = (0.03 \times 0.05) / 0.08 = 0.01875 \text{ mol dm}^{-3}$ $IP = [\text{Ca}^{2+}]^3[\text{PO}_4^{3-}]^2 = (0.01875)^3 \times (0.03125)^2$ $= 5.4373 \times 10^{-9} \text{ mol}^5 \text{ dm}^{-15} > K_{sp}$ $\text{Ca}_3(\text{PO}_4)_2$ ppt will form.	
	[Total: 21]	

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2	Chloric acid, $\text{HClO}$ is both a strong acid and an oxidising agent. It is corrosive and will accelerate the burning of combustible materials.	
(a)	When reacted with excess aqueous potassium hydroxide, $\text{HClO}$ is converted into water and two chloro-containing products, one of which is a chloro-oxo anion.  In an experiment, 0.5 mol of chloro-oxo anion was reacted with excess potassium iodide to form a brown solution and chloride ion. It was discovered that the brown solution required 3 moles of sodium thiosulfate for complete reaction.	
(i)	Calculate the number of moles of electrons gained by 1 mole of chloro-oxo anion in the reaction with potassium iodide. Hence, prove that the chloro-oxo anion is $\text{ClO}_3^-$ . [3]	$\text{I}_2 + 2\text{S}_2\text{O}_3^{2-} \rightarrow \text{S}_4\text{O}_6^{2-} + 2\text{I}^-$ Amount of $\text{I}_2$ formed = $3/2 = 1.5 \text{ mol}$ Amount of $\text{I}^-$ reacted = $1.5 \times 2 = 3 \text{ mol}$ Chloro-oxo anion : $\text{I}^-$ 0.5 : 3 1 : 6 Given $2\text{I}^- \rightarrow \text{I}_2 + 2e^-$ Amount of electron gained by 1 mole of chloro-oxo anion = 6 Oxidation number of Cl in chloro-oxo anion = $-1 + 6 = +5$ Oxoanion = $\text{ClO}_3^-$
(ii)	The other chloro-containing product formed a white precipitate with silver nitrate solution.  Identify this other chloro-containing product. Write an equation for the reaction between chloric acid and excess potassium hydroxide. [2]	Other product = $\text{Cl}^-$ Equation: $3\text{HClO} + 3\text{KOH} \rightarrow \text{KClO}_3 + 2\text{KCl} + 3\text{H}_2\text{O}$ OR $3\text{H}^+ + 3\text{ClO}^- + 3\text{OH}^- \rightarrow \text{ClO}_3^- + 2\text{Cl}^- + 3\text{H}_2\text{O}$ OR $3\text{ClO}^- \rightarrow \text{ClO}_3^- + 2\text{Cl}^-$

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(b)	Use of Data Booklet is relevant to this question. An experiment was carried out to determine the enthalpy change of neutralisation of chloric acid. 25 cm <sup>3</sup> of 1 mol dm <sup>-3</sup> chloric acid was mixed with 25 cm <sup>3</sup> of 1.5 mol dm <sup>-3</sup> potassium hydroxide and there was an increase in temperature by 8 °C.	
(i)	Explain the term <u>standard enthalpy change of neutralisation</u> . The standard enthalpy change of neutralisation, $\Delta H_{\text{neut}}^\ominus$ , is the enthalpy change when <u>an acid reacts with a base</u> to form <u>one mole of water</u> in dilute aqueous solution at <u>standard conditions</u> / <u>298 K and 1 bar</u> .	[1]
(ii)	Calculate the enthalpy change of neutralisation. Assume that the specific heat capacity of all solutions is the same as that of water. $q = mc\Delta T = (50)(4.18)(8) = 1672 \text{ J}$ Amount of H <sub>2</sub> O formed = amount of chloric acid = $(25/1000)(1) = 0.025 \text{ mol}$ $\Delta H_n = -(1672/1000)/0.025 = -66.88 \text{ kJ mol}^{-1} \approx \underline{-66.9 \text{ kJ mol}^{-1}}$	[2]
(iii)	The enthalpy change of neutralisation between a strong acid and a strong base is $-57.3 \text{ kJ mol}^{-1}$ . Suggest a reason for the difference between this value and your answer in b(ii). In the presence of (excess) strong base, <u>chlorate(I) ion undergoes disproportionation</u> and the <u>enthalpy change of the disproportionation reaction could have caused <math>\Delta H_n</math> to be more exothermic</u> . / <u>Heat evolved from disproportionation is factored into the experimental <math>\Delta H_n</math></u> . OR More exothermic because the <u>reaction in (a)(ii) took place</u> .	[1]
(g)	Glutamic acid is often used as a food additive and a flavour enhancer. The structure of a fully protonated glutamic acid is as shown, with the pK <sub>a</sub> values (2.1, 4.1 and 9.5) assigned.	



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(i)	Explain the assignment of pK <sub>a</sub> values to the respective acidic groups. <u>(most acidic) <math>\alpha</math>-COOH &gt; side chain -COOH &gt; <math>\text{-NH}_3^+</math></u> <u>Stability of conjugate base: (most stable) <math>\alpha</math>-COO<sup>-</sup> &gt; side chain -COO<sup>-</sup> &gt; <math>\text{-NH}_2</math></u> The -COOH on the side chain <u>is further away from the electron withdrawing <math>\text{-NH}_2</math> / <math>\text{-NH}_3^+</math> / N</u> . Hence the <u>negative charge of its conjugate base (-COO<sup>-</sup>) is dispersed to a smaller extent</u> as compared to the <u>conjugate base of the <math>\alpha</math>-COOH</u> . Hence, the pK <sub>a</sub> of the side chain -COOH is 4.1 while that of the $\alpha$ -COOH is 2.1 as the $\alpha$ -COO <sup>-</sup> is a more stable conjugate base. The <u>lone pair of electrons on <math>\text{-NH}_2</math> is localised and will readily accept H<sup>+</sup></u> and hence, is less stable than -COO <sup>-</sup> .	[3]
(ii)	Suggest the structural formulae of the major species present in solutions of glutamic acid with the pH values of 3.0, 6.0, and 10.0. pH = 3  pH = 6  pH = 10 	[3]
(iii)	The structure of compound H is as shown. 	

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H has 2  $pK_a$  values.

- $pK_{a1} = 4.5$
- $pK_{a2} = 11.9$

Calculate the pH of a  $0.50 \text{ mol dm}^{-3}$  solution of H. Ignore the effect of  $pK_{a2}$  on pH. [1]

$$[\text{OH}^-] = \sqrt{(10^{-4.5})(0.50)} = 0.003976 \text{ mol dm}^{-3}$$

$$p\text{OH} = -\lg(0.003976) = 2.40$$

$$p\text{H} = 14 - 2.40 = \underline{11.6}$$

(iv) Sketch the pH-volume curve that you would expect to obtain when  $25 \text{ cm}^3$  of  $0.50 \text{ mol dm}^{-3}$  compound H is titrated with  $60 \text{ cm}^3$  of  $0.50 \text{ mol dm}^{-3}$  chloric acid. Briefly describe how you have calculated the various key points on the curve. [3]

Amount of  $\text{H}^+$  to completely react with H =  $0.025 \times 0.5 \times 2 = 0.025 \text{ mol}$

Volume of chloric acid to reach 2<sup>nd</sup> equivalence point =  $0.05 \text{ dm}^3$

Amount of  $\text{H}^+$  to react with  $-\text{NH}_2 = 0.025 / 2 = 0.0125 \text{ mol}$

Volume of chloric acid needed to reach 1<sup>st</sup> equivalence point =  $0.025 \text{ dm}^3$

At 1<sup>st</sup> MBC:  $p\text{H} = pK_a = 14 - 4.5 = 9.5$

Volume of chloric acid to reach 1<sup>st</sup> MBC =  $0.025 / 2 = 0.0125 \text{ dm}^3$

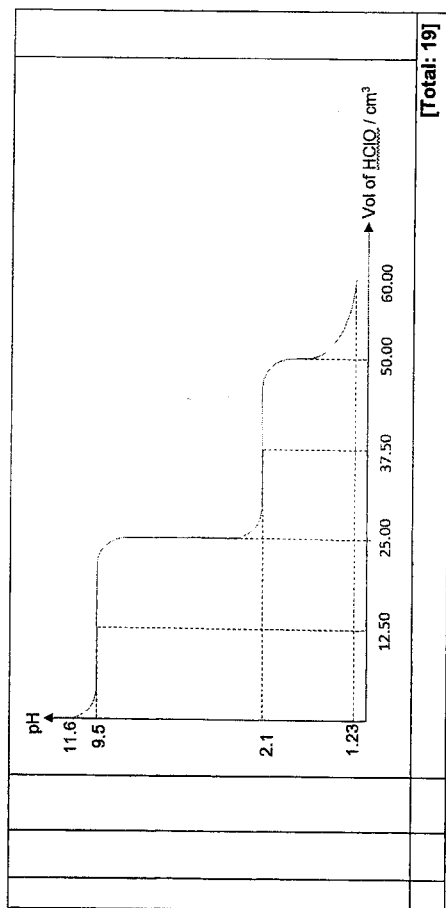
At 2<sup>nd</sup> MBC:  $p\text{H} = pK_a = 14 - 11.9 = 2.1$

Volume of chloric acid to reach 2<sup>nd</sup> MBC =  $(0.0125 + 0.025) / 2 = 0.0375 \text{ dm}^3$

Amount of excess  $\text{H}^+$  =  $10/1000 \times 0.50 = 0.005 \text{ mol}$

$[\text{H}^+] = 0.005 / 0.085 = 0.05882 \text{ mol dm}^{-3}$

Final  $p\text{H} = -\lg 0.05882 = 1.23$



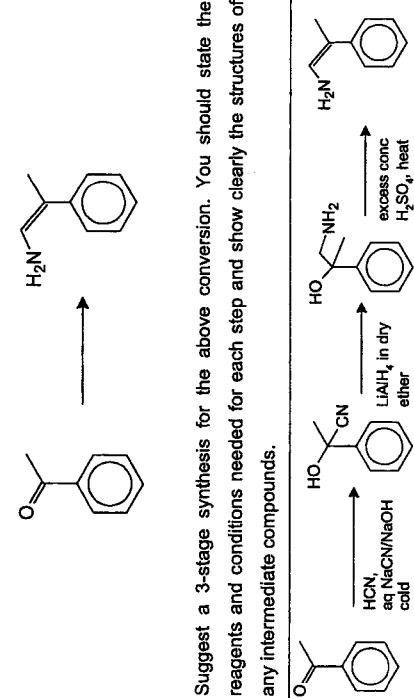
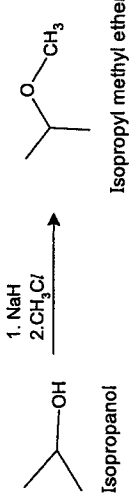
3 (a)	$\text{LiAlH}_4$ and $\text{H}_2$ are useful reducing agents in organic chemistry. Esters are reduced by $\text{LiAlH}_4$ and the equation is as shown. $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OR} + 4[\text{H}] \longrightarrow \text{R}-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-\text{OH} + \text{R}-\text{OH}$	
<p>Compound <b>I</b> contains an ester functional group and undergoes the following reactions with <math>\text{LiAlH}_4</math> and <math>\text{H}_2</math>:</p>	<p style="text-align: center;"> <math>\text{I} \xrightarrow{\text{H}_2 + \text{Ni}} \text{J}</math>  <math>\text{I} \xrightarrow{\text{LiAlH}_4} \text{K} + \text{L}</math> </p>	
(i)	<p>Compounds <b>I</b>, <b>J</b>, <b>K</b> and <b>L</b> react with <math>\text{Na}</math>, as well as with alkaline aqueous iodine. Suggest the structures for <b>I</b>, <b>J</b> and <b>L</b>.</p>	[3]

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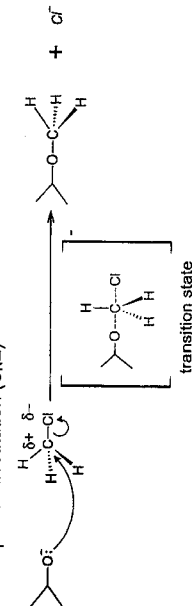

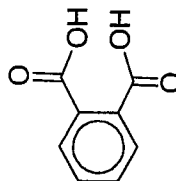
<p>Note: The following CANNOT be <b>I</b> as they will not agree with the change in molecular formula from <b>I</b> to <b>J</b> (ie. + 6H).</p>	(ii) Sodium boron hydride, $\text{NaBH}_4$ , is used in the reduction of compound <b>M</b> to form compound <b>K</b> . Given that <b>M</b> reacts with 2,4-DNPH but not Fehling's solution, suggest the structure for <b>M</b> .	[1]
(b) Both $\text{NaBH}_4$ and $\text{LiAlH}_4$ produce the hydride ion, $\text{H}^-$ , as the reacting species during reduction.		[1]
(i) Explain why $\text{LiAlH}_4$ is a stronger reducing agent than $\text{NaBH}_4$ . <b>A-H</b> is weaker than <b>B-H</b> due to <b>A</b> having a larger atomic radius than <b>B</b> and hence, easier production of hydride ions. OR The electronegativity difference between <b>A</b> and <b>H</b> is greater, causing the <b>H</b> to be more electron-rich in <b>A-H</b> than in <b>B-H</b> . OR <b>Li</b> has a stronger polarising power as it has a higher charge density and thus, <b>A-H</b> is weaker.		[1]
(ii) When $\text{NaBH}_4$ is added to propanal and propanone separately, it was found that propanal reacts faster than propanone. Suggest two reasons for this observation. 1) More electron-donating alkyl groups in propanone reduce the partial positive charge on the carbonyl carbon and attract $\text{H}^-$ less readily. 2) There are more bulky alkyl groups about the carbonyl C in propanone, hence there is greater steric hindrance, hindering the approach of the $\text{H}^-$ .		[2]

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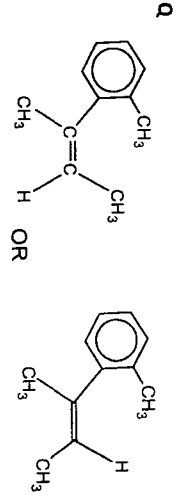
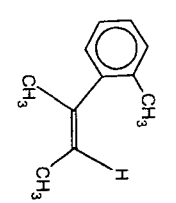
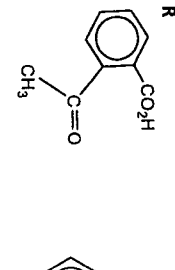
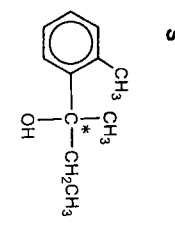


<p>(iii) <math>\text{LiAlH}_4</math> is used in the following synthesis.</p>  <p>Suggest a 3-stage synthesis for the above conversion. You should state the reagents and conditions needed for each step and show clearly the structures of any intermediate compounds.</p> <p>[4]</p> <p>Note: If elimination is carried out before reduction of nitrile, the concentrated acid may also hydrolyse nitrile.</p>	
<p>(c) Sodium hydride is a strong base commonly used in the Williamson Ether Synthesis. An example is the synthesis of isopropyl methyl ether from isopropanol.</p>  <p>Isopropanol <math>\xrightarrow[2. \text{CH}_3\text{I}]{1. \text{NaH}}</math> Isopropyl methyl ether</p> <p>The mechanism is as follows:</p> <p><b>Step 1:</b> Hydride ion removes a <math>\text{H}^+</math> from isopropanol to form an alkoxide, <math>\text{CH}(\text{CH}_3)_2\text{O}^-</math> and hydrogen gas.</p> <p><b>Step 2:</b> The alkoxide acts attacks the electron deficient carbon atom of chloromethane to form the ether and <math>\text{Cl}^-</math>.</p>	<p>(f) Outline the mechanism for <b>step 2</b> of the Williamson Ether Synthesis of isopropyl methyl ether. Label the partial charges on the reacting species and use curly arrows to show the flow of electrons during the reaction.</p> <p>[2]</p>

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<p>Nucleophilic substitution (<math>\text{S}_{\text{N}}2</math>)</p> 	<p>(ii) <math>\text{CH}_2\text{C}(\text{CH}_3)\text{OH}</math> reacts with sodium hydride via the Williamson Ether Synthesis to form an ether with the molecular formula <math>\text{C}_2\text{H}_4\text{O}</math>. Draw the structure of this ether.</p> <p>[1]</p> 
<p>(d) Compound <b>Q</b>, <math>\text{C}_{11}\text{H}_{14}</math>, exists as a mixture of two stereoisomers but it contains no chiral centre. <b>Q</b> decolourises hot acidified potassium manganate(VII) to give <b>R</b>, <math>\text{C}_9\text{H}_8\text{O}_3</math>, as one of the organic products. <b>R</b> reacts with alkaline aqueous iodine to give a yellow precipitate and a soluble salt. Upon acidification, the soluble salt forms benzene-1,2-dicarboxylic acid as shown.</p>  <p><b>Q</b> also reacts with cold concentrated sulfuric acid followed by steam to give <b>S</b>, <math>\text{C}_{11}\text{H}_{16}\text{O}</math>. <b>S</b> is able to rotate plane-polarised light but does not react with aqueous alkaline iodine.</p> <p>Deduce the structures of <b>Q</b>, <b>R</b> and <b>S</b>, explaining the reactions described.</p> <p>[6]</p>	<p>Observations</p> <p>Deductions</p> <p><b>Q</b> <math>\text{C}_{11}\text{H}_{14}</math> <math>\text{C}:\text{H} \approx 1:1</math>. <b>Q</b> has <u>benzene ring</u>.</p>

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<p><b>Q</b> has 2 stereoisomers with no chiral centre</p> <p><b>Q</b>, <math>C_{11}H_{14}</math>, decolourises hot <math>KMnO_4</math> to give <b>R</b>, <math>C_9H_{10}O_3</math></p>	<p><b>Q</b> is an <u>alkene with cis and trans isomer</u>.</p> <p><b>Q</b> is <u>oxidised</u></p> <p><b>Q</b> contains <u>alkene</u> (no double awarding) and/or <u>a side chain with a benzylic H</u>. C:H <math>\approx</math> 1:1. <b>R</b> contains a <u>benzene ring</u> (no double awarding for <b>Q</b> and <b>R</b>)</p> <p><b>R</b> is a <u>ketone and/or -COOH</u> (both must be present)</p>
<p><b>R</b> reacts with alkaline <math>I_2</math> (aq)</p>	<p><b>R</b> is <u>oxidised</u>.</p> <p><b>R</b> has <u><math>CH_3C=O</math></u>.</p>
<p><b>Q</b>, <math>C_{11}H_{14}</math>, reacts with cold <math>H_2SO_4</math> followed by steam to give <b>S</b>, <math>C_{11}H_{16}O</math>.</p>	<p><b>Q</b> undergoes <u>electrophilic addition</u> to form <u>alcohol</u>. <b>S</b>.</p> <p><b>Q</b> has an <u>alkene or 1 C=C</u>: (no double awarding)</p>
<p><b>S</b> rotates plane-polarised light but does not react with aqueous alkaline iodine</p>	<p><b>S</b> contains <u>chiral C/centre</u></p> <p><b>S</b> does not contain <math>CH_2-CH(OH)-</math></p>
<p><b>Q</b></p> 	<p><b>S</b></p> 
<p><b>R</b></p> 	<p><b>S</b></p> 
[Total: 20]	

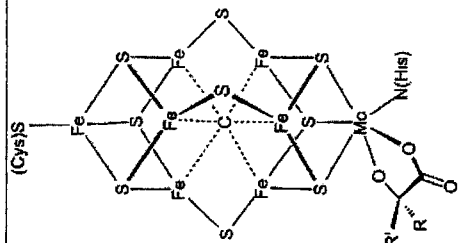
## Section B

Answer one question from this section.

<p><b>4</b> Nitrogen is a critical nutrient for the survival of all living organisms, as it is a necessary component of many biomolecules, such as proteins. Although nitrogen is very abundant in the atmosphere, it needs to be converted into ammonia for it to be available to primary producers, such as plants. This process is called nitrogen fixation. Only a select group of bacteria can carry out this energetically demanding process. The equation for nitrogen fixation is as shown.</p> $N_2 + 8H^+ + 8e^- \rightarrow 2NH_3 + H_2$	
<p><b>(a)</b> By using appropriate data from the <i>Data Booklet</i>, explain why nitrogen fixation is an energetically demanding process.</p> <p><math>BE(N \equiv N) = 944 \text{ kJ mol}^{-1}</math>. The <math>N \equiv N</math> is <b>strong / requires a lot of energy to break</b>.</p> <p>Examiners' comments:</p> <ul style="list-style-type: none"> <li>Quite well answered. Some students however did not comment how the bond energy quoted was a large value that needed a lot of energy to overcome to answer the question. A handful either did not quote or quoted the wrong data from the data booklet and the <math>N_2</math> is <math>N=N</math> instead of triple bond. There were also students who went to calculate <math>\Delta H</math> of the reaction based on bond energy not realising that an exothermic reaction does not answer the question.</li> </ul>	<b>[11]</b>
<p><b>(b)</b> Bacteria that carry out nitrogen fixation have an enzyme called nitrogenase. Nitrogenase contains an iron-sulfur-molybdenum metal cluster, as shown in Fig. 4.1. Histidine (His) and cysteine (Cys) are two important amino acids present in the active site of nitrogenase.</p>	

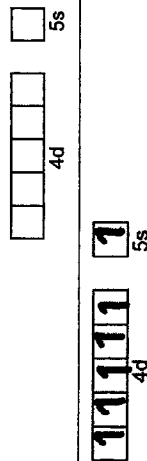
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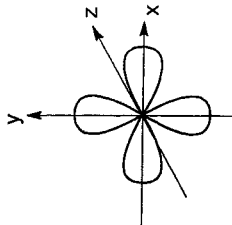


(i) Molybdenum,  $^{42}\text{Mo}$ , is in the same group as chromium and has a similar electronic configuration as chromium.

In the diagram below, show how the electrons are arranged in the 4d and 5s orbitals of Mo atom.



(ii) Draw a fully labelled diagram of a 4d orbital that lies along both the x and y axis.

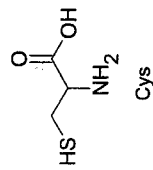


$4d_{x^2-y^2}$

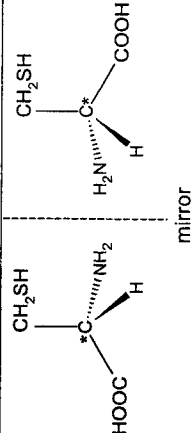
(iii) State the shape about Mo in Fig. 4.1.

Octahedral

(iv) The structure of cysteine (Cys) amino acid is given below.



Draw the stereoisomers of Cys.



(c) Nitrogenase are deactivated in the presence of oxygen, as oxygen and nitrogen can compete for binding to iron in the active site of the enzyme. Explain how oxygen is able to interact with nitrogenase in a similar manner as nitrogen.

Both oxygen and nitrogen have at least one lone pair of electrons that can be donated to iron via dative bond.

(d) Nitrogenase is stable when the temperature is between 20 °C to 40 °C.


<p>The kinetics of nitrogen fixation by nitrogenase was studied at 20 °C. The final concentration of <math>\text{NH}_3</math> formed was found to be <math>0.16 \text{ mol dm}^{-3}</math>.</p>		
<p><math>[\text{NH}_3] / \text{mol dm}^{-3}</math></p> <p style="text-align: center;">Fig. 4.2</p>		
(i)	<p>Explain the term <u>rate of reaction</u>.</p> <p>Rate of reaction is defined as the <u>change in concentration of reactant consumed / product formed per unit time</u>.</p>	[1]
(ii)	<p>Using Fig. 4.2, calculate the initial rate of reaction.</p> <p>Students are to <u>draw tangent at t = 0 (as long as does not cut the graph)</u> and calculate the gradient.</p> <p>Initial rate = <math>0.18 / 100 = 0.0018 \text{ mol dm}^{-3} \text{ s}^{-1}</math></p>	[1]
(iii)	<p>Use Fig. 4.2 to determine the order of reaction with respect to <math>[\text{N}_2]</math>. Hence, sketch a graph of rate against initial <math>[\text{N}_2]</math>.</p>	[3]

TURN OVER

<p>Show two constant <math>t_{1/2}</math> on the graph + <math>t_{1/2} = 50 \text{ s}</math></p> <p>Since <math>t_{1/2}</math> is constant at 50 s, the reaction is <u>first order</u> with respect to <math>[\text{N}_2]</math>.</p>		
<p>rate</p>		
(iv)	<p>On Fig. 4.2, sketch how the graph would look like when the experiment is carried out at 40 °C. Label this new graph as Y.</p> <p>Explain your answer using the Collision Theory.</p> <p>Graph: Y being steeper than X</p> <p>When temperature increases, kinetic energy of the reacting particles <u>increases</u>. The <u>number of particles with energy greater than or equal to activation energy increases</u>. Hence, <u>frequency of effective collision increases and rate increases</u>, which is shown by a steeper graph.</p>	[3]
(e)	<p>Denitrification is an important process because it converts nitrate back into nitrogen gas.</p> <p>A Latimer diagram shows the standard electrode potentials connecting various oxidation states of an element. The sum of the standard electrode potential for each reduction is the same as the standard electrode potential for the overall reduction.</p> <p>The Latimer diagram for some nitrogen-containing species in acidic medium is as shown below.</p> <p style="text-align: center;"> <math>\text{NO}_3^- \xrightarrow{+0.42\text{V}} \text{NO}_2^- \xrightarrow{+0.34\text{V}} \text{NO} \xrightarrow{+1.18\text{V}} \frac{1}{2}\text{N}_2\text{O} \xrightarrow{+1.35\text{V}} \frac{1}{2}\text{N}_2</math> </p> <p style="text-align: center;">                 Step 1                      Step 2                      Step 3                      Step 4             </p>	[2]
(i)	<p>Draw a dot-and-cross diagram of <math>\text{NO}_2^-</math>. State the bond angle of the ion.</p>	[2]

TURN OVER

	$\left[ \overset{\text{XX}}{\underset{\cdot}{\ddot{\text{O}}}} \cdot \overset{\cdot}{\text{N}} \overset{\cdot}{\text{X}} \overset{\cdot}{\text{X}} \overset{\cdot}{\text{O}} \overset{\cdot}{\text{O}} \right]^-$ <p>115° (bond angle ranging from 110 to 119°)</p>	
(ii)	Explain how the Latimer diagram shows that NO is an intermediate in the denitrification process. It is produced in step 2 and used in step 3.	[1]
(iii)	Write a half equation for the reduction of NO <sub>3</sub> <sup>-</sup> to N <sub>2</sub> in acidic medium. $2\text{NO}_3^- + 12\text{H}^+ + 10\text{e}^- \rightarrow \text{N}_2 + 6\text{H}_2\text{O}$	[1]
(iv)	Use the Latimer diagram to calculate the standard electrode potential for the reduction of NO <sub>3</sub> <sup>-</sup> to N <sub>2</sub> . Hence, calculate the standard Gibbs free energy change, ΔG°, per mole of N <sub>2</sub> formed. $E^\circ_{\text{cell}} = +0.42 + 0.34 + 1.18 + 1.35 = +3.29 \text{ V}$ $\Delta G^\circ = -10 \times 96500 \times 3.29 = -3174850 \text{ J mol}^{-1} \approx -3170 \text{ kJ mol}^{-1}$ (3sf)	[2]
	[Total: 20]	

5	This question is about the chemistry of titanium and its ions. (a) Titanium (II) oxide, TiO, and titanium (IV) dioxide, TiO <sub>2</sub> , are common sources of titanium ions with different oxidation states.	<table border="1"> <thead> <tr> <th>compound</th> <th>melting point / °C</th> </tr> </thead> <tbody> <tr> <td>TiO</td> <td>1750</td> </tr> <tr> <td>TiO<sub>2</sub></td> <td>1843</td> </tr> </tbody> </table>	compound	melting point / °C	TiO	1750	TiO <sub>2</sub>	1843	
compound	melting point / °C								
TiO	1750								
TiO <sub>2</sub>	1843								
(i)	State the electronic configuration of a Ti <sup>2+</sup> ion. $1s^2 2s^2 2p^6 3s^2 3p^6 3d^2$	[1]							
(ii)	Explain, in terms of structure and bonding, the difference in melting point between TiO and TiO <sub>2</sub> . Both have <b>giant ionic lattice</b> structure with <b>strong ionic bonds</b> between cations and anions. $ \text{Lattice Energy}  \propto \left  \frac{q^+ q^-}{r_+ + r_-} \right $ Since Ti <sup>4+</sup> has a <b>higher charge</b> and smaller cationic radius than Ti <sup>2+</sup> , and they have the same anion, the <b> LE  of TiO<sub>2</sub> is larger or LE of TiO<sub>2</sub> is more exothermic</b> . Hence, <b>more energy</b> is required to overcome the <b>stronger ionic bonds in TiO<sub>2</sub></b> and it has a higher melting point.	[2]							
(iii)	TiO <sub>2</sub> is a catalyst used in the anti-Markovnikov hydroxylation of gaseous alkenes with gaseous silane, SiH <sub>4</sub> . 	[2]							
	Outline the mode of action of TiO <sub>2</sub> catalyst in this reaction. TiO <sub>2</sub> is a heterogeneous catalyst. The alkene and silane are <b>adsorbed</b> onto the surface of TiO <sub>2</sub> by <b>forming weak interactions / bonds</b> . Besides increasing the surface concentration, <b>Si-H and π bond of alkenes are weakened</b> , <b>lowering the activation energy</b> for the reaction to take place, where the C-H and C-Si bonds are formed. The products then <b>desorb</b> from the TiO <sub>2</sub> surface.								

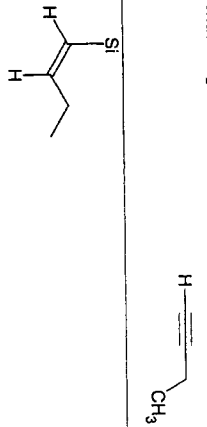
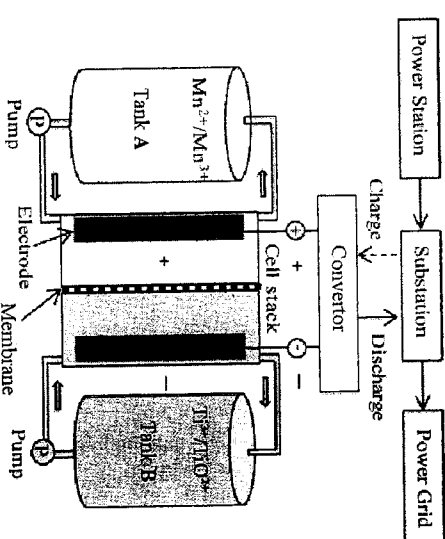
(iv)	Alkynes can react with silane in a similar way as alkenes. Suggest the alkene formed when the following alkyne undergoes hydroxylation with $\text{TiO}_2$ .		[1]
(b)	The use of renewable energy sources, such as solar energy, has been gaining momentum around the world with the aim of realising a carbon-zero society. However, climate change can affect the power output and therefore, there is a need to use large-scale batteries to store the power harnessed.  One such example is shown in Fig. 5.1. The battery uses the redox couple $\text{Mn}^{2+}/\text{Mn}^{3+}$ in one electrolyte tank and $\text{T}^{3+}/\text{TiO}^{2+}$ in another. Sulfuric acid is the electrolyte in both tanks.		
	The standard electrode potential for the reduction of $\text{TiO}^{2+}$ is as given. $\text{TiO}^{2+} + 2\text{H}^+ + \text{e}^- \rightleftharpoons \text{T}^{3+} + \text{H}_2\text{O} \quad E^\ominus = +0.10 \text{ V}$		

Fig. 5.1

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(i)	Write an equation to represent the discharging of this battery. $\text{T}^{3+} + \text{Mn}^{3+} + \text{H}_2\text{O} \rightarrow \text{TiO}^{2+} + 2\text{H}^+ + \text{Mn}^{2+}$		[1]						
(ii)	Use the Data Booklet to calculate the $E^\ominus_{\text{cell}}$ when the battery is discharged. Hence, calculate the standard Gibbs free energy change, $\Delta G^\ominus$ , per mole of $\text{Mn}^{3+}$ used in the discharging process.  $E^\ominus_{\text{cell}} = (+1.54) - (+0.10) = +1.44 \text{ V}$ $\Delta G^\ominus = -nFE^\ominus = -(1)(96500)(+1.44)$ $= -139860 \text{ J mol}^{-1}$ $\approx -139 \text{ kJ mol}^{-1}$		[2]						
(iii)	Suggest and explain the effect on $E_{\text{cell}}$ if an electrolyte of lower pH was used. $\text{TiO}^{2+} + 2\text{H}^+ + \text{e}^- \rightleftharpoons \text{T}^{3+} + \text{H}_2\text{O}$ At lower pH, $[\text{H}^+]$ is high and would cause the <u>position of equilibrium for the above to shift right</u> . $E(\text{TiO}^{2+}/\text{T}^{3+})$ would become <u>more positive</u> , causing $E_{\text{cell}}$ to become <u>less positive</u> . <i>Ecf from (ii) for <math>E_{\text{cell}}</math></i>		[2]						
(iv)	Sulfuric acid, which is a source of $\text{H}^+$ , will flow through the exchange membrane as the battery discharges. Suggest the direction of flow of $\text{H}^+$ through the membrane. Explain your answer. <u><math>\text{H}^+</math> flow from Tank B towards Tank A to maintain electrical neutrality as <math>\text{H}^+</math> is being produced in Tank B.</u>		[2]						
(v)	Suggest an advantage of using porous carbon electrodes. <u>It increases the surface area for exchange of electrons to occur faster.</u>		[1]						
(c)	(i) With reference to the table below, suggest the colour change in Tank B when the battery is charging.	<table border="1" data-bbox="207 1590 319 1836"> <thead> <tr> <th>Species</th> <th>Colour</th> </tr> </thead> <tbody> <tr> <td><math>\text{T}^{3+}</math> (aq)</td> <td>violet</td> </tr> <tr> <td><math>\text{TiO}^{2+}</math> (aq)</td> <td>colourless</td> </tr> </tbody> </table>	Species	Colour	$\text{T}^{3+}$ (aq)	violet	$\text{TiO}^{2+}$ (aq)	colourless	[1]
Species	Colour								
$\text{T}^{3+}$ (aq)	violet								
$\text{TiO}^{2+}$ (aq)	colourless								
	Tank B: colourless to violet		[1]						

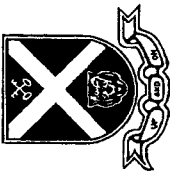
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(ii)	Explain what is meant by the term <i>transition element</i> . A transition element is a <u>d - block element</u> which forms <u>one or more stable ions</u> with <u>partially filled d subshells / d orbitals</u> .	[1]	
(iii)	Explain why $Ti^{3+}(aq)$ ions are coloured, but $TiO^{2+}(aq)$ ions are not. In the presence of water ligands, the <u>partially filled 3d orbitals</u> in $Ti^{3+}$ <u>split into two groups with a small energy gap between them</u> . When an electron <u>from the lower energy d orbital absorbs energy</u> from visible light range, it is <u>excited/promoted/transited to a higher energy d orbital</u> . <u>Energy that is not absorbed is reflected</u> , the reflected light is violet. $TiO^{2+}$ has <u>no 3d electrons</u> for d-d transition.	[3]	
(iv)	Two separate solutions of $Ti^{3+}$ and $Al^{3+}$ are acidic. Using relevant data from the <i>Data Booklet</i> , predict which solution of equal concentration, $Ti^{3+}$ or $Al^{3+}$ , will give a lower pH. <u><math>Al^{3+}</math>: 0.050 nm; <math>Ti^{3+}</math>: 0.067 nm</u> A solution of <u><math>Al^{3+}</math></u> is more acidic and has a lower pH. [1]  (Explanation for students during review): $Al^{3+}$ has a smaller ionic radius and higher charge density. $Al^{3+}$ has a higher polarising power and is able to polarise/distort the electron cloud of coordinated $H_2O$ to a larger extent, weakening the O-H bond more to form more $H^+$ .	[1]	
			[Total: 20]

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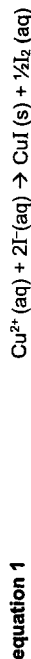


<b>Name:</b>	<b>Shift:</b>
<b>Class:</b> 21S	<b>Lab:</b>
<b>ST ANDREW'S JUNIOR COLLEGE</b>	
	
<b>JC2 PRELIMINARY EXAMINATION</b>	
<b>CHEMISTRY</b>	9729/04
<b>Paper 4 Practical</b>	18 Aug 2022
	2 hours 30 minutes
<b>Additional Materials: Qualitative Analysis Notes</b>	
<b>READ THESE INSTRUCTIONS FIRST.</b>	
Write your name and class on all the work you hand in.	
Give details of the practical shift and laboratory in the boxes provided above.	
Write in dark blue or black pen.	
You may use a soft pencil for any diagrams or graphs.	
Do not use staples, paper clips, highlighters, glue or correction fluid.	
Answer all questions in the spaces provided on the Question Paper.	
The use of an approved scientific calculator is expected, where appropriate.	
<b>You may lose marks if you do not show your working or if you do not use appropriate units.</b>	
The number of marks is given in the brackets [ ] at the end of each question or part question.	
This document consists of 22 printed pages, including 1 blank page.	

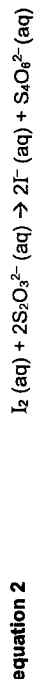
**1 Determination of water of crystallisation in a sample of hydrated copper(II) sulfate**

The formula of hydrated copper(II) sulfate is  $\text{CuSO}_4 \cdot x\text{H}_2\text{O}$ , where  $x$  refers to the number of moles of water of crystallisation. In 1(a)(i), you will perform titration to determine the value of  $x$ .

Excess aqueous KI is first added to copper(II) sulfate solution. This will produce a white precipitate in a brown solution of  $\text{I}_2$ .



The liberated iodine is then titrated against sodium thiosulfate.



You are provided with:

- solid **FA 1**, hydrated copper(II) sulfate
- **FA 2**, 0.100 mol dm<sup>-3</sup> sodium thiosulfate,  $\text{Na}_2\text{S}_2\text{O}_3$
- **FA 3**, potassium iodide solution, KI
- **Solution S**, starch solution.

**Note: Solution S will also be used in Question 2.**

**(a) (i) Procedure**

1. Fill a burette with **FA 2**.
2. Weigh accurately about 5 g of **FA 1**. Record the mass on page 3. Transfer all the solids into a 100 cm<sup>3</sup> beaker. Add about 75 cm<sup>3</sup> of deionised water and stir with a glass rod to dissolve them.
3. Transfer the solution into a 250 cm<sup>3</sup> volumetric flask. Rinse the beaker with deionised water and pour the washings into the volumetric flask.
4. Make up to the 250 cm<sup>3</sup> mark with deionised water. Stopper the volumetric flask and shake well to mix. Label this solution as **FA 4**.
5. Pipette 25.0 cm<sup>3</sup> of **FA 4** into a conical flask and use a measuring cylinder to add 15 cm<sup>3</sup> of **FA 3** into the same conical flask.
6. Titrate this solution with **FA 2** until the mixture becomes pale brown. An off-white precipitate is also present in the conical flask.

For Examiner's Use	
1	19
2	14
3	14
4	8
Total	55

3

7. Add approximately 1 cm<sup>3</sup> of solution S to the conical flask and continue titration until the blue-black colour just disappears, with the off-white precipitate remaining in the conical flask.
8. Discard the contents and rinse the conical flask with water.
9. Repeat the titration to obtain consistent results. Record your titration results in the space below.

**Results**

Mass of empty weighing bottle / g	
Mass of FA 1 and weighing bottle / g	
Mass of emptied weighing bottle / g	<b>OPTIONAL</b>
Mass of FA 1 / g	<b>5.03 / 5.00 / 5.03</b>

	1	2	3
final burette reading / cm <sup>3</sup>			
initial burette reading / cm <sup>3</sup>			
volume of FA 2 used / cm <sup>3</sup>	20.20	20.00	19.95
values used for calculating average titre			

- Mass of FA 1 used should be 5 +/- 0.05 g [1]
- Tabulates **correct headers and units for both mass and titration** [1]
- All values are recorded to 2 decimal places and to nearest 0.05 cm<sup>3</sup> [1]
- Two titre volumes within 0.10cm<sup>3</sup> [1]

[4]

4

- (ii) From your titrations, obtain a suitable volume of FA 2 to be used in your calculations. Show clearly how you obtained this volume.
- Average of 2 consistent titre volumes, recorded to 2 d.p [1]

Volume of FA 2 = ..... cm<sup>3</sup> [1]

- (b) (i) Calculate the amount, in moles, of Cu<sup>2+</sup> present in 25.0 cm<sup>3</sup> of FA 4.

Amount of S<sub>2</sub>O<sub>3</sub><sup>2-</sup> = (average titre volume / 1000) x 0.1= Amount of Cu<sup>2+</sup> in 25 cm<sup>3</sup> of FA 4 [1]

ecf from (a)(iii)

Amount of Cu<sup>2+</sup> = ..... mol [1]

- (ii) Calculate the concentration of Cu<sup>2+</sup> in FA 4.

Concentration of Cu<sup>2+</sup> in FA 4 = Ans from (b)(i) / 0.025 [1]

ecf from (b)(i)

Concentration of Cu<sup>2+</sup> = ..... mol dm<sup>-3</sup> [1]

- (iii) Given that the concentration of CuSO<sub>4</sub>.xH<sub>2</sub>O in FA 4 is 20.00 g dm<sup>-3</sup>, use your answer

in (b)(ii) to determine the value of x.

[A: H, 1.0 Cu, 63.5 S, 32.1 O, 16.0]

Molar mass of hydrated CuSO<sub>4</sub>= 20.00 / ans from (b)(ii) = ..... [1] g mol<sup>-1</sup>

Molar mass = (63.5 + 32.1 + 64 + x\*18)

x = 5 [1; rounded off to nearest whole number]

[1] for unit and 3 sf for (b)(i) and (b)(ii)

Accuracy mark [1] for x = 5 (from excel calculator)

x = ..... [4]

(iv) In step 5, FA 3 was added using a 25 cm<sup>3</sup> measuring cylinder. Calculate the percentage error in the measurement of the specified volume in step 5.

% error =  $\pm (0.25 / 15) \times 100\% = \pm 1.67\%$  [1]

Annotate if student did not calculate to 3 sf and annotate  $\pm$

Percentage error = ..... % [1]

(c) (i) A student conducted the experiment as mentioned in (a)(i). After carrying out step 5, he left the conical flask containing FA 3 and FA 4 to stand for 30 minutes, before continuing with steps 6 to 8. It was noted that his titre volume was less than expected. Suggest a reason for this observation.

..... [1]  
 ..... [1]  
Iodine is volatile and some will escape from the conical flask. [1]  
**Or words to the effect, e.g. evaporation of iodine.**

(ii) Two other students conducted the same experiment in (a)(i) but with the following modifications to the procedures.

Student 2: In Step 5, add 30 cm<sup>3</sup> of FA 3 instead of 15 cm<sup>3</sup>.

Student 3: In Step 7, omit the use of solution S.

Explain how each of these modifications will affect the accuracy of the results.

Student 2:

Potassium iodide was already added in excess in (a)(i) / The amount of iodine formed will be the same for both 15 cm<sup>3</sup> and 30 cm<sup>3</sup> of FA 3 / Cu<sup>2+</sup> is limiting reagent.

Hence, it will not be affected the accuracy of the results / the results will be the same. [1]

Student 3:

The colour change at end-point from yellow / pale brown to colourless will not be sharp / obvious, thus leading to inaccuracy in the titre volumes recorded. [1]

(iii) Another student proposed the following modification.

- Filtering the contents in the conical flask after step 5, before carrying out the titration in step 6.

State an advantage and a disadvantage of this modification.

Advantage: Easier to see the colour change at end-point without the interference of white ppt. [1]

Disadvantage: Some iodine may be lost OR remain on the filter paper, thus reducing the accuracy of titration results. [1]

(d) Table 1.1 shows some standard electrode potential values.

Table 1.1

electrode reaction	$E^\ominus / V$
$Cu^{2+} + e^- \rightleftharpoons Cu^+$	+0.15
$I_2 + 2e^- \rightleftharpoons 2I^-$	+0.54

The  $E^\ominus_{cell}$  for equation 1 is -0.39 V. Explain why the reaction occurred in (a)(i) despite the negative  $E^\ominus_{cell}$  value.

When CuI ppt is formed, [Cu<sup>+</sup>] / amount of Cu<sup>2+</sup> decreases. By Le Chatelier's Principle, the position of equilibrium for Cu<sup>2+</sup> + e<sup>-</sup>  $\rightleftharpoons$  Cu<sup>+</sup> shifts right [1] to form more Cu<sup>+</sup>, resulting in its  $E_{cathode}$  (or words to the effect) to be more positive and hence,  $E_{cell}$  will become positive. [1]

[Total: 19]

**Determination of the kinetics of the iodide-peroxodisulfate redox reaction**

This question seeks to investigate the kinetics of the redox reaction between iodide ions, I<sup>-</sup>, and peroxodisulfate ions, S<sub>2</sub>O<sub>8</sub><sup>2-</sup>. The redox reaction may be represented by the equation below.



In order to measure the rate of this reaction, a fixed volume of aqueous sodium thiosulfate, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, is added to the reaction mixture. Starch is also added to the reaction mixture. When the sodium thiosulfate completely reacts with the iodine produced, the remaining iodine reacts with starch to form a dark blue complex.



The rate of reaction is studied by measuring the time taken for the solution to turn dark blue, *t*, in a series of five experiments. You will then graphically analyse your results to determine the order of reaction with respect to [I<sup>-</sup>].

**FA 5** is 0.100 mol dm<sup>-3</sup> potassium iodide, KI.

**FA 6** is 0.500 mol dm<sup>-3</sup> sodium peroxodisulfate, Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>.

**FA 7** is 0.00500 mol dm<sup>-3</sup> sodium thiosulfate, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>.

You will also need **Solution S** from **Question 1**.

(a) Prepare a table in the space provided on page 9 to record, to an appropriate level of precision:

- volume of **FA 5**, *V*<sub>FA5</sub>
- volume of deionised water,
- all values of *t*,
- all calculated values of 1/*t*, lg(1/*t*) and lg(*V*<sub>FA5</sub>).

**Experiment 1**

1. Fill the burette with **FA 5**.
2. Transfer 20.00 cm<sup>3</sup> of **FA 5** into a 250 cm<sup>3</sup> conical flask.
3. Using separate 10 cm<sup>3</sup> measuring cylinders, add 10.0 cm<sup>3</sup> of **FA 7** and 1.0 cm<sup>3</sup> of **Solution S** into the same conical flask.

**Solution S** into the same conical flask.

4. Using a 25 cm<sup>3</sup> measuring cylinder, measure 20.0 cm<sup>3</sup> of **FA 6**.
5. Start the stopwatch upon adding **FA 6** into the conical flask. Swirl the reaction mixture and place the conical flask on a white tile.

6. Stop the stopwatch when the solution first turns dark blue.
7. Record the time taken, *t*, to the nearest second in your table.
8. Discard the reaction mixture and wash out the conical flask. Stand it upside down on a paper towel to drain.

**Experiments 2 to 5**

Repeat experiment 1 four times, using 18.00 cm<sup>3</sup>, 16.00 cm<sup>3</sup>, 14.00 cm<sup>3</sup> and 12.00 cm<sup>3</sup> of **FA 5** respectively at step 2.

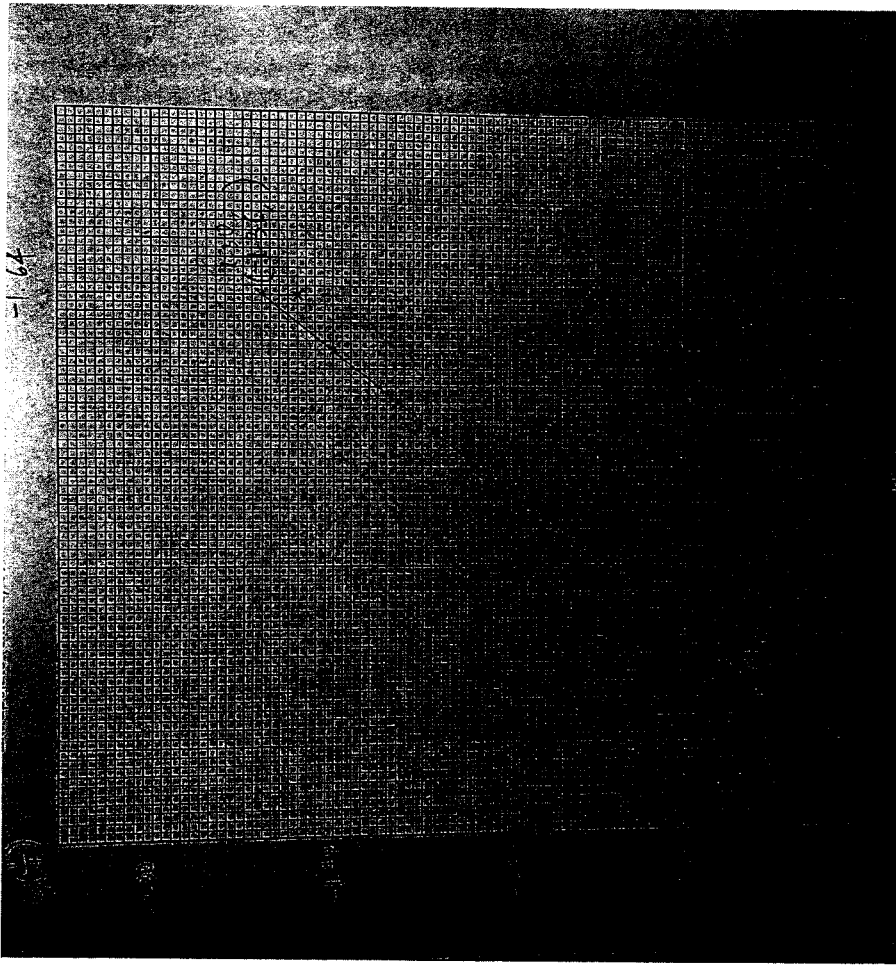
In each experiment, you will need to ensure that the same total volume of reaction mixture is used by adding appropriate volumes of deionised water.

You should alternate the use of the two conical flasks.

**Results**

<i>V</i> <sub>FA5</sub> / cm <sup>3</sup>	Vol of deionised water / cm <sup>3</sup>	<i>t</i> / s	1/ <i>t</i> / s <sup>-1</sup>	lg (1/ <i>t</i> )	lg ( <i>V</i> <sub>FA5</sub> )
20.00	0.0	24	0.0417	-1.38	1.30
18.00	2.0	25	0.0400	-1.40	1.26
16.00	4.0	30	0.0333	-1.48	1.20
14.00	6.0	36	0.0278	-1.56	1.15
12.00	8.0	44	0.0227	-1.64	1.08

- All headers with correct units and no units for log [1]
- Correct dp and sf [1]
- Correct calculations [1]
- 5 complete sets of data AND Vol of FA5 + deionised water = 20 cm<sup>3</sup> [1]



- Labelled axes and suitable scale for plotted points to cover at least half the grid [1]
- Best-fit straight line (not more than 2 anomalous points, allow 2 small squares away from plot) [1]
- Any 2 correctly plotted points [1]

(ii) Calculate the gradient of the line to three significant figures, showing clearly how you did this. Hence, deduce the order of reaction with respect to [I].

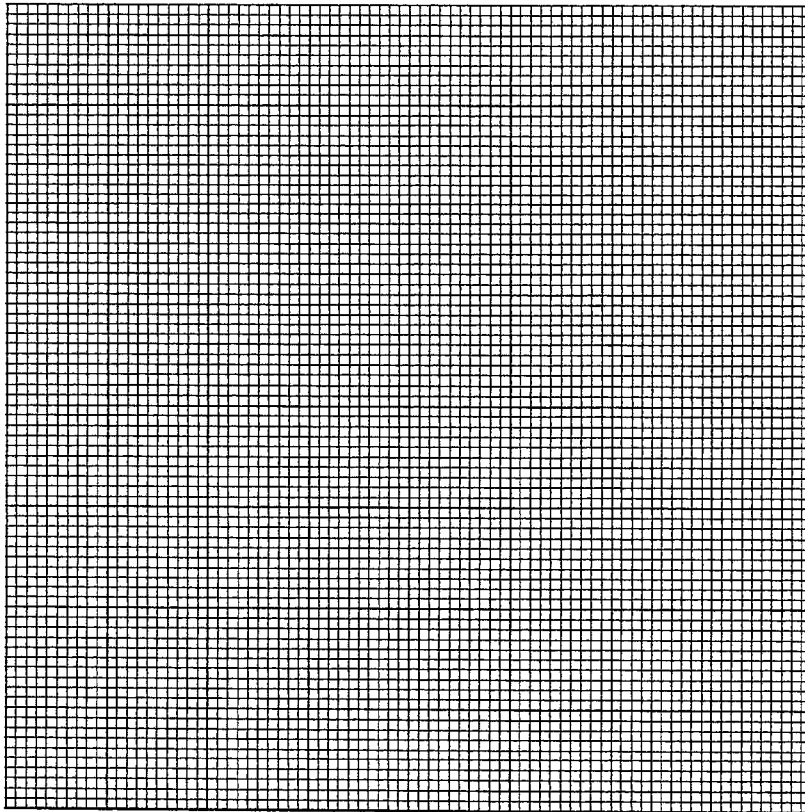
$$\text{Gradient} = \frac{(-1.36) - (-1.63)}{(1.30 - 1.09)} = 1.29 \text{ (3 s.f.)}$$

[1 showing 2 coordinates on the graph or in working]

[1 for correct calculation]

- (b) (i) Plot a graph of  $\lg(1/t)$  on the y-axis against  $\lg(V_{\text{FAS}})$  on the x-axis.  
Draw a best-fit straight line through your plotted points.

[3]



11

$$\text{Rate} = k[\text{I}]^x$$

$$1/t = k(V_{\text{FAS}})^x$$

$$\lg(1/t) = \lg k + x \lg(V_{\text{FAS}})$$

$$x = \frac{\text{gradient}}{\text{slope}} \quad [1]$$

$$\text{Gradient} = \dots \dots \dots [3]$$

Order of reaction with respect to  $[\text{I}] = \dots \dots \dots$

- (iii) Explain why the total volume of the reaction mixture needs to be kept constant in all five experiments in (a).

..... [1]

By keeping total volume constant, the concentration of each reactant after mixing is directly proportional to the volume used. [1]

- (c) (i) Iron(III) salts are sometimes used as a catalyst for the reaction you performed in (a). Suggest why there is a need for a catalyst.

..... [1]

The negatively charged reactants experience repulsion and hence the rate of reaction is too slow / high activation energy. [1]

- (ii) Using data from Table 2.1 below, show how iron(III) ions can perform this role and write relevant equation(s).

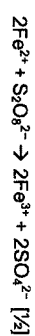
Table 2.1

electrode reaction	$E^\ominus/\text{V}$
$\text{Fe}^{3+} + 3\text{e}^- \rightleftharpoons \text{Fe}$	-0.04
$\text{Fe}^{3+} + \text{e}^- \rightleftharpoons \text{Fe}^{2+}$	+0.77
$\text{I}_2 + 2\text{e}^- \rightleftharpoons 2\text{I}^-$	+0.54
$\text{S}_2\text{O}_8^{2-} + 2\text{e}^- \rightleftharpoons 2\text{SO}_4^{2-}$	+2.01

12



$$E_{\text{cell}} = (+0.77) - (+0.54) = +0.23\text{V} \quad [1/2]$$



$$E_{\text{cell}} = (+2.01) - (+0.77) = +1.24\text{V} \quad [1/2]$$

[Total: 14]

[2]

### 3 Investigation of some inorganic reactions

(a) **FA 8** is a solid which contains one cation and one anion from those listed in the **Qualitative Analysis Notes**.

Perform the tests described in **Table 3.1**. Record your observations in the table. In all the tests, the reagent should be added gradually until no further change is observed, with shaking after each addition. Test and identify any gases evolved. No additional or confirmatory tests for ions present should be attempted.

**Table 3.1**

Tests		Observations for FA 8
1.	Place a spatula of <b>FA 8</b> in a dry boiling tube and heat.	Blue crystals become form <b>white powder/solid</b> . ✓  Note: No mark for "blue crystals form white ppt" as ppt is only used for solids forming in solution.  <b>Colourless liquid droplets</b> can be found near the opening of the boiling tube. ✓
2.	Add a spatula of <b>FA 8</b> in a test-tube.  Add 1 cm depth of $H_2O_2$ , followed by 1 cm depth of aqueous sodium hydroxide.	Blue solid dissolved to form <b>blue solution</b> . ✓  Upon adding sodium hydroxide, a <b>black / brown / greenish-brown / green ppt</b> ✓ is formed.  <b>Effervescence</b> ✓ is seen, which <b>relights a glowing splint</b> ✓.  Gas is <b>oxygen</b> ✓.
3.	Add half a spatula of <b>FA 8</b> into a test-tube.  Add aqueous ammonia dropwise until it is in excess.	A (pale) <b>blue ppt</b> is formed ✓  Ppt is <b>soluble in excess <math>NH_3</math></b> , ✓ forming a <b>deep blue/dark blue solution</b> . ✓

<p><b>4.</b> Add half a spatula of <b>FA 8</b> into a test-tube and dissolve with 1 cm depth deionised water. Use a glass rod to stir if necessary.</p> <p>Add aqueous sodium carbonate dropwise to the resultant solution until it is in excess.</p>	<p>Blue solid dissolves to form a <b>blue solution</b> ✓.</p>
---	---

[4]

- 10-13 points – 4 marks
- 7-9 points – 3 marks
- 4-6 points – 2 marks
- 2 to 3 points – 1 mark
- 0 to 1 point – 0 mark

(b) Consider your observations in **Table 3.1**.

(i) Based on your observations for test 2, suggest the role of **FA 8**.

..... [1]

Oxidising agent [1]

(ii) **Table 3.2** shows the  $K_{sp}$  values for both copper(II) carbonate and copper(II) hydroxide.

**Table 3.2**

	$K_{sp}$
$\text{CuCO}_3$	$1.4 \times 10^{-10} \text{ mol}^2 \text{ dm}^{-6}$
$\text{Cu}(\text{OH})_2$	$4.8 \times 10^{-20} \text{ mol}^3 \text{ dm}^{-9}$

Calculate the solubility of each salt. Hence, suggest the identity of the species responsible for the observations seen in test 4.

.....  
 .....

..... [3]

Let the solubility of  $\text{CuCO}_3$  be  $x \text{ mol dm}^{-3}$

$$1.4 \times 10^{-10} = x^2 \rightarrow x = \underline{1.18 \times 10^{-5} \text{ mol dm}^{-3}} \text{ [1]}$$

Let the solubility of  $\text{Cu}(\text{OH})_2$  be  $y \text{ mol dm}^{-3}$

$$4.8 \times 10^{-20} = 4y^3 \rightarrow y = 2.289 \times 10^{-7} \approx \underline{2.29 \times 10^{-7} \text{ mol dm}^{-3}} \text{ (to 3 sf) [1]}$$

Since  $\underline{\text{Cu}(\text{OH})_2}$  [1] has a lower solubility, it is precipitated first and seen in test 4.

(c) To determine the identity of anion in **FA 8**, a student added barium nitrate solution to a solution of **FA 8**. A white ppt is formed.

(i) Based on the observations given, state the possible identities of the anions.

..... [1]

$\text{CO}_3^{2-}, \text{SO}_3^{2-}, \text{SO}_4^{2-}$

[1] for all 3 anions

(ii) Suggest a test to confirm the identity of the anion in **FA 8**. **DO NOT** carry out the test.

Test: ..... [1]

Add HCl(aq) or HNO<sub>3</sub>(aq) to the white ppt. [1]

(d) Note: You are NOT given **FA 9**.

**FA 9** is a solid which contains one cation and one anion from those listed in the **Qualitative Analysis Notes**. **Table 3.3** shows a test which is performed on **FA 9** and the corresponding observations.

**Table 3.3**

Test	Observations for <b>FA 9</b>



To 1 cm depth of a solution of FA 9, add aqueous ammonia dropwise until it is in excess.	A white ppt is formed. It dissolves in excess aqueous ammonia to give a colourless solution.
--	--

- (i) Suggest the identity of the cation present in FA 9.

..... [1]  
 $Zn^{2+}$  [1]

- (ii) Suggest an explanation for the observations in Table 3.3 in terms of the species present.

..... [1]  
 .....

Award 1 mark if students give the identities of white solid is  $Zn(OH)_2$  and it dissolves to form  $Zn(NH_3)_4^{2+}$ .

- (iii) Assuming you have an aqueous solution of FA 9.

There is no observable change when barium nitrate solution is added to FA 9 solution.

Devise a series of simple tests to identify the anion in FA 9. Your tests should be based on the Qualitative Analysis Notes and should use only the bench reagents provided. Record your tests in the space below.

Test
Add 1 cm depth of NaOH(aq) to 1 cm depth of FA 9 solution and a piece of Al foil. Heat the mixture. [1]
Add 1 cm depth of AgNO <sub>3</sub> (aq) to 1 cm depth of FA 9 solution. Add NH <sub>3</sub> (aq) to the resulting mixture. [1]

[2]

[Total: 14]

#### 4 Planning

The labels for a bottle of carbonic acid and a bottle of citric acid were mixed up. Both acids have the same concentration of 1.00 mol dm<sup>-3</sup>. Carbonic acid is dibasic and citric acid is tribasic. In order to identify the correct acids, a series of six experiments will be performed, where different volumes of the acid from one of the bottles and sodium hydroxide are chosen to ensure there are sufficient points before and after the equivalence point. The total volume for each experiment should be kept constant at 60.0 cm<sup>3</sup>.

The temperature change,  $\Delta T$ , for each neutralisation is calculated using the formula below:

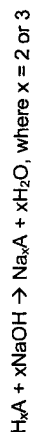
$$\Delta T = T_{\text{final}} - T_{\text{average}}$$

where  $T_{\text{average}}$  is the weighted average of the initial temperatures of the acid and sodium hydroxide:

$$T_{\text{average}} = \frac{(V_{\text{acid}} \times T_{\text{acid}}) + (V_{\text{NaOH}} \times T_{\text{NaOH}})}{V_{\text{acid}} + V_{\text{NaOH}}}$$

A suitable graph can then be plotted to determine the basicity of the acid.

Let the unknown acid be H<sub>x</sub>A. The neutralisation reaction is shown below.



You are provided with:

- 1.00 mol dm<sup>-3</sup> sodium hydroxide, NaOH
- 1.00 mol dm<sup>-3</sup> acid from one of the bottles, H<sub>x</sub>A
- the equipment normally found in a school or college laboratory.

- (a) (i) Calculate the volumes of acid required for complete reaction if the acid is dibasic and tribasic respectively. [1]

If acid is dibasic, mole ratio of acid : NaOH = 1 : 2

Since [acid] = [NaOH], volume of acid : volume of NaOH = 1 : 2.

For complete reaction within a total volume of 60 cm<sup>3</sup>, volume of acid = 20 cm<sup>3</sup>

If acid is tribasic, mole ratio of acid : NaOH = 1 : 3

Since [acid] = [NaOH], volume of acid : volume of NaOH = 1 : 3.

For complete reaction within a total volume of 60 cm<sup>3</sup>, volume of acid = 15 cm<sup>3</sup>

- (ii) Using your answers in (i), fill in the volumes of acid and NaOH in the table below.

Experiment	Volume of acid / cm <sup>3</sup>	Volume of NaOH / cm <sup>3</sup>
1	5.0	55.0
2	10.0	50.0
3	15.0	45.0
4	20.0	40.0
5	25.0	35.0
6	30.0	30.0

(ignore d.p., Total volume in each experiment must be 60 cm<sup>3</sup>)

There should be 3 volumes less than/equal to 15 cm<sup>3</sup> and 3 volumes larger than/equal 20 cm<sup>3</sup>, (eaf based on student's answer in (i)).

[11]

(b) In your plan to determine the basicity of H<sub>2</sub>A, you should include brief details of:

- the apparatus you would use;
- the procedure you would follow;
- the measurements you would make.

[4]

1. Place a clean and dry Styrofoam cup inside another Styrofoam cup placed in a 250 cm<sup>3</sup> beaker.
2. Using a measuring cylinder, measure 5.0 cm<sup>3</sup> of acid, H<sub>2</sub>A, into the Styrofoam cup.
3. Using another measuring cylinder, measure 55.0 cm<sup>3</sup> of NaOH.
4. Record the initial temperatures of each solution with a thermometer.
5. Pour the NaOH into the Styrofoam cup with H<sub>2</sub>A and stir the mixture with the thermometer.
6. Record the highest temperature reached with the thermometer.
7. Wash the Styrofoam cup and dry with a paper towel.
8. Repeat Steps 1 to 6 with the volumes in the table in (a)(iii).

Apparatus [3A = 1 mark]:

- Styrofoam cup,
- measuring cylinder of suitable capacity/burette (volume must have corresponding d.p.)

- thermometer

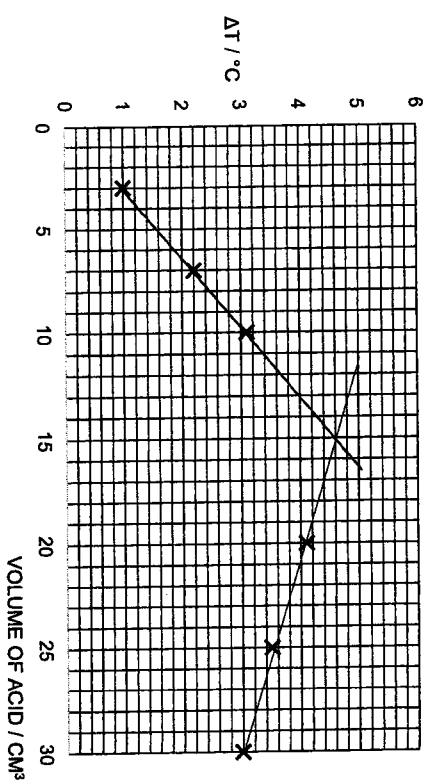
Procedure [3P = 1 mark; 0-2P = 0 marks]:

- Pour one of the solutions into a Styrofoam cup.
- Pour the other solution into same Styrofoam cup.
- Stir (with the thermometer)

Measurements [3M = 2 marks; 1-2M = 1 mark; 0M = 0 marks]

- Initial temperature of acid
- Initial temperature of NaOH
- Highest temperature reached after mixing

(b) A student conducted the experiment and obtained the following graph of  $\Delta T$  against volume of acid.



(b)

Draw 2 best-fit straight lines and extrapolate both lines to find volume of acid required to completely react with NaOH.

Hence, deduce the identity of the acid.

[1 for 2 best-fit straight lines that intersect]

Volume of acid used to completely react with NaOH = 0.015 dm<sup>3</sup> [½]

[2]

Based on calculation in (a)(i), acid is tribasic and the acid is citric acid. [ $\frac{1}{2}$ ]

FYI:

Volume of NaOH used = 0.060 – 0.015 = 0.045 dm<sup>3</sup>

Amount of unknown acid used = 0.015 mol

Amount of NaOH used = 0.045 mol

The ratio of NaOH : acid = 3 : 1

[Total: 8]

iron(II), Fe <sup>2+</sup> (aq)	green ppt. turning brown on contact with air insoluble in excess	giving dark blue solution green ppt. turning brown on contact with air insoluble in excess
iron(III), Fe <sup>3+</sup> (aq)	red-brown ppt. insoluble in excess	red-brown ppt. insoluble in excess
magnesium, Mg <sup>2+</sup> (aq)	white ppt. insoluble in excess	white ppt. insoluble in excess
manganese(II), Mn <sup>2+</sup> (aq)	off-white ppt. rapidly turning brown on contact with air insoluble in excess	off-white ppt. rapidly turning brown on contact with air insoluble in excess
zinc, Zn <sup>2+</sup> (aq)	white ppt. soluble in excess	white ppt. soluble in excess

(a) Reactions of aqueous cations

Cation	reaction with	
	NaOH(aq)	NH <sub>3</sub> (aq)
aluminium, Al <sup>3+</sup> (aq)	white ppt. soluble in excess	white ppt. insoluble in excess
ammonium, NH <sub>4</sub> <sup>+</sup> (aq)	ammonia produced on heating	–
barium, Ba <sup>2+</sup> (aq)	no ppt. (if reagents are pure)	no ppt.
calcium, Ca <sup>2+</sup> (aq)	white ppt. with high [Ca <sup>2+</sup> (aq)]	no ppt.
chromium(III), Cr <sup>3+</sup> (aq)	grey-green ppt. soluble in excess giving dark green solution	grey-green ppt. insoluble in excess
copper(II), Cu <sup>2+</sup> (aq)	pale blue ppt. insoluble in excess	blue ppt. soluble in excess

Qualitative Analysis Notes

[ppt. = precipitate]

## (b) Reactions of anions

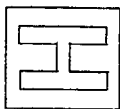
ion	reaction
carbonate, $\text{CO}_3^{2-}$	$\text{CO}_2$ liberated by dilute acids
chloride, $\text{Cl}^-$ (aq)	gives white ppt. with $\text{Ag}^+$ (aq) (soluble in $\text{NH}_3$ (aq))
bromide, $\text{Br}^-$ (aq)	gives pale cream ppt. with $\text{Ag}^+$ (aq) (partially soluble in $\text{NH}_3$ (aq))
iodide, $\text{I}^-$ (aq)	gives yellow ppt. with $\text{Ag}^+$ (aq) (insoluble in $\text{NH}_3$ (aq))
nitrate, $\text{NO}_3^+$ (aq)	$\text{NH}_3$ liberated on heating with $\text{OH}^-$ (aq) and Al foil
nitrite, $\text{NO}_2^+$ (aq)	$\text{NH}_3$ liberated on heating with $\text{OH}^-$ (aq) and Al foil NO liberated by dilute acids (colourless $\text{NO} \rightarrow$ (pale) brown $\text{NO}_2$ in air)
sulfate, $\text{SO}_4^{2-}$ (aq)	gives white ppt. with $\text{Ba}^{2+}$ (aq) (insoluble in excess dilute strong acids)
sulfite, $\text{SO}_3^{2-}$ (aq)	$\text{SO}_2$ liberated on warming with dilute acids; gives white ppt. with $\text{Ba}^{2+}$ (aq) (soluble in dilute strong acids)

## (c) Tests for gases

gas	test and test result
ammonia, $\text{NH}_3$	turns damp red litmus paper blue
carbon dioxide, $\text{CO}_2$	gives a white ppt. with limewater (ppt. dissolves with excess $\text{CO}_2$ )
chlorine, $\text{Cl}_2$	bleaches damp litmus paper
hydrogen, $\text{H}_2$	"pops" with a lighted splint
oxygen, $\text{O}_2$	relights a glowing splint
sulfur dioxide, $\text{SO}_2$	turns aqueous acidified potassium manganate(VII) from purple to colourless

## (d) Colour of halogens

Halogen	colour of element	colour in aqueous solution	colour in hexane
chlorine, $\text{Cl}_2$	greenish yellow gas	pale yellow	pale yellow
bromine, $\text{Br}_2$	reddish brown gas / liquid	orange	orange-red
iodine, $\text{I}_2$	black solid / purple gas	brown	purple



**TEMASEK JUNIOR COLLEGE**  
**2022 JC2 PRELIMINARY EXAMINATION**  
**Higher 2**



**TEMASEK JUNIOR COLLEGE**

**Chemistry** 9729/01

Paper 1 Multiple Choice 16 September 2022

1 hour

Additional Materials: Multiple Choice Answer Sheet (OMS) Data Booklet

**READ THESE INSTRUCTIONS FIRST**

Write in soft pencil.

Do not use staples, paper clips, glue or correction fluid.

There are thirty questions on this paper. Answer all questions. For each question there are four possible answers A, B, C, D.

Choose the one you consider correct and record your choice in soft pencil on the separate OMS.

Read the instructions on the OMS very carefully.

Write your name & Civics Group on the OMS. Shade your index number in the appropriate boxes.

1. Enter your NAME (as in MRIC).

2. Enter the SUBJECT TITLE.

3. Enter the TEST NAME.

4. Enter the CLASS.

Write your name and Civics Group

WRITE																	
I	M	X	H	J	K	L	N	O	P	Q	R	S	SHADE APPROPRIATE BOXES				
1	2	3	4	5	6	7	8	9	0	A	B	C	D	Index number (refer to entry proof)			

5. Enter your CLASS NUMBER or INDEX NUMBER.

6. Now SHADE the corresponding box in the grid for EACH DIGIT or LETTER.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer. Any rough working should be done in this booklet. The use of an approved scientific calculator is expected, where appropriate.

This document consists of 16 printed pages.

1 Use of the Data Booklet is relevant to this question.

Atoms or ions that contain the same number of neutrons are isotonic.

Which of the following pairs of ions fulfil both criteria below?

- The two ions are isotonic.
- The first ion deflects more than the second ion when passed through an electric field.

A  $^{35}\text{Cl}^-$ ,  $^{31}\text{P}^-$

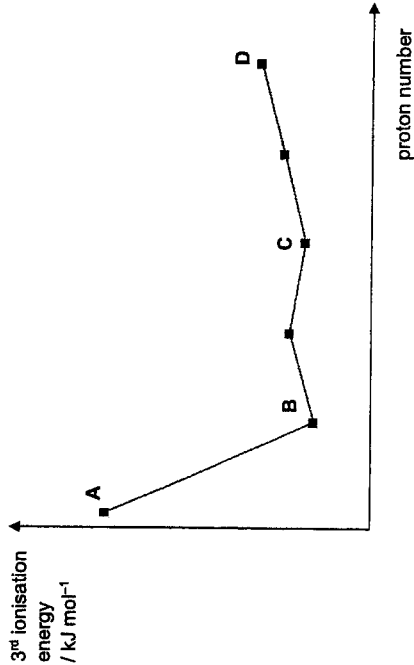
B  $^{31}\text{P}^-$ ,  $^{31}\text{P}^{3-}$

C  $^{31}\text{P}^{3-}$ ,  $^{32}\text{P}^{2-}$

D  $^{31}\text{P}^{3-}$ ,  $^{32}\text{S}^{2-}$

2 The variation in the third ionisation energy of six consecutive elements in the Periodic Table is shown in the graph.

Which of these elements is a Group 15 element?



3 Which group of particles is in order of increasing first ionisation energy?

- 1 Ga Ge As
- 2 As Se Br
- 3 Se Br Kr
- 4 P As Sb

- A 1 and 3
- B 2 and 4
- C 2 and 3
- D 1 and 4

4 Carbon forms double bonds with oxygen, and with two other Group 16 elements, Y and Z. In the molecules CO<sub>2</sub>, COY and COZ, the polarities of these double bonds do not necessarily cancel.

	overall polarity of molecule
CO <sub>2</sub>	0
COY	0.71
COZ	0.73

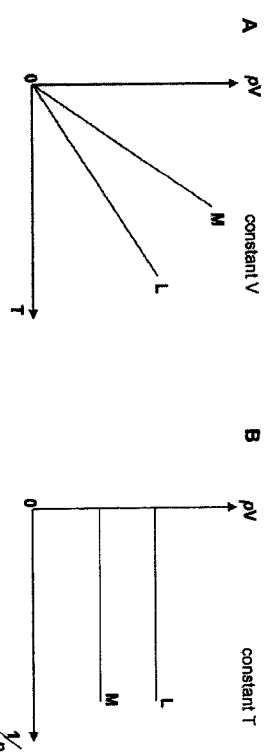
Which factor best accounts for these observations?

- A The C=O bond is the least polar, while the C=Z bond is the most polar.
- B Electronegativity increases in the order: Z < Y < O
- C The C=O, C=Y and C=Z bonds are all polar.
- D Bond length increases in the order: C=O < C=Y < C=Z

5 Which of the following best describes the change in bond angle when SO<sub>2</sub> is converted to SO<sub>3</sub>?

- A Decreases to 107°
- B Increases to 107°
- C Decreases to 120°
- D Increases to 120°

6 Which graph correctly describes the behaviour of fixed masses of the ideal gases L and M where the number of moles of L is greater than number of moles of M?



7 X, Y and Z are elements in Period 3 of the Periodic Table. The table below shows the changes in pH when compounds of these elements are added to water.

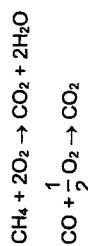
element	change in pH of solution when oxide of element is added to water	change in pH of solution when chloride of element is added to water
X	increases	no change
Y	decreases	decreases
Z	no change	decreases

What could be the identities of X, Y and Z?

	X	Y	Z
A	Na	Al	Mg
B	Na	P	Al
C	Si	P	Al
D	P	Na	Si

- 8 Which of the following statements about Group 2 elements is correct?
- A Solubility of hydroxides decreases down the group.  
 B Covalent character of chlorides increases down the group.  
 C Thermal stability of carbonates increases down the group.  
 D Electrode potential,  $E^\ominus(M^{2+}/M)$ , becomes more positive down the group.
- 9 Which of the following statements about the Group 17 elements and compounds is **incorrect**?
- A When aqueous sodium chloride is added to aqueous bromine, the orange solution is decolourised.  
 B When aqueous silver nitrate is added to aqueous sodium chloride followed by nitric acid, a white precipitate remains.  
 C When aqueous chlorine is added to excess sodium thiosulfate, followed by barium nitrate, a white precipitate is formed.  
 D When chlorine gas is bubbled through potassium iodide, the solution turns brown.

- 10 A 15 cm<sup>3</sup> mixture of carbon monoxide and methane was mixed with excess oxygen and exploded.



There was a contraction in volume of 15 cm<sup>3</sup> at room temperature and pressure after the reaction.

What is the percentage by volume of methane in the mixture?

- A 33 %      B 50 %      C 60 %      D 75 %

- 11 Magnesium reacts readily with dilute hydrochloric acid to form magnesium chloride and hydrogen.
- $$\text{Mg(s)} + 2\text{HCl(aq)} \rightarrow \text{MgCl}_2\text{(aq)} + \text{H}_2\text{(g)}$$
- The standard enthalpy change for this reaction can be measured in the laboratory. What further information is needed in order to calculate the standard enthalpy change of formation of magnesium chloride?

- 1  $\Delta H_f^\ominus$  for  $\text{HCl(aq)}$   
 2 lattice energy of  $\text{MgCl}_2$   
 3 enthalpy change of solution of  $\text{MgCl}_2$

- A 1, 2 and 3      B 1 and 2 only      C 2 and 3 only      D 1 only

- 12 The mechanism for the above reaction involves the following steps.



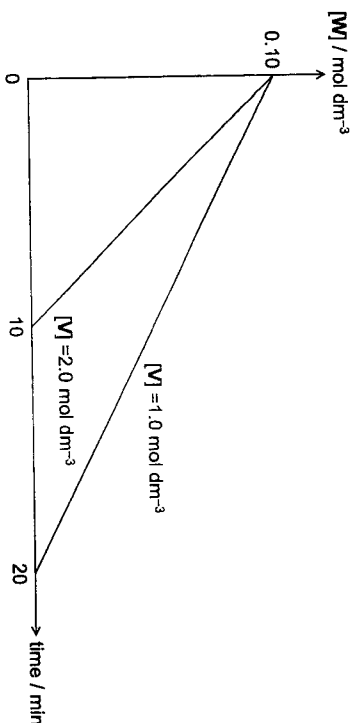
Based on the information, what is the rate equation for this reaction?

- A rate =  $k[\text{A}]^2[\text{B}]^2$   
 B rate =  $k[\text{B}][\text{C}]$   
 C rate =  $k[\text{A}]^2[\text{B}]$   
 D rate =  $k[\text{A}][\text{B}]^2$

13 Consider the reaction



Two separate experiments were carried out using  $1.0 \text{ mol dm}^{-3}$  and  $2.0 \text{ mol dm}^{-3}$  of V respectively. A graph of the variation of the concentration of W with time is plotted.



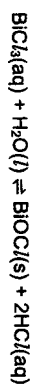
Which of the following statements can be determined from the above information?

- 1 The reaction is first order with respect to V.
- 2 The reaction is zero order with respect to W.
- 3 The reaction is first order with respect to X.

- A 1, 2 and 3  
 B 1 and 2 only  
 C 2 and 3 only  
 D 1 only

14 When  $0.1 \text{ mol}$  of bismuth chloride is added to  $2 \text{ dm}^3$  of water, it reacts to form  $0.02 \text{ mol}$  of white precipitate of bismuth oxychloride and a solution of hydrochloric acid.

The equation for the reaction is as follows:



What is the correct expression for the equilibrium constant  $K_c$ ?

- A  $\frac{(2 \times 0.02)^2}{0.08}$       B  $\frac{(0.02)(2 \times 0.02)^2}{0.08}$   
 C  $\frac{(0.02) \left( \frac{2 \times 0.02}{2} \right)^2}{\frac{0.08}{2}}$       D  $\frac{(2 \times 0.02)^2}{\frac{0.08}{2}}$

15 The enthalpy change of dissociation of ethanoic acid in water is  $+1.0 \text{ kJ mol}^{-1}$ . Which correctly describes the value of acid dissociation constant and degree of dissociation when temperature increases?

	acid dissociation constant	degree of dissociation
A	Increase	remain constant
B	Increase	Increase
C	decrease	remain constant
D	decrease	Increase



- 18 Both cyclohexene and benzene react with bromine, but under different conditions. Cyclohexene reacts readily with liquid bromine while benzene requires a catalyst before a reaction with bromine can occur.

Which of the following explains why cyclohexene is more reactive than benzene?

- A The localised  $\pi$  electron cloud in cyclohexene makes the molecule more susceptible to attack by electrophiles.  
 B Cyclohexene is not a planar molecule while all atoms in benzene lie on the same plane.  
 C The delocalised  $\pi$  electron cloud in benzene repels electrophiles.  
 D Cyclohexene has a higher boiling point than benzene.

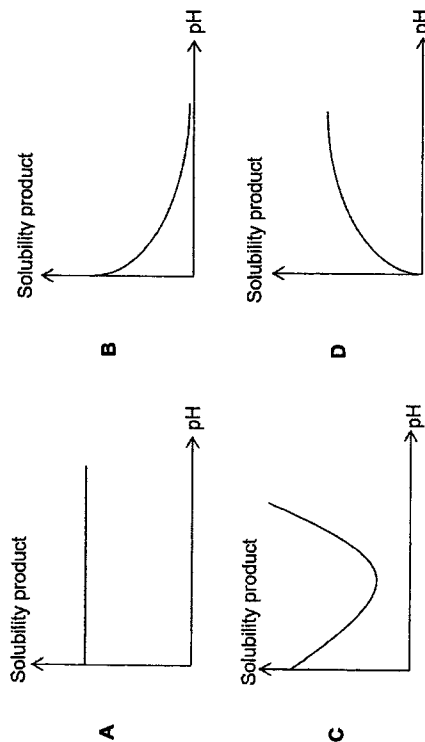
- 19 Chloroalkane **W**,  $C_8H_{11}Cl$ , rotates plane polarised light. On heating **W** with alcoholic  $NaOH$ , two alkenes **U** and **X** are formed, with **U** being formed in larger amount.

A yellow precipitate is produced when aqueous alkaline iodine is warmed with one of the products of the reaction between **U** and hot acidified  $KMnO_4$ .

Which of the following is **W**?

- A  $CH_3CH_2CHClCH_2CH_2CH_3$   
 B  $CH_3CH(CH_3)CHClCH_3$   
 C  $CH_3CH_2CHClCH_2CH_3$   
 D  $CH_3CCl(CH_3)CH_2CH_3$

- 16 The numerical value of the solubility product of copper(I) iodide is  $1.27 \times 10^{-12}$ . Given that  $HI$  is a strong acid, which diagram shows how the solubility product of  $CuI$  will vary with  $pH$  at constant temperature?



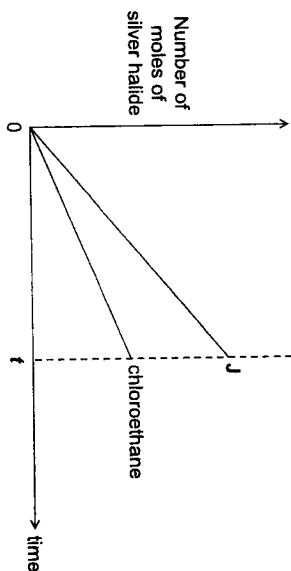
- 17 Buta-1,3-diene,  $CH_2=CH-CH=CH_2$ , reacts completely with two moles of hydrogen chloride. Which of the following about the products formed is correct?

	No. of constitutional isomers	No. of products that are secondary chloroalkanes
A	2	1
B	3	1
C	3	2
D	4	2

11

20 When haloalkanes are heated with ethanolic silver nitrate, insoluble silver halides are formed.

A student investigated the rate of formation of silver halides when the same amount of chloroethane and J were reacted separately with hot ethanolic silver nitrate. Each reaction was monitored till time,  $t_1$  and the following graphs were obtained.



Which of the following compounds could be J?

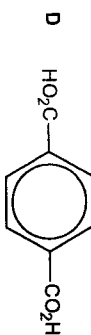
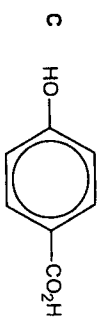
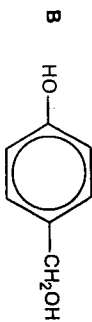
- 1  $C/CH_2CH_2Cl$
- 2  $CH_3CH_2Br$
- 3  $CH_3CH_2I$

- A 1, 2 and 3
- B 1 and 2
- C 2 and 3
- D 1 only

21 1 mole of each of the following four compounds is reacted separately with

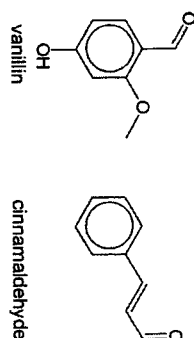
- an excess of Na, and
- an excess of  $NaHCO_3$ .

Which compound produces the same volume of gas with each of the two reagents?



12

22 Vanillin and cinnamaldehyde are some naturally occurring flavouring agents.



Which reagent, when added separately to the two compounds, would enable them to be distinguished from one another?

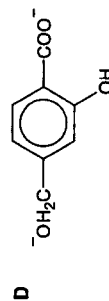
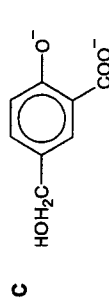
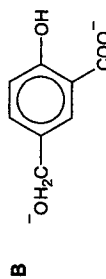
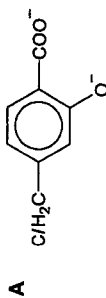
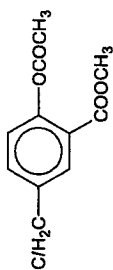
- A 2,4-dinitrophenylhydrazine
- B Fehling's solution
- C Hot acidified  $K_2Cr_2O_7$
- D Tollens' reagent

23 What is the relative order of decreasing acidity for the following compounds?

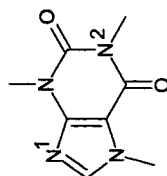
- 1 2-nitrophenol
- 2 benzoic acid
- 3 2-chlorobenzoic acid
- 4 cyclohexanol

	most acidic	—————>		least acidic
A	2	3	4	1
B	2	3	1	4
C	3	2	4	1
D	3	2	1	4

24 Which one of the following represents the organic product when an excess of hot aqueous sodium hydroxide is added to compound R?



25 Caffeine is a central nervous system stimulant and is used as a cognitive enhancer to increase alertness. All the atoms in the 2 rings are planar.



Which of the following statements about caffeine are correct?

- 1 N<sup>1</sup> is more basic than N<sup>2</sup>.
- 2 Caffeine undergoes a condensation reaction with ethanoyl chloride.
- 3 1 mole of caffeine reacts with excess hot aqueous sodium hydroxide to form 2 moles of methylamine.

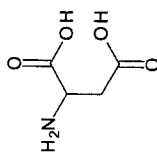
A 1 only

B 2 only

C 1 and 3

D 1, 2 and 3

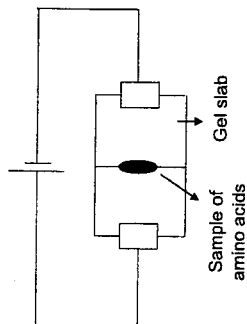
26 Aspartic acid is an  $\alpha$ -amino acid that occur naturally in the body.



Aspartic acid

The three  $pK_a$  values associated with aspartic acid are 1.88, 3.65 and 9.60.

Electrophoresis is a technique of separating amino acids. Samples are placed on a gel slab containing a buffer and the ends of the gel slab are connected to charged electrodes. Positively charged species migrate towards the negative electrode while negatively charged species migrate towards the positive electrode. Ions of higher charge to mass ratio will migrate at a faster rate.



A solution of aspartic acid buffered at  $pH = 4$  was placed in the electrophoresis set-up. Which of the following is correct?

- A The major species has a net charge of +1.
- B The major species present will migrate to the cathode.
- C The major species present will migrate to neither electrodes.
- D The major species will migrate faster if the  $pH$  was 11.

27

Use of the Data Booklet is relevant to this question.

Which of the following is the strongest reducing agent?

- A hexacyanoferrate(II)
- B manganese(II)
- C nitrogen dioxide
- D vanadyl,  $\text{VO}^{2+}$

28

Use of the Data Booklet is relevant to this question.

The reaction between iodide,  $\text{I}^-$  and peroxydisulfate,  $\text{S}_2\text{O}_8^{2-}$  is very slow at room conditions.

Which of the ions is unable to alter the rate of reaction between iodide and peroxydisulfate?

- A  $\text{Co}^{2+}$
- B  $\text{Cu}^{2+}$
- C  $\text{Fe}^{3+}$
- D  $\text{Fe}^{2+}$

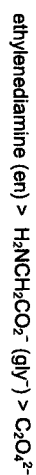
29

Use of the Data Booklet is relevant to this question.

Which one of the following is true about vanadium and its compounds?

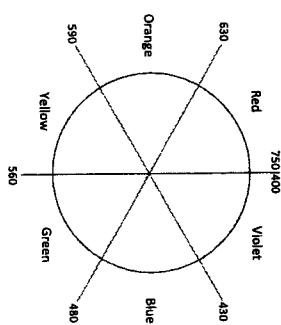
- A The maximum oxidation state of vanadium is found in  $\text{VO}^{2+}$ .
- B  $\text{V}_2\text{O}_6$  is used as a catalyst in the manufacture of ammonia.
- C Zinc reduces  $\text{VO}_2^+(\text{aq})$  to  $\text{V}^{2+}(\text{aq})$ .
- D Vanadium is less dense than calcium.

30 A partial spectrochemical series with ligands arranged in order of decreasing field strength is given below.



Stronger field ligands are known to give rise to a larger energy gap between the two sets of d-orbitals in a transition metal complex.

The figure below shows a colour wheel with approximate wavelength values (in nm) for different colour light. As wavelength decreases, the energy of the light increases.



An aqueous solution containing the  $[\text{Co}(\text{gly})_3]$  complex is violet.

Which combination could be the colours of  $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}(\text{aq})$  and  $[\text{Co}(\text{en})_3]^{3+}(\text{aq})$ ?

	$[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}(\text{aq})$	$[\text{Co}(\text{en})_3]^{3+}(\text{aq})$
A	green	yellow
B	yellow	orange
C	red	blue
D	blue	green