

# PAPER 1 ANSWERS

BP~727

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



Answer all the questions in this section.

- 1 (a) Figure 1.1 shows the third ionisation energies of eight consecutive elements A to H, in the Periodic Table. [Note that letters A to H are not the atomic symbols of the elements concerned.]

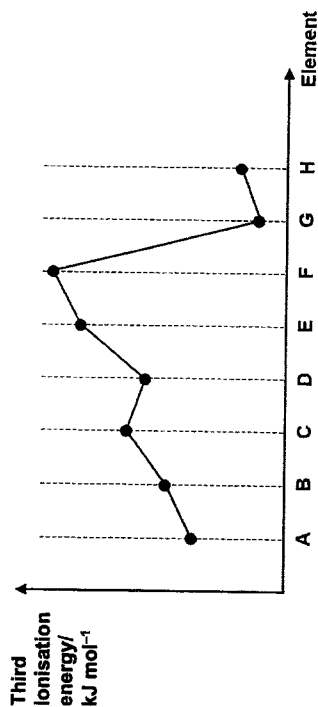
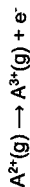


Figure 1.1

- (i) Write an equation, including state symbols, to represent the third ionisation energy of element A. [1]



- (ii) From Figure 1.1, suggest the identity of B. Explain how you arrived at your answer. [2]

The large decrease in 3<sup>rd</sup> IE from F to G implies that G<sup>2+</sup> has 1 more quantum shell of electrons than F<sup>2+</sup> / 3<sup>rd</sup> electron to be removed from F is from the inner quantum shell.

The valence shell configuration of G<sup>2+</sup> is ns<sup>1</sup> and hence, the valence shell configuration of G is ns<sup>2</sup> np<sup>1</sup> (i.e. Al).

OR

This also implies that the valence shell configuration of B<sup>2+</sup> is (n-1)s<sup>2</sup> np<sup>2</sup> and hence, the valence shell configuration of B is ns<sup>2</sup> np<sup>4</sup>.

OR

F is in group 2 / G is in group 13

Hence, B is oxygen.

Cannot accept sulfur.

- (iii) Explain why the third ionisation energy of element D is slightly lower than that of element C. [1]



The inter-electronic repulsion / repulsion between the paired 2p electrons in D<sup>2+</sup> makes it easier to remove a paired electron than an unpaired 2p electron of C<sup>2+</sup> which do not experience such repulsion.

Hence, the 3<sup>rd</sup> IE of D is lower than that of element C.

NAME \_\_\_\_\_

CLASS 21S

**JURONG PIONEER JUNIOR COLLEGE**  
**JC2 PRELIMINARY EXAMINATION 2022**



**CHEMISTRY**

**Higher 2**

Paper 2 Structured Questions

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

**9729/02**

**14 September 2022**

**2 hours**

**READ THESE INSTRUCTIONS FIRST**

Write your name, class and exam index number on all the work you hand in.  
 Write in dark blue or black pen on both sides of the paper.  
 You may use a HB pencil for any diagrams, 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.

For Examiner's Use	
1	10
2	10
3	17
4	10
5	11
6	12
7	5
<b>Penalty</b> (delete accordingly)	
Bond linkages	-1 / NA
Significant figures & units	-1 / NA
<b>Total</b>	<b>75</b>

This document consists of 20 printed pages.

(b) Nitrogen and phosphorus are elements of Group 15 in the Periodic Table. Nitrogen exists naturally as gaseous diatomic  $N_2$  molecules whereas phosphorus is a solid and exists as  $P_4$  molecules comprising of P-P single bonds.

(i) Account for the difference in their physical states in terms of structure and bonding. [2]

Both  $N_2$  and  $P_4$  have simple molecular structures.

As  $P_4$  has larger number of electrons/ bigger electron cloud to be polarised, more energy is required to overcome the stronger instantaneous dipole-induced dipole interactions/attractions between the  $P_4$  molecules.

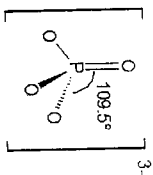
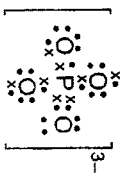
This results in higher melting point in  $P_4$ , hence  $P_4$  exists as solid.

(ii) Suggest why phosphorus does not occur naturally as  $P=P$  molecules. [1]

Phosphorus is a relatively big atom with diffused orbitals, side-on overlap of its p orbitals to form  $\pi$  bonds is much less effective than head-on overlap to form sigma bond.

(iii) Nitrate,  $NO_3^-$ , and phosphate,  $PO_4^{3-}$ , are oxoanions of nitrogen and phosphorus respectively. [3]

Draw a dot-and-cross diagram to show the bonding  $PO_4^{3-}$ , deducing the shape and the bond angle around the phosphorous atom. Hence explain why it is not possible for nitrogen to form an oxoanion with formula  $NO_4^{3-}$ .



4 bond pairs around central atom P  
Shape of  $PO_4^{3-}$  is tetrahedral, angle  $O-P-O: 109.5^\circ$

To form  $NO_4^{3-}$ , N must be able to accommodate 10 electrons in its valence shell. Since N is in Period 2, it has no energetically accessible/low lying d orbital to expand its octet.

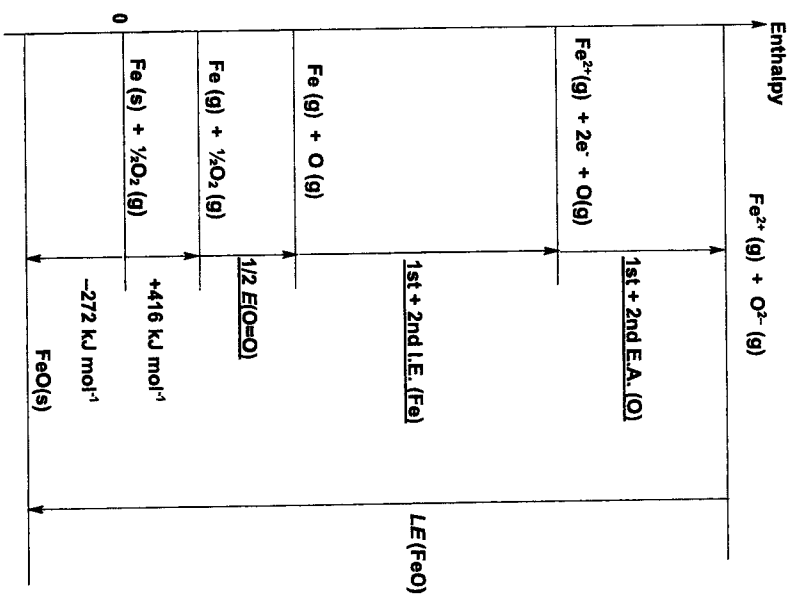
[Total: 10]

2 Iron oxides are chemical compounds composed of iron and oxygen. Most iron ores are oxides, making them important precursors to iron metal and its many alloys.

(a) Iron (II) compounds are generally only stable in neutral, non-oxidising conditions. It is difficult to determine the lattice energy of  $FeO$  experimentally.

(i) Given the following data in Table 2.1 and data from the Data Booklet, use the energy diagram below to calculate the lattice energy of  $FeO(s)$  in  $kJ\ mol^{-1}$ . [3]

Table 2.1	
standard enthalpy change of atomisation of Fe(s)	+416 $kJ\ mol^{-1}$
standard enthalpy change of formation of $FeO(s)$	-272 $kJ\ mol^{-1}$
Sum of 1 <sup>st</sup> and 2 <sup>nd</sup> Electron Affinity of oxygen	+157 $kJ\ mol^{-1}$



By Hess Law,  
 $-272 = +416 + \frac{1}{2}(496) + 762 + 1560 + 157 + LE(FeO)$   
 $LE(FeO) = -3415$  (or  $-3420$ )  $kJ\ mol^{-1}$

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- (ii) Most naturally occurring samples of iron(II) oxides are found as the mineral Wüstite. [1]

Wüstite has the formula  $\text{Fe}_2\text{O}_x$ . It contains both  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions. 90% of the iron is present as  $\text{Fe}^{2+}$  and the remaining as  $\text{Fe}^{3+}$ .

Deduce the value of  $x$ .

Balancing of charges:

$$20 \times [0.9(+2) + 0.1(+3)] - 2x = 0$$

Solving  $x = 21$

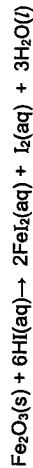
- (iii) State and explain how the lattice energies of FeO compares with the lattice energies of  $\text{Fe}_2\text{O}_3$ . [2]

$\text{Fe}^{3+}$  ion has a higher (ionic) charge and smaller radius/size than  $\text{Fe}^{2+}$  ion.

Since  $|\text{LE}| \propto \frac{q_+ \times q_-}{r_+ + r_-}$ , hence, the magnitude of LE for  $\text{Fe}_2\text{O}_3$  is larger /

LE for  $\text{Fe}_2\text{O}_3$  is more exothermic than that in FeO.

- (b) Another common iron oxide is hematite,  $\text{Fe}_2\text{O}_3$  is the main source of iron for the steel industry.  $\text{Fe}_2\text{O}_3$  will readily react with acids to form soluble salts such as the following reaction. [1]



- (i) Define standard enthalpy change of solution. [1]

It is the heat change when 1 mole of a substance is completely dissolved in water under the standard conditions of 298 K and 1 bar so that there is no further heat change upon adding more water.

- (ii) Use the data in Table 2.2 to calculate the enthalpy change of solution of iron (II) iodide,  $\text{FeI}_2$ . [1]

$\Delta H_{\text{f, int}}(\text{FeI}_2(\text{s}))$	- 2440 kJ mol <sup>-1</sup>
$\Delta H_{\text{hyd}}(\text{Fe}^{2+}(\text{g}))$	- 1950 kJ mol <sup>-1</sup>
$\Delta H_{\text{hyd}}(\text{I}^-(\text{g}))$	- 308 kJ mol <sup>-1</sup>

Table 2.2

$$\Delta H_{\text{soln}} = -(-2440) + (-1950) + (2(-308))$$

$$= -126 \text{ kJ mol}^{-1}$$

- (iii) A yellow precipitate of  $\text{PbI}_2$  forms when 25 cm<sup>3</sup> of  $x$  mol dm<sup>-3</sup>  $\text{Pb}^{2+}$  ions are added to 10 cm<sup>3</sup> of 0.100 mol dm<sup>-3</sup>  $\text{FeI}_2$  (aq). [2]

Given that the solubility product,  $K_{\text{sp}}$ , of  $\text{PbI}_2 = 9.8 \times 10^{-9} \text{ mol}^3 \text{ dm}^{-9}$ , find the minimum value for  $x$ , concentration of  $\text{Pb}^{2+}$ .

For ppt to occur,

Ionic product >  $K_{\text{sp}}$   $[\text{Pb}^{2+}][\text{I}^-]^2$

$$[\text{Pb}^{2+}][\text{I}^-]^2 > 9.8 \times 10^{-9}$$

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$$\left( \frac{25}{1000} \times x \right) \left( \frac{2 \times \frac{10}{1000} \times 0.100}{\frac{35}{1000}} \right)^2 > 9.8 \times 10^{-9}$$

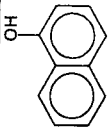
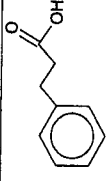
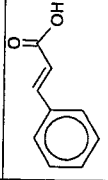
(diluted conc to be given mark)

$$x > 4.20 \times 10^{-8} \text{ mol dm}^{-3}$$

- 3 Carboxylic acids and their derivatives are classes of organic compounds that play important roles in our everyday lives. Some of their uses include the manufacturing of polymers, production of pharmaceutical drugs, as food additives and industrial solvents. [Total: 10]

This question deals with some of the properties of acidic organic compounds, including carboxylic acids and their derivatives.

- (a) The table below shows three organic compounds that can be found in nature.

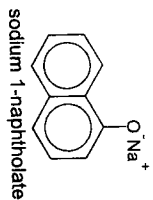
Name	1-naphthol	hydrocinnamic acid	cinnamic acid
Where it can be found	<i>Selaginella sinensis</i> tree	cowberries	cinnamon
Structural Formula			
$\text{p}K_{\text{a}}$	9.51	4.70	4.37

- (i) By reference to the structures, explain why cinnamic acid will be the first to react when aqueous potassium hydroxide is added dropwise to a mixture containing both cinnamic acid and hydrocinnamic acid. [2]

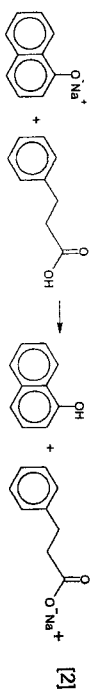
Cinnamic acid is a stronger acid than hydrocinnamic acid, as can be seen from its lower  $\text{p}K_{\text{a}}$  value.

There is overlap between the  $p$  orbital of the O atom of the anion of cinnamic acid and the  $p$  orbitals of the  $-\text{C}=\text{O}$ ,  $\text{C}=\text{C}$ , benzene, and  $-\text{OH}$  groups. This allows the negative charge on the O of the anion of cinnamic acid to be delocalised/dispersed. This stabilises the anion and hence is it a stronger acid.

- (ii) With the aid of balanced equation(s), explain any reaction(s) that occurs when a solution containing sodium 1-naphtholate is added to a solution containing hydrochloric acid.



Hydrochloric acid is a stronger acid (lower  $pK_a$ ) than 1-naphthol. It will dissociate in water to protonate/donate its  $H^+$  to the 1-naphtholate ion to form back 1-naphthol.

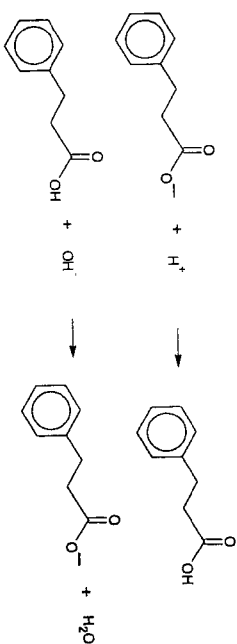


A laboratory technician was tasked to prepare a buffer solution made up of hydrocinamic acid and aqueous potassium hydroxide.

- (iii) What is a buffer solution? [1]

A buffer solution is made up of a weak acid/weak base and its conjugate acid / base OR salt, and it is able to resist changes in pH when a small amount of acid/base is added to it, or upon dilution.

- (iv) Write equations to show how a mixture of hydrocinamic acid and its salt can function as a buffer. [2]



- (v) Using appropriate data from the table in (a), determine the volume of  $0.100 \text{ mol dm}^{-3} \text{ KOH(aq)}$  the student needs to add to  $0.100 \text{ dm}^3$  of  $0.100 \text{ mol dm}^{-3}$  hydrocinamic acid to form a buffer of pH 5.50. [2]

Let HA be hydrocinamic acid. Let the volume of  $\text{KOH(aq)}$  to be added be  $v \text{ dm}^3$ .

To form a buffer, you need to add limited  $\text{KOH}$ , so that the final mixture will contain HA and  $\text{KA}$ .

HA	+	KOH	→	KA	+	$\text{H}_2\text{O}$
1 / mol		0.1v		0		-
c / mol		-0.1v		+0.1v		-
f / mol		0.01-0.1v		0		0.1v

Acidic buffer:

$$\text{pH} = \text{p}K_a + \lg \left( \frac{[\text{KA}]}{[\text{HA}]} \right)$$

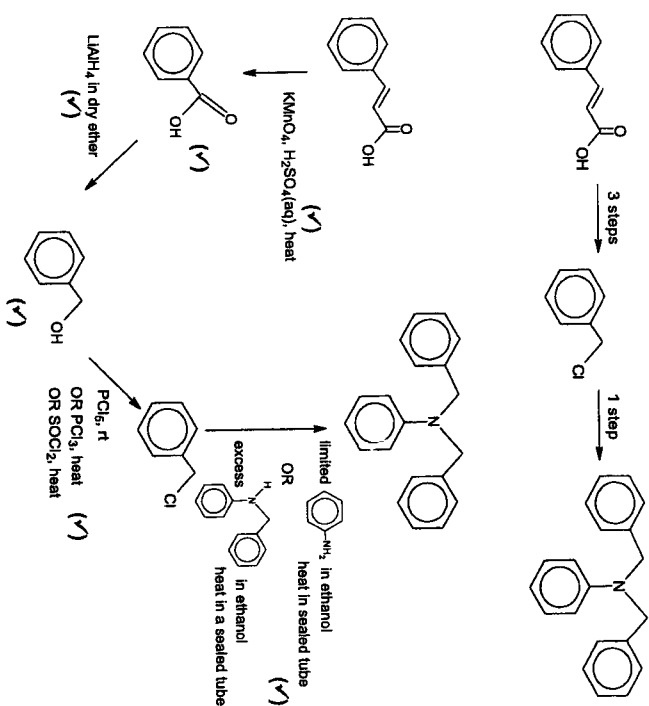
$$5.50 = 4.70 + \lg \left( \frac{0.1v / (0.1+v)}{(0.01-0.1v) / (0.1+v)} \right)$$

$$5.50 - 4.70 = 0.8 = \lg \left( \frac{0.1v}{0.01-0.1v} \right)$$

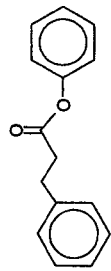
$$0.1v = 0.063096 - 0.63096v$$

$$v = 0.08632 \text{ dm}^3 = 86.3 \text{ cm}^3$$

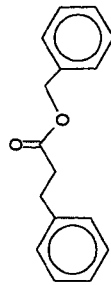
- (b) The diagram below shows a reaction scheme involving cinamic acid. Suggest a possible synthetic pathway involving 4 steps, stating clearly the reagents and conditions required, and the intermediate organic compounds formed for every step. [3]



- (c) Hydrocinamic acid form many different types of esters that have great commercial uses. Two such esters are shown below:



ester P



ester Q

- (i) Suggest a simple chemical test that would enable the laboratory technician to distinguish between the two esters. [2]

Test 1:

Reagents and conditions: 1)  $\text{H}_2\text{SO}_4(\text{aq})$  or  $\text{HCl}(\text{aq})$ , heat  
2)  $\text{Br}_2(\text{aq})$

Observations: Orange  $\text{Br}_2(\text{aq})$  decolourises, and a white ppt forms for P but not for Q.

Test 2: Reagents and conditions:  $\text{K}_2\text{Cr}_2\text{O}_7$ ,  $\text{H}_2\text{SO}_4(\text{aq})$ , heat

Observations: Orange  $\text{K}_2\text{Cr}_2\text{O}_7$  turns green for Q but not for P.

- (ii) State the type of reaction that occurred when hydrocinamic acid forms these esters. [1]

Nucleophilic Acyl Substitution OR Condensation

- (d) Describe and explain the trend observed in the thermal stability of the carbonates of the Group 2 elements.

$\text{MCO}_3 \rightarrow \text{MO} + \text{CO}_2$  Let  $M^{2+}$  represent the Group 2 cation.

Down the group, the radius/size of  $M^{2+}$  increases and

- hence, the charge density of  $M^{2+}$  decreases .
- Thus, the ability of  $M^{2+}$  to polarise the large carbonate ion decreases and
- the C-O bond is weakened to decreasing extent.
- Therefore, the thermal stability of  $\text{MCO}_3$  increases down the group.

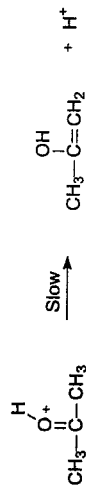
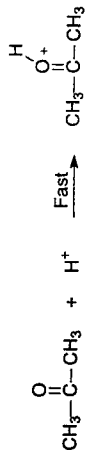
[Total: 17]

- 4 Carbonyl compounds can react with halogens in acidic or alkaline medium to form different products. Kinetic studies are conducted to investigate the orders of reaction and the mechanisms of these reactions.

In acidic medium, propanone reacts with bromine to form bromopropanone as shown in the equation below:



The kinetic studies of the above reaction suggest that a three-step mechanism is involved in this reaction.



- (a) Based on the mechanism above, construct the rate equation for the above reaction. [1]

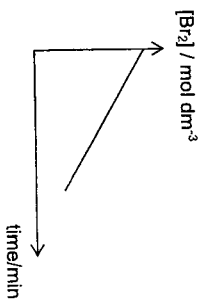
Rate =  $k [\text{CH}_3\text{COCH}_3] [\text{H}^+]$

- (b) From the mechanism of the reaction, how can you deduce that  $\text{H}^+$  is acting as a catalyst? [1]

$\text{H}^+$  is consumed/reacted in step 1 but is regenerated in step 2.

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- (c) Sketch, in the space below, the graph of  $[\text{Br}_2]$  against time in minutes, given that the initial concentration of bromine is  $0.008 \text{ mol dm}^{-3}$  and the initial concentration of propanone is  $0.80 \text{ mol dm}^{-3}$ . [1]



$$\text{Rate} = k [\text{CH}_3\text{COCH}_3] [\text{H}^+] [\text{Br}_2]^0$$

Given:  $[\text{Br}_2] = 0.008 \text{ mol dm}^{-3}$  and  $[\text{CH}_3\text{COCH}_3] = 0.80 \text{ mol dm}^{-3}$

Since  $\text{CH}_3\text{COCH}_3$  is used in large excess, its conc. remains effectively constant as only a small fraction of  $\text{CH}_3\text{COCH}_3$  reacted during the reaction.

Since  $\text{H}^+$  is a catalyst, its conc. remains constant throughout the reaction.

$\therefore$  the rate equation can be simplified as

$$\text{rate} = k' [\text{Br}_2]^0, \text{ where } k' = k [\text{CH}_3\text{COCH}_3] [\text{H}^+] = \text{constant}$$

Hence the reaction is an overall zero order. Any change in  $[\text{Br}_2]$  has no effect on the reaction rate. So the graph of  $[\text{Br}_2]$  vs time graph is a straight line with a constant negative gradient.

- (d) Explain what will happen to the rate of reaction if chlorine is used in place of bromine, assuming that the mechanism remains unchanged? [1]

There will be no change to the rate of reaction

as halogen is not involved in the rate determining/slow step

(or  $[\text{X}_2]$  is not in the rate equation)

(or the reaction is zero order with respect to  $[\text{X}_2]$ )

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- (e) The kinetics data for the experiment may be collected using a continuous sampling method, which requires a sample of the chemical reaction to be extracted at various time intervals from a reaction mixture followed by titration. Briefly describe a physical property that you can use to determine the  $[\text{Br}_2]$  at various times. [1]

The colour intensity of the reaction solution can be measured at various time using a colorimeter/spectrometer.

As the  $[\text{Br}_2]$  decreases, the orange-brown colour intensity of the reaction solution decreases.

Hence, the absorbance measured at various time  $t$  is directly proportional to the  $[\text{Br}_2]$  left at  $t$ .

- (f) The reaction between propanone and bromine was carried out in experiments 1 and 2, and the following results were obtained: [2]

Experiment	Initial $[(\text{CH}_3)_2\text{CO}] / \text{mol dm}^{-3}$	Initial $[\text{H}^+] / \text{mol dm}^{-3}$	Initial $[\text{Br}_2] / \text{mol dm}^{-3}$	Half-life / min
1	0.40	0.30	0.20	22.5
2	0.60	0.10	0.20	S

The half-life of propanone in experiment 1 was found to be constant at about 22.5 minutes. Predict the half-life of propanone in experiment 2, s, giving your reasoning.

rate =  $k [\text{H}^+] [\text{propanone}]$ , an overall second order reaction.

Since  $\text{H}^+$  is a catalyst,  $[\text{H}^+]$  remains constant throughout the reaction.

$\therefore$  rate =  $k' [\text{propanone}]$  where  $k' = k [\text{H}^+] = \text{constant}$ .

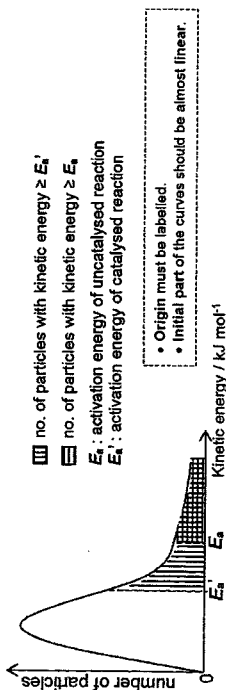
It is an overall pseudo first order reaction

$$\text{and } t_{1/2} = \frac{\ln 2}{k'} = \frac{\ln 2}{k [\text{H}^+]} \text{ or } t_{1/2} \propto \frac{1}{[\text{H}^+]}$$

Since  $[\text{H}^+]$  decreases by a factor of  $1/3$  from expt 1 to expt 2,  $t_{1/2}$  would increase by a factor of 3, from 22.5 min in expt 1 to 67.5 min in expt 2.

- (g) With the aid of a labelled Boltzmann distribution diagram, explain how the presence of a catalyst affects the rate of a chemical reaction. [3]





- A catalyst provides an alternative reaction pathway/mechanism of lower activation energy ( $E_a'$ ) than that of the uncatalysed reaction.
- There is a greater proportion/number of particles of reactant molecules with kinetic energy  $\geq E_a'$  (as indicated by the larger shaded area). Hence the frequency of effective collision between reactant particles increases and the rate of reaction increases.

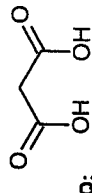
- 5 (a) Compound **P**,  $C_5H_{10}O_2$  is optically active. It reacts with 2,4-dinitrophenylhydrazine to give an orange precipitate. However, **P** does not react with Tollens' reagent.

Upon reaction with sodium metal, **P** produces effervescence that extinguishes a lighted splint with pop sound. **P** forms a yellow precipitate when treated with alkaline aqueous iodine, and upon acidification, **Q**,  $C_3H_4O_4$  is formed as the resulting compound.

**Q** reacts with  $Na_2CO_3(aq)$  to produce effervescence that forms white precipitate with limewater.

- (i) Suggest the structure of **Q**.

[1]



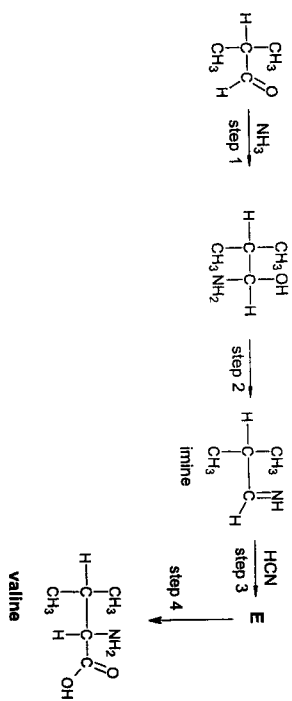
- (ii) Suggest a structure of **P** that is consistent with the information provided, giving your reasoning. [3]

<b>P</b> , $C_5H_{10}O_2$ is optically active	<b>P</b> has at least 1 chiral carbon
<b>P</b> undergoes condensation with 2,4-dinitrophenylhydrazine.	$\rightarrow$ <b>P</b> contains aldehyde or ketone
<b>P</b> does not undergo oxidation with Tollens' reagent	<b>P</b> is not aldehyde OR (thus, <b>P</b> is ketone)
<b>P</b> undergoes redox reaction with Na	$\rightarrow$ <b>P</b> contains alcohol group (BOD: accept -OH group)
<b>P</b> undergoes oxidation with alkaline aqueous iodine	<b>P</b> contains either $\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3 - \text{C} - \end{array}$ Or $\begin{array}{c} \text{OH} \\   \\ \text{R} - \text{C} - \text{CH}_3 \\   \\ \text{H} \end{array}$
<b>Q</b> undergoes acid base reaction with $Na_2CO_3(aq)$	<b>Q</b> contains carboxylic acid

*Link to reagent must be clearly stated*

**P** is  $CH_3COCH_2CH(OH)CH_3$

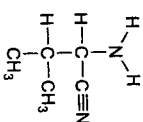
(b) The Strecker synthesis is a method to prepare  $\alpha$ -amino acids. The amino acid valine can be prepared from 2-methylpropanal via Strecker synthesis as shown below.



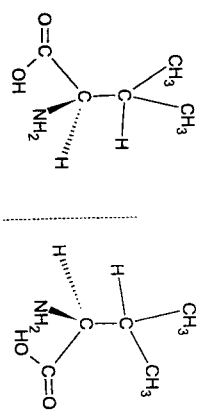
(i) Suggest the type of reaction occurring in step 2. [1]

Step 2: Elimination

(ii) Given that the reaction of the imine in step 3 with HCN is similar to the reaction of a carbonyl compound with HCN, suggest the structure of E. [1]

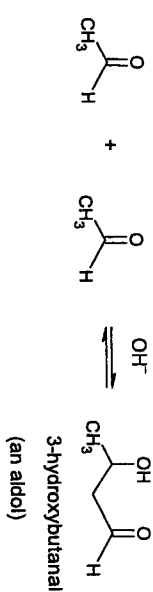


(iii) Valine can exist as a pair of stereoisomers. [2]  
Draw the 2 stereoisomers of valine.



(c) The aldol reaction is a useful method of making new carbon-carbon bonds in organic chemistry. It involves combining two molecules of the same aldehyde to form a product which contains both an aldehyde and alcohol functional groups. Thus, it is also known as the aldol reaction.

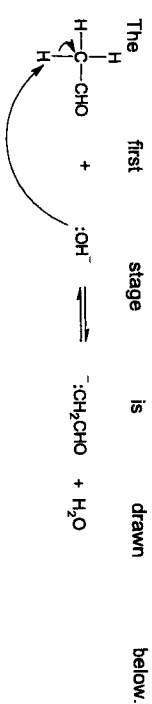
Ethanal undergoes base-catalysed aldol reaction as shown below.



The aldol synthesis involved the following reactions in two stages:

Stage 1:

An acid-base reaction takes place between the  $\text{OH}^-$  base and the acidic H atom bonded to alpha C of an ethanal molecule, forming a carbanion.

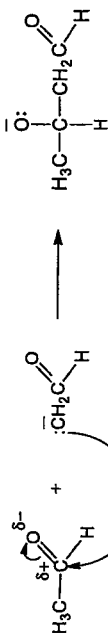


Stage 2:

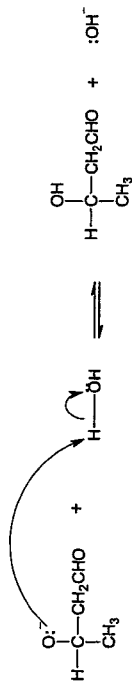
The carbanion formed in stage 1 attacks the delta positive carbon of another ethanal molecule, forming a tetrahedral intermediate which is negatively charged. The tetrahedral intermediate rapidly reacts with  $\text{H}_2\text{O}$  to form the aldol product and regenerates back the  $\text{OH}^-$  catalyst.

Name and outline the mechanism for stage 2.

## Nucleophilic addition



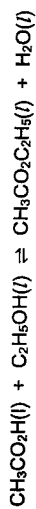
step 3



[3]

[Total:11]

6 (a) The value of the equilibrium constant is 4.0 for the reaction below:



(i) Write an expression for the equilibrium constant,  $K_c$ , of the reverse reaction, i.e. the hydrolysis of ethyl ethanoate, stating its numerical value. [2]

$$K_c = \frac{[\text{CH}_3\text{CO}_2\text{H}][\text{C}_2\text{H}_5\text{OH}]}{[\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5][\text{H}_2\text{O}]} = \frac{1}{4} = 0.25$$

(ii) In an experiment, 2 mol of ethyl ethanoate and 2 mol of water are mixed. Calculate the number of moles of each substance present when equilibrium is reached. [2]

	$\text{CH}_3\text{CO}_2\text{H}$	$+ \text{C}_2\text{H}_5\text{OH}$	$\rightleftharpoons$	$\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5$	$+ \text{H}_2\text{O}$
Initial amount/mol	0	0		2	2
Change in amount/mol	+x	+x		-x	-x
Equilibrium amount/mol	x	x		2-x	2-x
Equilibrium conc /mol dm <sup>-3</sup> .	x/v	x/v		(2-x)/v	(2-x)/v

$$K_c = \frac{(x/v)^2}{((2-x)/v)^2} = 0.25$$

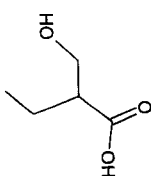
$$\therefore x = 0.667$$

Therefore, amount of acid = amount of alcohol = 0.667 mol  
Amount of water = amount of ester = 1.33 mol

- (b) The following shows a flow scheme involving a chloro-carboxylic acid to form compounds X, Y and Z.

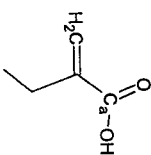


- (i) Suggest the structure of compound X. [1]



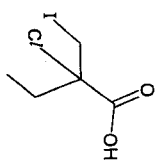
- (ii) Give the reagents and conditions for step 1. [1]  
 $NaOH(aq)$ , heat

- (iii) State the hybridisation of  $C_a$  in the structure of Y below. [1]

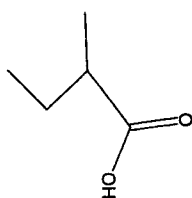


$sp^2$  hybridised

- (iv) Give the structure of compound Z. [1]



- (v) Give the structure of the product formed when compound Y is reacted with hydrogen with nickel, upon heating.



Only  $C=C$  is reduced by  $H_2$ , Ni, heat,  $-COOH$  is not reduced.

Aluminium objects that have had the aluminium oxide layer removed may then be oxidised.

- (c) (i) State why aluminium objects are anodised. [1]

To increase the thickness of a protective corrosion-resistant  $Al_2O_3$  layer on the surface of Al object.

- (ii) Complete Table 6.1 below to show the type of reaction occurring, with the relevant half-equations, during the anodising of an aluminium object. [2]

	Type of reaction	Half-equation(s)
Anode	Oxidation	$2Al(s) + 3H_2O(l) \rightarrow Al_2O_3(s) + 6H^+(aq) + 6e^-$
Cathode	Reduction	$2H^+(aq) + 2e^- \rightarrow H_2(g)$

Table 6.1

[Total: 12]

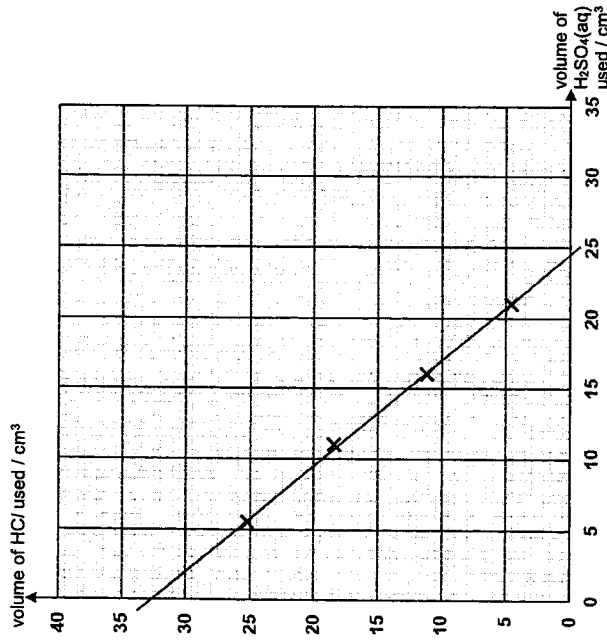
- 7 (a) Baryta water, barium hydroxide,  $Ba(OH)_2(aq)$  is a Bronsted base. Define what is meant by a Bronsted base.

21

Bronsted base is  $H^+$  or proton acceptor.

- (b)  $Ba(OH)_2(aq)$  neutralises both  $H_2SO_4$  and  $HCl$  acid. In an experiment, a student prepared 4 mixtures, each containing the same volume of  $25.0\text{ cm}^3$  of  $Ba(OH)_2$  solution, but with different volumes of sulfuric acid added.

In each mixture, neutralisation has not been completed, the solution remains alkaline and is neutralised by titration with  $0.150\text{ mol dm}^{-3}$   $HCl$  acid. A graph of volume of  $HCl$  on the y-axis was plotted against volume of  $H_2SO_4$  for each of the 4 mixtures. The graph is extrapolated until it touches both axes.



- (i) Read from the graph, and record the volume of  $HCl$  (Vol. $HCl$ ) (max), required to exactly neutralise  $25.0\text{ cm}^3$  of  $Ba(OH)_2$ .  
 $V_{HCl}(\text{max}) = 32.50\text{ cm}^3$  read correctly from the graph to  $\pm\frac{1}{2}$  small square

[1]

- (ii) Calculate the concentration of  $Ba(OH)_2$ .

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Using  $[HCl]$  and Vol.  $HCl$  (max):

$$n(HCl)_{\text{used}} = 0.150 \times \frac{32.50}{1000} = 0.004875\text{ mol}$$

$$\text{Since } 1\text{ Ba(OH)}_2 = 2HCl,$$

$$nBa(OH)_2 \text{ in } 25.0\text{ cm}^3 = \frac{1}{2} \times 0.004875 = 0.002438\text{ mol}$$

$$[Ba(OH)_2] = \frac{0.002438}{25.0} = 0.0975\text{ mol dm}^{-3}$$

[2]

- (iii) Explain in terms of the chemistry involved, why the direction of the slope of the graph is negative.

Negative gradient because the more sulfuric acid is added to  $25.0\text{ cm}^3$  of sodium carbonate, the less sodium carbonate remaining, the less hydrochloric acid is required for neutralisation (or words to that effect).

[1]

[Total:5]

End of paper

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Section A  
Answer all the questions in this section.

**JURONG PIONEER JUNIOR COLLEGE**  
**JC2 PRELIMINARY EXAMINATION 2022**

**CHEMISTRY**

**Higher 2**

**9729/03**

**19 September 2022**

**2 hours**

Paper 3 Free Response Questions

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

**READ THESE INSTRUCTIONS FIRST**

Write your name and class on all the work you hand in.  
Write in dark blue or black pen on both sides of the paper.  
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 end of this booklet. The question number must be clearly shown.

Answer all questions in Section A.  
Answer 1 question in Section B.

The use of an approved scientific calculator is expected, where appropriate.  
A Data Booklet is provided.

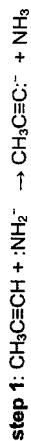
At the end of the examination, fasten all your work securely together.  
The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiner's Use	
1	21
2	20
3	19
4 or 5	20
<b>Penalty</b> (delete accordingly)	
Lack 3sf in final answer	-1 / NA
Missing/wrong units in final ans	-1 / NA
Bond linkages	-1 / NA
<b>Total</b>	<b>80</b>

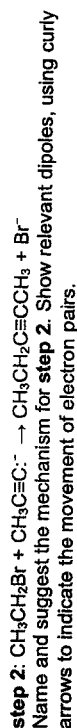
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- 1 (a) Bromoethane reacts with "acetylide" anion,  $\text{CH}_3\text{C}\equiv\text{C}^-$  to form new carbon-carbon bonds. This reaction takes place in two steps.

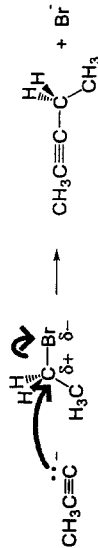
In step 1, an acid-base reaction occurs.  $\text{CH}_3\text{C}\equiv\text{C}^-$  is formed from the reaction of propyne and a strong base, sodium amide,  $\text{NaNH}_2$ .



In step 2, the intermediate anion reacts with bromoethane to form the product.



Type of mechanism: nucleophilic substitution



- (b) 4-bromopentanol can be used to synthesise Compound C by the three-step route shown in Fig. 1.1. [3]

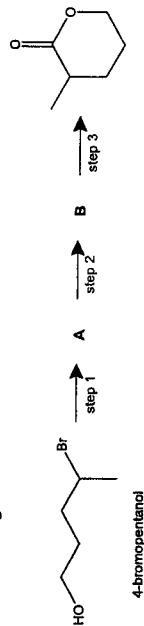
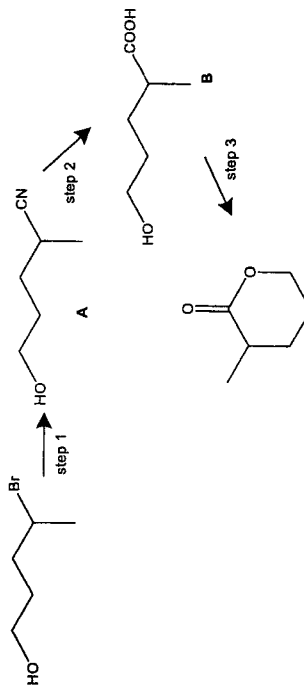


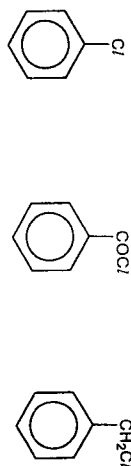
Fig. 1.1

State the structures for compounds A and B, and reagents and conditions for steps 1, 2 and 3 in this route. [4]



step 1 :  $\text{NaCN}$  (or  $\text{KCN}$ ), ethanol, heat ( $\checkmark$ )  
step 2 :  $\text{H}_2\text{SO}_4(\text{aq})$  (or  $\text{HC}(\text{aq})$ ), heat ( $\checkmark$ )

- step 3 : concentrated sulfuric acid, heat(✓)
- (c) Describe and explain the relative ease of hydrolysis of the following three [3]  
chlorine-containing compounds.



Ease of hydrolysis of  $C_6H_5Cl < C_6H_5CH_2Cl < C_6H_5COCl$

$C_6H_5Cl$  is inert or unreactive to hydrolysis as the p-p orbital overlap results in the delocalisation of lone pair of electrons on Cl atom of  $C_6H_5Cl$  into the π-electrons system of benzene ring, leading to the formation of partial double bond character of C-Cl bond and hence, strengthening C-Cl bond. Thus,  $C_6H_5Cl$  is resistant towards nucleophilic attack.

$C_6H_5COCl$  is most readily hydrolysed because the C of -COCl is highly electron-deficient or has the highest partial positive charge as it is bonded to two electronegative atoms, O and Cl. Hence,  $C_6H_5COCl$  is more susceptible towards nucleophilic attack than  $C_6H_5CH_2Cl$ .

- (d) Ethanol is formed when bromoethane is heated with NaOH(aq). The standard enthalpy change of combustion of ethanol is  $-1367 \text{ kJ mol}^{-1}$ . In an experiment, 0.23 g of ethanol was burned under a container, using a spirit lamp. An unknown mass of water was heated from 30 °C to its boiling point. The process was found to be 70 % efficient. Calculate the mass of water that could be brought to the boiling point by burning this amount of ethanol.

[Given specific heat capacity of water is  $4.18 \text{ J g}^{-1}\text{K}^{-1}$ ]

$$\text{Amount of ethanol burnt} = \frac{0.23}{46.0} = 5.00 \times 10^{-3} \text{ mol}$$

Heat evolved by combustion of ethanol =  $5.00 \times 10^{-3} \times 1367 = 6.835 \text{ kJ}$

Heat absorbed by x g of water  
=  $70/100 \times 5.00 \times 10^{-3} \times 1367$

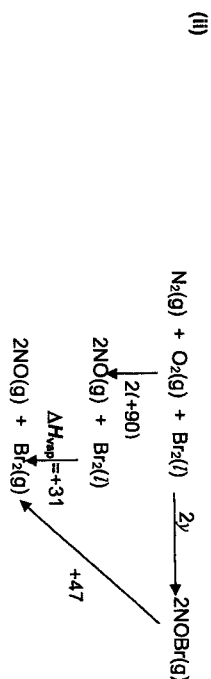
$$= 4.78 \text{ kJ} \quad \text{mass of water, } x = 4.78 \times 10^3 / (4.18 \times 70) = 16.3 \text{ g}$$

- (e) (i) Nitrosyl bromide, Br-N=O is an inorganic halogen-containing compound. It decomposes to NO and Br<sub>2</sub> as shown below. [2]
- $$2\text{NOBr(g)} \rightarrow 2\text{NO(g)} + \text{Br}_2\text{(g)}, \quad \Delta H_f$$
- Given that the bond energy of N-Br is  $+120 \text{ kJ mol}^{-1}$ , use appropriate bond energy data from the Data Booklet to calculate the enthalpy change of decomposition of nitrosyl bromide.
- (ii) Enthalpy changes of formation of NOBr(g) and NO(g) and the enthalpy change of vapourisation of Br<sub>2</sub>(l) are given below. [3]

$\Delta H_f$ (NOBr(g))	$y \text{ kJ mol}^{-1}$
$\Delta H_f$ (NO(g))	$+90 \text{ kJ mol}^{-1}$
$\Delta H_{\text{vap}}$ (Br <sub>2</sub> (l))	$+31 \text{ kJ mol}^{-1}$

With the aid of an energy cycle, use your answer in (i) and the given data to calculate the enthalpy change of formation of NOBr(g).

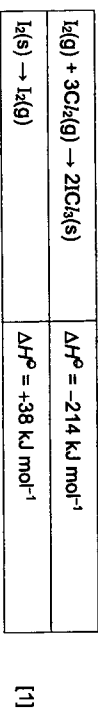
- (e) (i)  $2\text{O}=\text{N}-\text{Br}(\text{g}) \rightarrow 2\text{N}=\text{O}(\text{g}) + \text{Br}-\text{Br}(\text{g}), \quad \Delta H_f = 2 \times \Delta H_{\text{decomposition}}(\text{NOBr})$   
 $\Delta H_f = +2E(\text{N}=\text{O}) + 2E(\text{N}-\text{Br}) - 2E(\text{N}=\text{O}) - E(\text{Br}-\text{Br})$   
 $= 2E(\text{N}-\text{Br}) - E(\text{Br}-\text{Br})$   
 $= 2(+120) - (+193)$   
 $= +47 \text{ kJ mol}^{-1}$   
 $\Delta H_{\text{decomposition}}(\text{NOBr}) = \frac{1}{2} (+47) = +23.5 \text{ kJ mol}^{-1}$



By Hess' Law,  
 $2y = 2(+90) + (+31) - (+47)$   
 $y = \Delta H_f(\text{NOBr}) = +82.0 \text{ kJ mol}^{-1}$

- (i) State how the reactivity of the halogens as oxidising agents varies down the group, and relate this variation to relevant  $E^\circ$  values. [2]
- (ii) Describe a reaction that illustrates the relative oxidising abilities of two halogens of your choice. [1]

- (iii) Iodine and chlorine react together to form solid iodine trichloride, ICl<sub>3</sub>. Given the following enthalpy changes, calculate the standard enthalpy change of formation of ICl<sub>3</sub>(s).



- (i) Down the group,  $E^\circ$  ( $X_2/X^-$ ) becomes less positive, implying that the tendency of  $X_2$  to be reduced decreases. [2]

Hence, the oxidising power of  $X_2$  decreases down the group.

- (ii) Eg.  $\text{Br}_2 + 2\text{I}^- \rightarrow 2\text{Br}^- + \text{I}_2$

(Halogen displacement reaction where the stronger oxidising halogen can oxidise the halides of the weaker oxidising halogen. or  
 Eg.  $\text{Cl}_2 + 2\text{Fe}^{2+} \rightarrow 2\text{Cl}^- + 2\text{Fe}^{3+}$   
 Reaction of  $X_2$  with  $\text{Fe}^{2+}$ .)

- (iii) Let  $x = \Delta H_f^\circ(\text{ICl}_3(\text{s}))$

$\Delta H^\circ = \sum \Delta H_f^\circ(\text{products}) - \sum \Delta H_f^\circ(\text{reactants})$

$$-214 = 2x - 3(+38)$$

$$x = \Delta H_f^\circ(\text{ICl}_3(\text{s})) = -88.0 \text{ kJ mol}^{-1}$$

[Total: 21]



The presence of ligands causes the d orbitals to split into 2 different energy levels with a small energy gap.

Visible light is absorbed when an electron transits from a lower energy d orbital to a higher energy d orbital which is partially filled.

Hence, transition element complexes are coloured and the colour observed is the complement of the colours absorbed.

- (b) In a given electroplating experiment, a solution of  $\text{CrCl}_3(\text{aq})$  is electrolysed using a current of 3.50 A. Calculate the time, in min, required to produce 4.60 g of chromium by this electrolysis.

$$\text{Amount of Cr} = 4.60 / 52.0 = 0.0885 \text{ mol}$$



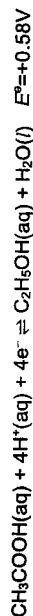
$$Q = n_e F = It$$

$$\text{Hence } Q = 3 \times 0.0885 \times 96500$$

$$= 25621 \text{ C}$$

$$\text{Time taken} = 25621 / 3.50 = 7320\text{s} = 122 \text{ min}$$

- (c) The half reaction involving conversion of ethanol to ethanoic acid is given below:

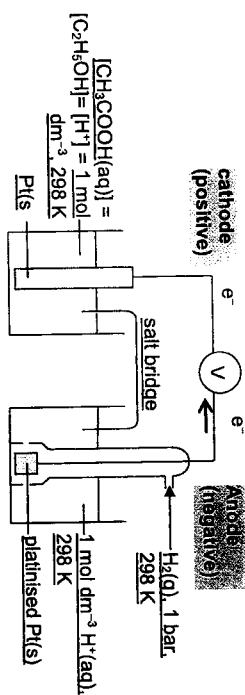


- (i) Using *Data Booklet* and the above information, draw a fully labelled diagram of the experimental set-up used to measure the standard electrode potential of the  $\text{CH}_3\text{COOH}/\text{C}_2\text{H}_5\text{OH}$  half-cell. Indicate the direction of movement of electrons in the external circuit when the cell is operating. [3]
- (ii) The amount of ethanol in a person's breath is measured with a breathalyzer.  $\text{C}_2\text{H}_5\text{OH}$  is oxidised to  $\text{CH}_3\text{COOH}$  and potassium dichromate,  $\text{K}_2\text{Cr}_2\text{O}_7$  is reduced to  $\text{Cr}^{3+}$  in acidic medium. The colour change observed is orange to green. Calculate  $E^{\ominus}_{\text{cell}}$  for the above reaction. [1]
- (iii) Using the  $E^{\ominus}_{\text{cell}}$  calculated in (c)(ii), calculate  $\Delta G^{\ominus}$ , with units, for the cell reaction. [1]
- (iv) State and explain how the e.m.f. of the cell would change if  $\text{HC}_2\text{O}_4(\text{aq})$  is added to the cathode half-cell in (c)(ii). [2]
- (c) (i)  $\text{CH}_3\text{COOH}(\text{aq}) + 4\text{H}^{+}(\text{aq}) + 4\text{e}^{-} \rightleftharpoons \text{C}_2\text{H}_5\text{OH}(\text{aq}) + \text{H}_2\text{O(l)} \quad E^{\ominus} = +0.58\text{V}$

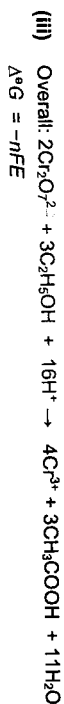
- 2 (a) Explain why transition element complexes are usually coloured.

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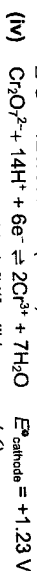


$$(ii) \quad E^{\circ}_{\text{cell}} = (+1.33) - (+0.58) = +0.75 \text{ V} \quad [1\text{m}]$$



$$n = 12$$

$$\Delta^{\circ}G = -12 \times 96500 \times (+0.65) = -753\,000 \text{ J mol}^{-1} \approx -753 \text{ kJ mol}^{-1}$$



- When  $\text{H}^+$  is added,  $[\text{H}^+]$  will increase ( $\checkmark$ ).
- By Le Chatelier's Principle, the equilibrium position will shift to the right ( $\checkmark$ ), so as to remove some  $[\text{H}^+]$  to re-establish equilibrium.
- Cathode becomes more positive ( $\checkmark$ ).
- Since  $E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$ , thus  $E_{\text{cell}}$  will become more positive ( $\checkmark$ ).

(d) A solution of  $\text{XeF}_2$  is a strong oxidising agent. A solution containing  $25.0 \text{ g dm}^{-3}$  of  $\text{XeF}_2$  is reacted with another solution containing  $0.150 \text{ mol dm}^{-3}$  of a  $\text{Cr(III)}$  salt. In an experiment,  $15.20 \text{ cm}^3$  of the  $\text{XeF}_2$  solution is required to completely react with  $10.0 \text{ cm}^3$  of the  $\text{Cr(III)}$  solution.  $\text{XeF}_2$  is reduced to  $\text{Xe}$  in the reaction. Determine the final oxidation state of Cr after the reaction.

$$\text{Amount of } \text{XeF}_2 = \frac{15.2}{1000} \times \frac{25}{169} = 0.002249 \text{ mol}$$

$\text{XeF}_2$  is reduced to  $\text{Xe}$  and oxidation state of Xe changes from +2 to 0.

Amount of electrons transferred =  $2 \times 0.002249 = 0.004497 \text{ mol}$

$$\text{Amount of Cr(III)} = \frac{10}{1000} \times 0.150 = 0.00150 \text{ mol}$$

$$\text{Amount of electrons lost from 1 mol of Cr(III)} = \frac{0.004497}{0.00150} = 3 \text{ mol}$$

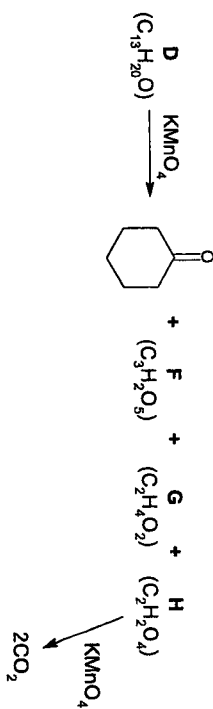
$\therefore$  oxidation state of Cr increases by 3 units

$\therefore$  oxidation state of Cr is +6 after reaction.

(e) Hot acidified  $\text{KMnO}_4$  oxidises several classes of organic compounds to ketones, carboxylic acids or carbon dioxide. By this means, the structures of compounds

8

can be determined. Some compounds are easily oxidized while others require longer heating. The following scheme shows the reaction with hot acidified  $\text{KMnO}_4$  of compound D and its oxidation products.



- Compound D effervesces with sodium metal. D also reacts with hot acidified potassium dichromate(VI) to give compound  $\text{C}_{13}\text{H}_{18}\text{O}$ .
- Compound F gives an orange precipitate with 2,4-dinitrophenylhydrazine.
- Both compounds F and H dissolve in  $\text{NaOH(aq)}$ .

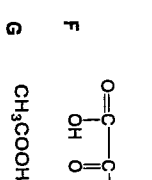
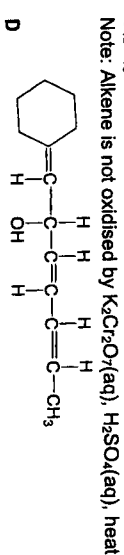
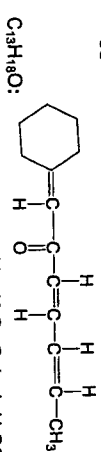
(i) Explain these observations.

[2]

D undergoes redox reaction with Na and oxidation with warm acidified potassium dichromate(VI). D contains secondary alcohol.  
 F undergoes condensation with 2,4-DNPH to give orange ppt.  
 F contains ketone.  
 F and H undergo acid-base reaction with  $\text{NaOH(aq)}$ . F and H contain carboxylic acid.

(ii) Suggest the structures of compounds D, F and G.

[3]



[Total: 20]

3 Nitrogen is the most abundant element in our planet's atmosphere. The various nitrogen-containing organic compounds play an important role in our lives, as they serve as the building materials for amino acids, proteins and even in our DNA.

- (a) Table 3.1 below shows some aromatic organic nitrogen compounds that have important uses in both chemical and pharmaceutical industries.

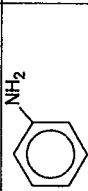
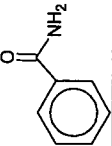
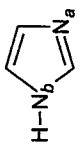
Name of compound	Structure	$K_b$
phenylamine		$3.98 \times 10^{-10}$
benzamide		$1.00 \times 10^{-14}$
imidazole		-

Table 3.1

- (i) Using the data provided in Table 3.1, suggest an explanation for the difference in the relative basicities of phenylamine and benzamide. [2]
- (ii) Based on the structure of a molecule of imidazole, suggest an explanation why nitrogen  $N_a$  would have a higher  $K_b$  value than  $N_b$ . [1]
- (i) Phenylamine is a stronger base than benzamide because it has higher  $K_b$ . The lone pair on nitrogen in benzamide is delocalised completely over C=O through p-p orbital and due to the electronegative oxygen atom hence it is totally not available ( $\checkmark$ ) to be donated to a proton/ $H^+$ .
- (ii)  $N_b$  has higher  $K_b$  value because:  
The lone pair on  $N_a$  atom is in the  $sp^2$  hybrid orbital which is not delocalised OR not in the same plane as the  $\pi$  electron cloud / p-orbitals of the carbon atoms in the molecule. As such, the lone pair is not delocalised and is more available to be donated to a proton/ $H^+$ .  
OR  
p-p overlap between the orbitals of  $N_b$  and the  $\pi$  electron cloud / p-orbitals of the carbon atoms results in the delocalisation of the lone pair on  $N_b$ , reduces its availability to donate to acid/ $H^+$ .

- (b) Amino acids are sometimes referred to as the "building blocks of life". In human beings, there are 20 amino acids that are used to manufacture the proteins required by the body.

One such essential  $\alpha$ -amino acid is histidine, that is required to maintain good mental and physical states of the human body. Food sources such as fish, poultry and nuts are good sources of histidine.

- (i) In terms of bonding, explain why histidine has a much higher melting point than 4-nitrophenylamine, despite having similar  $M_r$  in Table 3.2 [2]

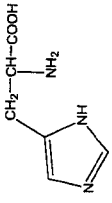

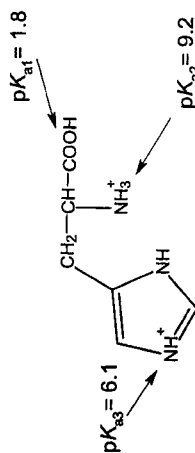
compound	Structure	melting point/ $^{\circ}C$
histidine		285
4-nitrophenylamine		146

Table 3.2

- (ii) The diagram below shows the protonated form of histidine, which can be represented by  $H_3A$ , and the respective acid dissociation constants for its three acidic groups. [2]



Predict the structure of the major species that would be present when histidine is placed into buffer solutions with the following pH values:

- pH = 7
- pH = 12

(iii) A chemist invented two new enzymes:

- "histidinase-C" that can hydrolyse at the C-terminal of the histidine (His) amino acid residue;
- "lysinase-N" that can hydrolyse at the N-terminal of the lysine (Lys) amino acid residue;

A polypeptide chain from a liver protein consists of a total of 11 amino acids. This polypeptide was subjected to partial hydrolysis by these two enzymes separately, and the following fragments were obtained.

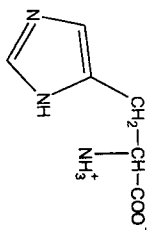
Amino acid fragments obtained with histidinase-C:	Amino acid fragments obtained with lysinase-N:
Ala-Lys-Ser-His	Lys-Cys-His
Ser-Lys-His	Lys-Ser-His-Ser
Ser-Lys-Cys-His	Ser
	Lys-His-Ala

Table 3.3

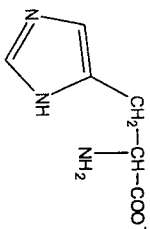
Using the above information, deduce the correct sequence of the 11 amino acid residues in the polypeptide chain. [2]

(i) Histidine exists as zwitterions in the solid state, which are held by stronger electrostatic forces of attraction / ionic bonds, while molecules of 4-nitrophenylamine are held by weaker hydrogen bonds. More energy is required to overcome the stronger ionic bonds between the zwitterions of histidine.

(ii) • pH = 7



• pH = 12



For  
Examiner's  
Use

(iii) Working:

Find the "head" of the polypeptide: Ser appears on both columns in the table.  
Find the "tail" of the polypeptide: His appears on both columns in the table.  
Hence, Ser-2-3-4-5-6-7-8-9-10-His

Using histidinase-C:  
Ser-Lys-His

Ala-Lys-Ser-His  
Ser-Lys-Cys-His

Using lysinase-C:

Ser  
Lys-His-Ala  
Lys-Ser-His-Ser  
Lys-Cys-His

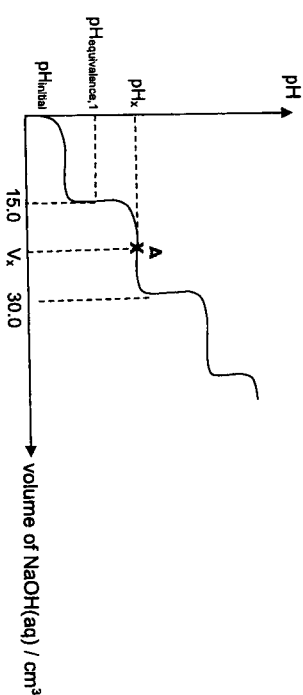
Ser-Lys-His-Ala-Lys-Ser-His-Ser-Lys-Cys-His

(e) Information from 2(f)(ii) would be useful for this part of the question.

Intrigued by his newly found knowledge on amino acids after completing his SLS lesson on Organic Nitrogen Compounds, a H2 Chemistry student from Jurong Pioneer JC decided to seek help from his chemistry tutor to conduct a more in-depth analysis.

He prepared a fresh sample containing 15.0 cm<sup>3</sup> of 0.100 mol dm<sup>-3</sup> fully protonated histidine and titrated it against 0.100 mol dm<sup>-3</sup> NaOH(aq).

The following graph was obtained:



(i) Calculate the initial pH of the 0.100 mol dm<sup>-3</sup> fully protonated histidine, pH<sub>initial</sub>. (Ignore the effect of pK<sub>a2</sub> and pK<sub>a3</sub> on the pH). [1]

(ii) An amphiprotic species is one that is able to donate and accept a proton. The pH of a solution containing an amphiprotic species is given by the following expression.

$$\text{pH} = \frac{1}{2}(\text{pK}_1 + \text{pK}_2)$$

In the titration above, an amphiprotic species is formed at the first equivalence point, when 15.0 cm<sup>3</sup> of NaOH(aq) was added to the sample of protonated histidine.

Calculate the pH of the amphiprotic species formed at the first equivalence point and draw its structure. [2]

- (iii) Using your answer to 3(c)(ii) and information from Table 3.4 given below, choose the best indicator to detect the 1<sup>st</sup> end-point of the titration. Briefly explain your answer. [1]

indicator	thymol blue	methyl yellow	methyl red
$pK_a$	1.7	3.1	5.2

Table 3.4

- (iv) Point A on the titration graph represents a solution of maximum buffering capacity that is equally effective in removing small amounts of H<sup>+</sup> and OH<sup>-</sup> ions added. [2]

State the value of  $V_x$ , the volume of NaOH(aq) added and the value of pH<sub>x</sub>, at point A. [1]

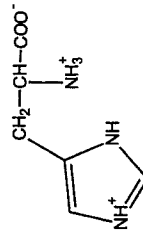
(i)  $pK_{a1} = 1.8$   
 $K_a = 10^{-1.8}$

$K_a = 10^{-1.8} = x^2 / (0.100 - x) \approx x^2 / 0.100$

Solving,  $x = [H^+] = 0.03981 \text{ mol dm}^{-3}$

$pH_{\text{initial}} = -\lg(0.03981) = 1.40$

(ii)  $pH \approx (pK_{a1} + pK_{a2}) / 2 = (1.8 + 6.1) / 2 = 3.95$  or 4.0



- (iii) The best indicator would be methyl yellow.

Working range of indicators:  $pK_a \pm 1$

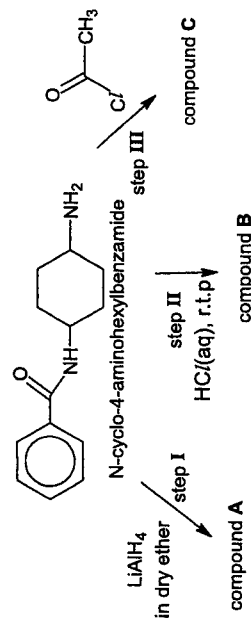
Hence, the working range for methyl orange is between 2.1 to 4.1, which coincides with the pH at the first equivalence point.

- (iv) Volume at 1<sup>st</sup> equivalence point = 15.0 cm<sup>3</sup>

Volume at 2<sup>nd</sup> equivalence point = 30.0 cm<sup>3</sup>

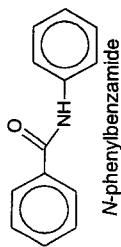
$V_x = (15.0 + 30.0) / 2 = 22.50 \text{ cm}^3$

- (d) The diagram below shows some reactions involving N-cyclo-4-amino hexylbenzamide.

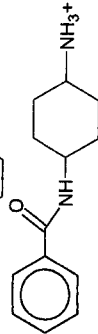
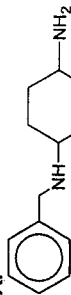


- (i) Give the structures of compounds A, B and C. [3]

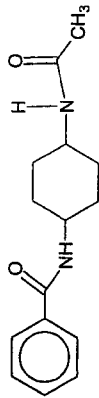
- (ii) Suggest a simple chemical test that could be used to distinguish between N-cyclohexylbenzamide and N-phenylbenzamide. [2]



- (i)



- B:



- C:

[Total: 20]

## Answer one question from this section.

- 4 (a) Phosphoryl chloride is a colourless liquid with the formula
- $\text{POCl}_3$
- .

Table 4.1 shows the electronegativity values of the atoms in  $\text{POCl}_3$ .

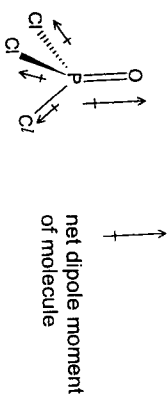
atom	electronegativity / pauling units
phosphorus	2.2
chlorine	3.0
oxygen	3.5

Table 4.1

- (i)  $\text{POCl}_3$  hydrolyses in moist air releasing phosphoric acid and fumes of hydrogen chloride.  
Write an equation to show the reaction of  $\text{POCl}_3$  with water. [1]
- (ii) Draw the shape of  $\text{POCl}_3$ .  
Indicate clearly the polarity of each bond it contains, and its overall net polarity. [2]
- (iii) Predict all possible intermolecular forces which could exist between  $\text{POCl}_3$  molecules.  
Explain how these forces arise. [2]



(iii)



There are instantaneous dipole-induced dipole attractions (id-id) and permanent dipole-permanent dipole attractions (pd-pd) between phosgene molecules.

id-id attraction arises due to the constant motion of electrons, a molecule develops an instantaneous dipole within itself when its electrons are distributed unevenly instantaneously. This instantaneous dipole then induces a temporary dipole on another molecule close to it, giving rise to id-id

pd-pd attraction arises due to the electrostatic attraction between polar molecules which have permanent dipoles (or has net dipole moment within each molecule). [2]

For Examiner's Use

- (b) The boiling points of phosphorus trichloride,
- $\text{PCl}_3$
- and nitrogen trichloride,
- $\text{NCl}_3$
- are given below in Table 4.2.

At 373 K, both  $\text{PCl}_3$  and  $\text{NCl}_3$  exist as gases. Predict with reasons, which of the two gases will deviate more from ideal gas behavior.

compound	Formula	$M_r$	boiling point/ K
phosphorus trichloride	$\text{PCl}_3$	137.5	350
nitrogen trichloride	$\text{NCl}_3$	120.5	344

Table 4.2

Both phosphorus trichloride and nitrogen trichloride are simple molecular structures with net dipole moment.

1<sup>st</sup> mark:  
However, phosphorus trichloride has a larger electron cloud/larger number of electrons which results in stronger intermolecular instantaneous dipole-induced dipole interactions.

OR  
phosphorus trichloride has stronger pd-pd attractions between its molecules as P-Cl bond is more polar than N-Cl bond (difference in electronegativity between P and Cl is larger than that between N and Cl).

Phosphorus trichloride will show a greater relative deviation from ideality than nitrogen trichloride.

(c)

X, Y and Z are Period 3 elements.  
Element X forms a white oxide that is insoluble in water.  
Element Y forms an oxide which forms a white precipitate when shaken with excess aqueous  $\text{Ba}(\text{NO}_3)_2$  solution.  
The oxide of element X dissolves when a solution of oxide of element Y is added to it.  
Element Z forms an oxide that dissolves readily in water and the resulting solution turns moist red litmus blue.  
The oxide of element X dissolves when a solution of oxide of element Z is added to it.  
Identify the elements Y, Z and the oxide of X in the above reactions.

Write equations to account for the dissolution of the oxide of X in the two reactions above. [4]

- Element Y: Sulfur

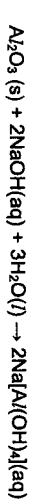
- Element Z: Sodium

- Oxide of Element X: Aluminium oxide or  $\text{Al}_2\text{O}_3$

- white ppt correspond to  $\text{BaSO}_4$



White ppt



State symbols not required

- (d) Dinitrogen tetroxide,  $N_2O_4$ , is a useful reagent in chemical synthesis. It forms an equilibrium mixture with nitrogen dioxide according to the equation below.



- (i) At 318 K and 1 atm, the degree of dissociation of  $N_2O_4$  is 37.8%.

Calculate the equilibrium constant,  $K_p$ . [2]

- (ii) The degree of dissociation is found to be 28% when total pressure is increased.

Comment on why is there a difference in the degree of dissociation compared to (i)(i).

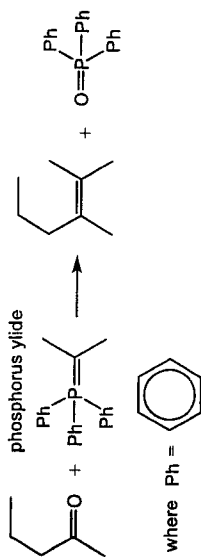
[1]

	$N_2O_4(g)$	$\rightleftharpoons$	$2NO_2(g)$
Initial amount/mol	1		0
Change in amount/mol	-0.378		$2 \times 0.378$
Equilibrium amount/mol	0.622		0.756
Equilibrium pressure/atm	$\frac{0.622}{1.378} \times 1 = 0.451$		$\frac{0.756}{1.378} \times 1 = 0.549$

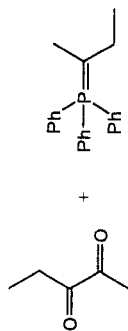
$$K_p = \frac{(0.549 \text{ atm})^2}{0.451 \text{ atm}} = \underline{0.668 \text{ atm}}$$

- (ii) When pressure increase, the position of equilibrium shifts to the left to reduce the total no. of moles of gas in the system to decrease pressure which results in smaller degree of dissociation.

- (e) A phosphorous ylide is used in the Wittig reaction which converts a carbonyl compound to an alkene. An example of a Wittig reaction is shown below.

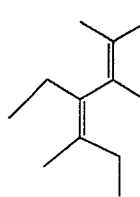
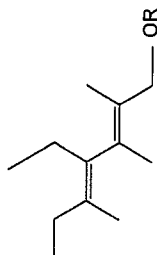


- (i) Suggest the structure formed when 1 mole of the following carbonyl compound reacts with 2 moles of the phosphorous ylide via the Wittig reaction.



Hence, suggest the total number of stereoisomers that can be formed. [2]

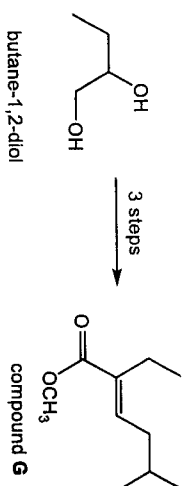
The product formed:



Since the product has two C=C double bonds, total number of isomers formed  $2^2 = 4$ .

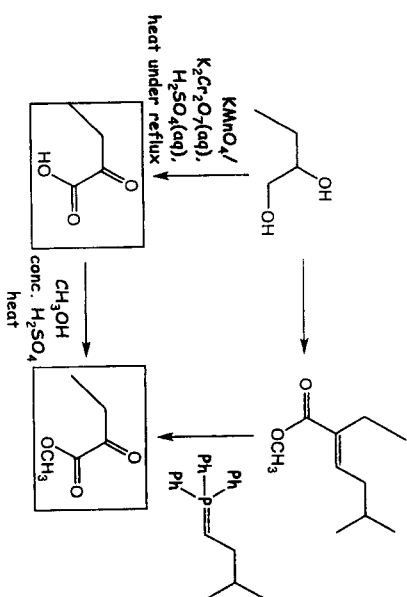
19

- (ii) Using the Wittig reaction as one of the steps in a three-step synthesis route, suggest suitable reagents and conditions to synthesise compound **G** from butane-1,2-diol.



In your answer, include the structure of the intermediates formed.  
In your answer, include the structure of the intermediates formed.

[4]



20

- 5 (a) The brown compound  $[\text{Fe}(\text{en})_2\text{Cl}_2]\text{Cl}$  contains 19.8% Fe, 19.8% of N and 37.7% of Cl.  
en is used to represent ethane-1,2-diamine  $\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{NH}_2$ .

(i) ethane-1,2-diamine, en, is a bidentate ligand. [1]  
What is meant by the term a bidentate ligand?

(ii) Calculate the values of p and q and hence determine the formula of the brown compound. [2]

(iii) On treatment with water over a long period of time, it is converted to an orange complex, which has octahedral geometry.

Treatment of 0.01 mol of the product with «excess aqueous  $\text{AgNO}_3$  results in the precipitation of 4.31 g of  $\text{AgCl}$ .  
Give the formula of the orange complex ion and suggest a balanced equation for its formation. [2]

(i) A bidentate ligand is an anion or neutral molecule that provides 2 lone pairs to form 2 dative bonds with central atom or ion. [1]

(ii) Let mass of the complex be 100 g.

	Fe	N	Cl
Mass / g	19.8	19.8	37.7
Amt / mol	0.3548	1.414	1.062
Relative amount/ mol	1	3.986	2.993
Simplest mole ratio	1	4	3

Since 1 en contains 2 N atoms, in 1 mole of brown compound, there are 4/2 = 2 en ligands

$$p = 2$$

Or in 1 mole of brown compound, there are 3  $\text{Cl}^-$  in total

$$q + 1 = 3$$

$$q = 2$$

$[\text{Fe}(\text{en})_2\text{Cl}_2]\text{Cl}$  is the brown compound. [2]

(iii) Amount of  $\text{AgCl}$  precipitated =  $4.31 / (108 + 35.5) = 0.0300$  mol  
1 mol of the brown-orange complex = 3 mol of free chloride ions (not dative bonded as ligands).

Formula of the brown-orange complex is  $[\text{Fe}(\text{en})_2(\text{H}_2\text{O})_2]^{3+}$ .

The treatment with water results in ligand exchange



[2]



(b) Brass is used to make window frames and other architectural models. Brass is a mixture of copper and zinc.

The process of etching brass involves dissolving the unprotected brass in aqueous iron (III) chloride until all the unwanted brass has been removed.

By using the relevant  $E^\ominus$  values, explain if one or both components of the brass are soluble in aqueous iron (III) chloride.

$$\text{Fe}^{3+}(\text{aq}) + \text{e}^- \rightleftharpoons \text{Fe}^{2+}(\text{aq}) \quad E^\ominus (\text{Fe}^{3+}/\text{Fe}^{2+}) = +0.77 \text{ V}$$

$$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Cu}(\text{s}) \quad E^\ominus (\text{Cu}^{2+}/\text{Cu}) = +0.34 \text{ V}$$

$$\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Zn}(\text{s}) \quad E^\ominus (\text{Zn}^{2+}/\text{Zn}) = -0.76 \text{ V}$$

For the reaction between Cu and  $\text{Fe}^{3+}$ ,  $E^\ominus_{\text{cell}} = +0.77 - 0.34 = +0.43 \text{ V} > 0$

For the reaction between Zn and  $\text{Fe}^{3+}$ ,  $E^\ominus_{\text{cell}} = +0.77 - (-0.76) = +1.53 \text{ V} > 0$

Both are spontaneous, as  $E^\ominus_{\text{cell}} > 0$ , thus  $\text{Fe}^{3+}$  oxidises Cu to  $\text{Cu}^{2+}(\text{aq})$ ,  $\text{Fe}^{3+}$  oxidises Zn to  $\text{Zn}^{2+}(\text{aq})$ , both metals dissolve forming metal ions.

[2]

(c) (i) Solid aluminium chloride,  $\text{AlCl}_3$ , may be produced by passing a stream of  $\text{Cl}_2$  gas over heated Al metal in a long hard-glass tube.

The pH of 1.0 mol  $\text{dm}^{-3}$  solution of  $\text{AlCl}_3$  in water is 3. Write equations where appropriate to account for the reactions of  $\text{AlCl}_3$  in water.

[1]

(ii) The pH values of a 1.0 mol  $\text{dm}^{-3}$  solution of  $\text{FeCl}_3$  in water is given as y.

compound	pH of 1.0 mol $\text{dm}^{-3}$ solution
$\text{FeCl}_3$	y

Table 5.1

With reference to the Data Booklet, quote relevant values and suggest whether the value of y is larger or smaller than 3. Explain your answer.

[2]

(i)  $\text{AlCl}_3$  dissolves to give  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$  which undergoes partial hydrolysis readily to form an acidic solution of pH 3.

Dissolving:  $\text{AlCl}_3(\text{s}) + 6\text{H}_2\text{O}(\text{l}) \rightarrow [\text{Al}(\text{H}_2\text{O})_6]^{3+}(\text{aq}) + 3\text{Cl}^-(\text{aq})$

Marker writes BOD for  $\text{Al}^{3+}(\text{aq})$  for dissolving.

Hydrolysis:  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}(\text{aq}) \rightleftharpoons [\text{Al}(\text{H}_2\text{O})_5\text{OH}]^{2+}(\text{aq}) + \text{H}^+(\text{aq})$

[1]

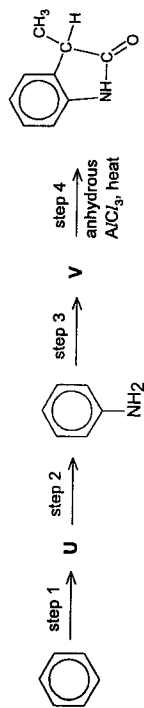
(ii)

Ion	Size or radius of cation
$\text{Fe}^{3+}$	0.055
$\text{Al}^{3+}$	0.050

y > 3 since  $\text{Fe}^{3+}$  has lower charge density/ $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$  has a lower polarising power and lower degree/ extent of hydrolysis in aq solution, resulting in higher pH.

[2]

(d) Compound W can be formed from benzene in the following reaction scheme.



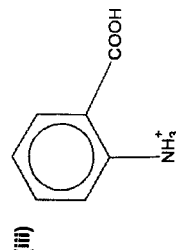
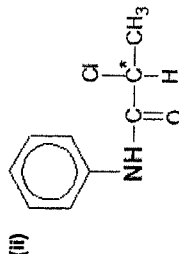
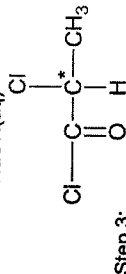
W

(i) Suggest the reagents and conditions for steps 1, 2 and 3.

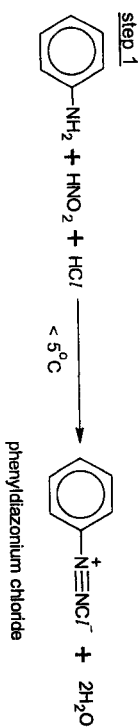
(ii) Draw the structure of compound V in the space provided below. [1]

(iii) Draw the organic product obtained when compound W is treated with hot, acidified potassium manganate(VII). [1]

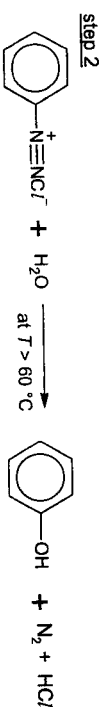
(i) Step 1: Concentrated  $\text{H}_2\text{SO}_4$ , concentrated  $\text{HNO}_3$ ,  $50^\circ\text{C}/55^\circ\text{C}$   
 Step 2: 1. Sn, concentrated  $\text{HCl}$ , heat, followed by  
 2.  $\text{NaOH}(\text{aq})$



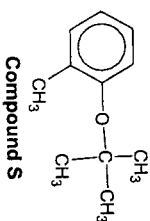
- (e) The following equations illustrate the formation of phenol from phenylamine, in two steps:
- In step 1, phenylamine reacts with cold nitrous acid,  $\text{HNO}_2$ , and hydrochloric acid,  $\text{HCl}$ , to form phenyldiazonium chloride.



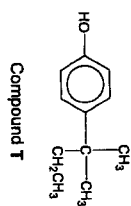
In step 2, phenyldiazonium chloride can react with water upon heating to give phenol:



- (i) By making use of the reactions above, propose a two-step synthetic pathway for the conversion of 2-methylphenylamine to compound **S** below.



- (ii) Compound **T**, an isomer of Compound **S**, reacted with  $\text{Br}_2$  in the presence of uv light to produce 3 different mono-brominated products, **X**, **Y** and **Z**.

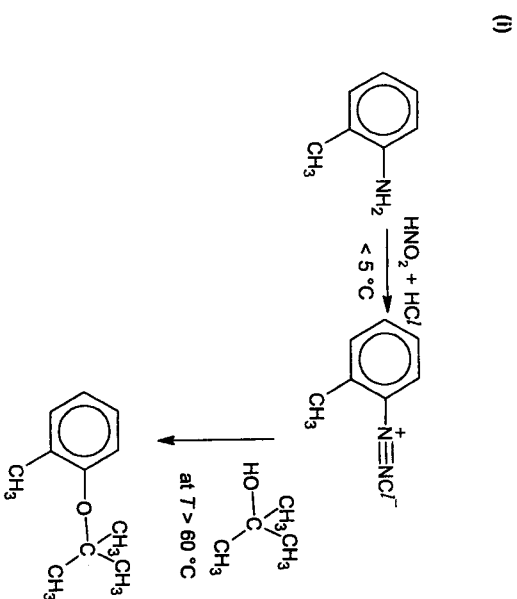


During free-radical substitution of alkanes, different types of hydrogen atoms are replaced by bromine atoms at different rates as shown in Table 5.2.

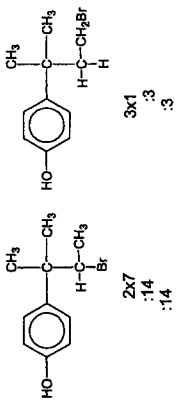
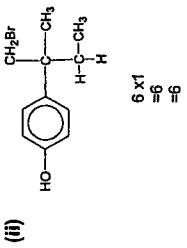
Table 5.2

Type of hydrogen atom	Reaction	Relative rate
Primary	$\text{RCH}_3 \rightarrow \text{RCH}_2\text{Br}$	1
Secondary	$\text{R}_2\text{CH}_2 \rightarrow \text{R}_2\text{CHBr}$	7
Tertiary	$\text{R}_3\text{CH} \rightarrow \text{R}_3\text{CBr}$	21

Using the information in Table 4.2 and considering the number and type of hydrogen atoms within the molecule **T**, draw the structures of the three monobrominated structural isomers formed and predict their relative ratio.



25



$3 \times 1 = 3$   
 $= 3$

[3]

[Total:20]



**JURONG PIONEER JUNIOR COLLEGE**  
**JC2 PRELIMINARY EXAMINATION 2022**

**CHEMISTRY**

**Higher 2**

Paper 4 Practical

**9729/04**

**16 August 2022**

**2 hours 30 minutes**

**Candidates answer on the Question paper.**

**Additional Materials:** As listed in the Confidential Instructions

**READ THESE INSTRUCTIONS FIRST**

Write your name, class and exam index number on all the work you hand in.  
 Give details of the practical shift and laboratory where appropriate, in the boxes provided.  
 Write in dark blue or black pen.  
 You may use a HB pencil for any diagrams, 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.  
 You may lose marks if you do not show your working or if you do not use appropriate units.  
 Qualitative Analysis Notes are printed on pages 18 and 19.

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.

Shift
Laboratory

For Examiner's Use	
1	
2	
3	
4	
Total	

This document consists of 19 printed pages.

Answer all the questions in the spaces provided.

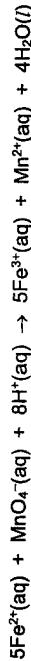
**1 Determination of the percentage by mass of iron in a sample of iron wire**

Iron wire contains impurities. You will investigate the percentage by mass of iron in a sample of iron wire.

A sample of iron wire is reacted with an excess of sulfuric acid to produce a solution of iron(II) sulfate.



You will titrate the solution of iron(II) sulfate with potassium manganate(VII) of known concentration to determine the amount of iron(II) ions present and hence the percentage by mass of iron in the wire. You may assume the impurities do not form any products that react with potassium manganate(VII).



**FA 1** is a solution of FeSO<sub>4</sub> prepared by reacting 3.03 g of iron wire with sulfuric acid to make 500 cm<sup>3</sup> of solution.

**FA 2** is 3.16 g dm<sup>-3</sup> potassium manganate(VII), KMnO<sub>4</sub>.

**FA 3** is 1.00 mol dm<sup>-3</sup> sulfuric acid, H<sub>2</sub>SO<sub>4</sub>.

**(a) Method**

1. Fill the burette labelled "FA 2" with FA 2.
2. Pipette 25.0 cm<sup>3</sup> of FA 1 into a conical flask.
3. Use the 50 cm<sup>3</sup> measuring cylinder to transfer 25 cm<sup>3</sup> of FA 3 to the same conical flask.
4. Titrate this mixture with FA 2 until a permanent pale pink colour is obtained.
5. Record your titration results, to an appropriate level of precision, in the space provided below.
6. Repeat points 2 to 5 until consistent results are obtained.

**Results**

Final burette reading / cm <sup>3</sup>	25.30	25.30
Initial burette reading / cm <sup>3</sup>	0.00	10.00
Volume of FA 2 used / cm <sup>3</sup>	25.30	25.30

[1] Gives a proper table with correct headings (burette must be stated) and units. Do not award if any final and initial burette readings are inverted.

[1] Records all burette readings to the nearest 0.05 cm<sup>3</sup> (2 d.p.) + computes all titres correctly. Do not award if 50 is used as initial burette reading or burette reading is > 50.

[1] Obtains two uncorrected titres within 0.10 cm<sup>3</sup> + places tick (✓) or shows selected titres in exact form in the average working in (b). [3]

- (b) From your titrations, obtain a suitable volume of FA 2,  $V_{FA 2}$ , to be used in your calculations. Show clearly how you obtained this volume.

$$V_{FA 2} = \frac{25.30 + 25.30}{2} = \underline{25.30 \text{ cm}^3}$$

[1] Obtains average correctly to 2.d.p. from any expts with uncorrected end-point titre values within 0.20 cm<sup>3</sup>.

Do not award this mark if the titres used are not identified either in the table (by ticks) or in the calculation.

Accuracy:

Round any burette readings to the nearest 0.05 cm<sup>3</sup>.

Check and correct subtractions in the titre table.

Select the "best" titre using the hierarchy:

two identical; titres within 0.05 cm<sup>3</sup>, titres within 0.10 cm<sup>3</sup> etc.

Supervisor's average titre = 25.20 cm<sup>3</sup>

[2] within 0.2

[1] within 0.4

$$V_{FA 2} = \underline{25.30} \quad [3]$$

- (c) (i) Calculate the amount of  $\text{KMnO}_4$  present in the volume of FA 2,  $V_{FA 2}$ , calculated in (b).

[A: O, 16.0; K, 39.1; Mn, 54.9]

$$n(\text{KMnO}_4) = \frac{3.16}{158.0} \times \frac{V_{FA 2}}{1000} \quad [1]$$

$$= \frac{3.16}{158.0} \times \frac{25.30}{1000} = 5.06 \times 10^{-4} \text{ mol}$$

amount of  $\text{MnO}_4^-$  present =  $5.06 \times 10^{-4}$  [1]

- (ii) Calculate the amount of  $\text{Fe}^{2+}$  ions in 25.0 cm<sup>3</sup> of FA 1.

$n(\text{Fe}^{2+})$  in 25.0 cm<sup>3</sup> of FA 1

$$= 5 \times \text{ans. (c)(i)} \quad [1]$$

$$= 5 \times 5.06 \times 10^{-4} = 2.53 \times 10^{-3}$$

amount of  $\text{Fe}^{2+}$  ions =  $2.53 \times 10^{-3}$  [1]

$\text{KMnO}_4 : \text{FeSO}_4$

1 : 5

- (iii) Calculate the percentage by mass of iron in the sample of iron wire.

[A: Fe, 55.8]

$n(\text{Fe}^{2+})$  in 500 cm<sup>3</sup> of FA 1

$$= \text{ans. (c)(ii)} \times \frac{500}{25.0} \quad [1]$$

$$= 2.53 \times 10^{-3} \times \frac{500}{25.0} = 0.0506 \text{ mol}$$

$$\% \text{ mass of Fe} = \frac{0.0506 \times 55.8}{3.03} \times 100 = 93.2 \% \quad [1] \text{ ecf}$$

percentage by mass of iron in the wire = 93.2 [3]

[1] Shows appropriate workings for (c)(i)-(iii) + gives [ ] for (b) and (c)(i)-(iii) + gives all final ans to 3sf in (c)(i)-(iii)

- (d) The maximum error in any single burette reading is  $\pm 0.05$  cm<sup>3</sup>.

(i) State the maximum possible error in the volume run from the burette recorded in any titration.

$\pm 0.10$  cm<sup>3</sup> [1] with sign

[1]

(ii) Explain how an error of  $(-0.10)$  cm<sup>3</sup> may arise when using a burette to obtain an individual titre value.

Initial burette reading has an error of  $+0.05$  cm<sup>3</sup> and the final burette reading has an error of  $-0.05$  cm<sup>3</sup>. [1]

$$\text{Total error} = \text{Final} - \text{initial} = (-0.05) - (+0.05) = -0.10 \text{ cm}^3$$

[1]

(e) A student suggested that when a piece of iron wire was dissolved in a known volume and concentration of sulfuric acid, the number of moles of iron that reacted with the acid could be determined by working out how much acid was left after the reaction. The amount of excess acid could be determined by titrating the mixture with a known concentration of sodium hydroxide.

Explain whether the student was correct.

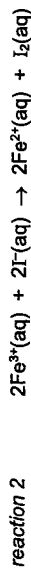
The student was incorrect as sodium hydroxide would also react with  $\text{Fe}^{2+}$  in the mixture to form  $\text{Fe}(\text{OH})_2$  ppt. [1]

Furthermore, the impurities in the wire might react with sodium hydroxide. [1]

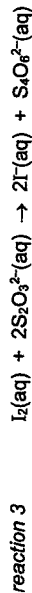
[Total: 14]

## 2 Investigation of the kinetics of the reaction between $I^-(aq)$ and $Fe^{3+}(aq)$

Iron(III) ions,  $Fe^{3+}(aq)$ , and iodide ions,  $I^-(aq)$ , react to give iodine,  $I_2(aq)$ , in the presence of acid.



If acidified iron(III) chloride and potassium iodide are mixed in the presence of starch indicator and sodium thiosulfate, the iodine liberated reacts immediately with the thiosulfate ions and is reduced back to iodide ions.



When all the thiosulfate ions have reacted, the iodine which continues to be produced then turns the starch indicator blue-black. The rate of reaction 2 may be determined by timing how long it takes for the reaction to turn blue-black.

You are to investigate how the rate of reaction is affected by changing the concentration of the iodide ions.

**FA 4** is 0.0500 mol dm<sup>-3</sup> potassium iodide, KI(aq)

**FA 5** is 0.0500 mol dm<sup>-3</sup> acidified iron(III) chloride, FeCl<sub>3</sub>(aq).

**FA 6** is 0.00500 mol dm<sup>-3</sup> sodium thiosulfate, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>(aq)

**FA 7** is starch indicator.

**Read through the whole method carefully and prepare a table for your results on page 6 before starting any practical work.**

### (a) Method

#### Experiment 1

1. Fill the burette labelled "FA 4" with FA 4.
2. Run 20.00 cm<sup>3</sup> of FA 4 into the 100 cm<sup>3</sup> beaker.
3. Use the 50 cm<sup>3</sup> measuring cylinder to add the following to the same 100 cm<sup>3</sup> beaker:
  - o 20.0 cm<sup>3</sup> of FA 6
  - o 10.0 cm<sup>3</sup> of FA 7
4. Place the beaker on the white tile and stir the contents of the beaker using a glass rod.
5. Use the 25 cm<sup>3</sup> measuring cylinder to measure 10.0 cm<sup>3</sup> of FA 5.
6. Add this FA 5 into the same 100 cm<sup>3</sup> beaker and start timing immediately at the instant of mixing.
7. Stir once. The reaction mixture will turn *light brown* and then *pale yellow* before a sudden intense blue-black colouration is observed. Stop timing as soon as the solution turns blue-black.
8. Record this reaction time,  $t$ , to the nearest 0.1 s.
9. Wash out the beaker and dry it with a paper towel.

#### Experiment 2

1. Fill another burette with deionised water.
2. Run 7.00 cm<sup>3</sup> of FA 4 into the 100 cm<sup>3</sup> beaker.
3. Run 13.00 cm<sup>3</sup> of deionised water into the beaker containing FA 4.
4. Use the 50 cm<sup>3</sup> measuring cylinder to add the following to the same 100 cm<sup>3</sup> beaker:
  - o 20.0 cm<sup>3</sup> of FA 6
  - o 10.0 cm<sup>3</sup> of FA 7
5. Place the beaker on the white tile and stir the contents of the beaker using a glass rod.
6. Use the 25 cm<sup>3</sup> measuring cylinder to measure 10.0 cm<sup>3</sup> of FA 5.
7. Add the FA 5 to the same 100 cm<sup>3</sup> beaker and start timing immediately at the instant of mixing.
8. Stir once and stop timing as soon as the solution turns blue-black.  
Note: This may take **more than 2 minutes**.
9. Record this reaction time,  $t$ , to the nearest 0.1 s.
10. Wash out the beaker and dry it with a paper towel.

#### Experiments 3 – 5

Carry out three further experiments to investigate how the reaction time,  $t$ , changes with different volumes of potassium iodide, FA 4. The combined volume of FA 4 and deionised water must always be 20.00 cm<sup>3</sup>. Do not use a volume of FA 4 that is less than 6.00 cm<sup>3</sup>.

Record all your results in a single table in the space provided below. You should include the experiment number, volume of FA 4, VFA 4, volume of water, V<sub>water</sub>, and the reaction time,  $t$ .

You should also include the 'rate of reaction' which is to be calculated as shown:

$$\text{rate} = \frac{1000}{\text{reaction time}}$$

For each experiment, the value of the 'rate of reaction' is to be recorded to 3 significant figures.

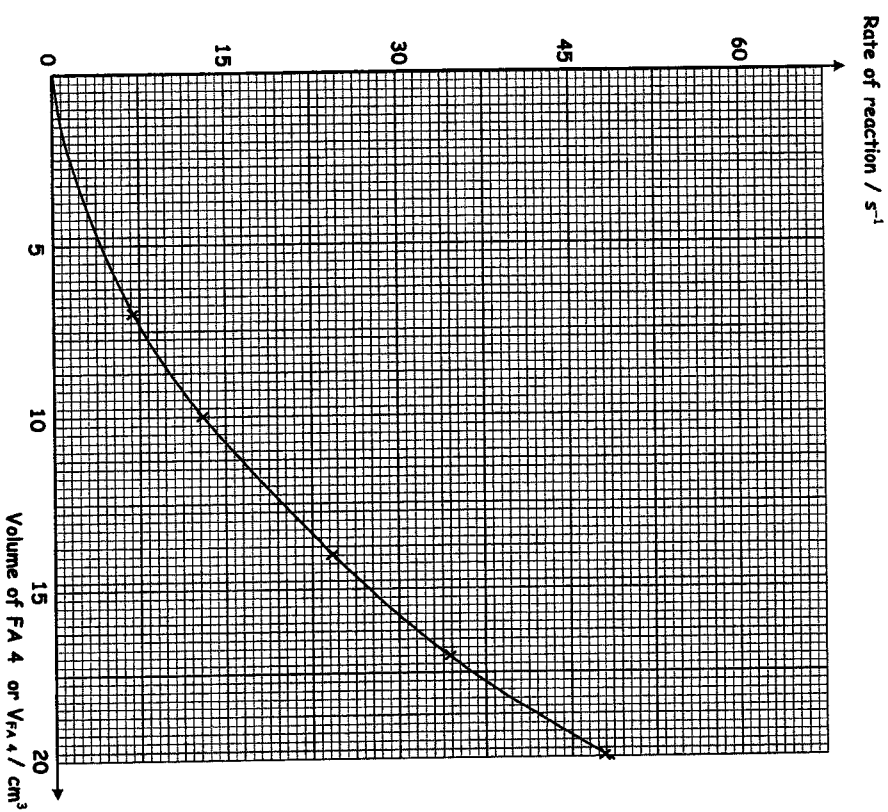
## Results

Experiment No.	V <sub>FA 4</sub> / cm <sup>3</sup>	V <sub>water</sub> / cm <sup>3</sup>	t / s	Rate of reaction / s <sup>-1</sup>
1	20.00	0.00	20.9	47.8
2	7.00	13.00	144.9	6.90
3	10.00	10.00	77.1	13.0
4	14.00	6.00	41.3	24.2
5	17.00	3.00	29.1	34.4

- [1] gives a single table with correct required headers with units.  
(units can be stated with each entry of data).
- [1] records all V<sub>FA 4</sub> and V<sub>water</sub> to the nearest 0.05 cm<sup>3</sup>  
+ all t to the nearest 0.1 s
- [1] correctly calculates all rates to 3 significant figures
- [1] gives three additional expts with 6.00 cm<sup>3</sup> < V<sub>FA 4</sub> < 20.00 cm<sup>3</sup>  
+ no V<sub>FA 4</sub> < 3 cm<sup>3</sup> close to another volume  
+ V<sub>FA 4</sub> + V<sub>water</sub> = 20.00 cm<sup>3</sup>
- [1] obtains correct trend of V<sub>FA 4</sub> increases, t decreases

[5]

- (b) (i) On the grid below, plot a graph of rate of reaction (y-axis) against volume of FA 4 (x-axis). Include the origin, (0,0), in your scale. Circle any points you consider anomalous and draw a line of best fit.



- [1] Labels axes correct way round with correct units + uses linear scales that include plotted points & (0,0) which cover more than half of the given grid in both directions + scale includes (0,0). Do not award this mark if awkward scale is used (e.g. 1 for 3/7).
- [1] Plots all points correctly within correct & small square.  
Do not award this mark if awkward scale is used or the scale used is too small such that plotting is done through estimation or non-linear scale is used.
- [1] Draws a straight-line or a smooth curve of best-fit (considered points should not be more than 1 small square from the chosen line and should not include the origin) + circle anomalous point if any (allows only one).



- (b) (ii) Explain, by referring to your graph, how the rate of reaction is affected by an increase in the concentration of aqueous potassium iodide, FA 4.

Since the total volume of each reaction mixture is kept constant, volume of FA 4 used is directly proportional to the initial  $[KI]$  in the reaction mixture.

- A straight line with positive gradient that passes through the origin [1] is obtained. Hence, the rate is directly proportional to  $[KI]$  (or rate  $\propto [KI]$  or rate is first order w.r.t.  $[KI]$ ) [1] OWTTE

- A straight line with positive gradient [1] that does not pass through the origin is obtained. Hence, the rate is proportional to  $[KI]$ . [1] OWTTE

- A curve with increasing gradient [1] is obtained. Hence, as the  $[KI]$  increases, the rate increases more. [1] OWTTE [2]

- (c) Thiosulfate ions can also react with acid to form sulfur, sulfur dioxide and water.

- (i) Write an ionic equation for the reaction between thiosulfate ions and hydrogen ions in aqueous solution. Include state symbols.



- (ii) A student carries out the same investigation as in (a) but the solutions are mixed in different order. The student places FA 4 and appropriate volume of deionised water in one beaker and all other reactants in a second beaker. The student then transfers the mixture from the second beaker to the first and starts timing.

Tick the box for the statement you consider correct. Explain your answer.

- The student's method is better than in (a).
- The two methods are equally good.
- The student's method is not as good as that in (a).

Reason:  $H^+/Fe^{3+}/FA\ 5$  will react away some  $S_2O_3^{2-}/FA\ 6$ .

Less  $S_2O_3^{2-}/FA\ 6$  will be left in the reaction mixture before starting the experiment. So the reaction time for each experiment will be shorter than expected. [1]

OR, The two methods are equally good. ✓

Reason: Concentration of  $S_2O_3^{2-}/FA\ 6$  is very small such that the reaction between  $S_2O_3^{2-}/FA\ 6$  and  $H^+/FA\ 5$  is very slow. So there is negligible/no effect on the reaction time/t for each expt. [1] [1]

- (d) Another student investigates the effect of iron(III) concentration on the rate of this reaction.

The student carries out another experiment, Experiment 6, and the rate is compared to that of Experiment 2.

In Experiment 2, the volumes used were:

reagent	Volume / cm <sup>3</sup>
FA 4	7.00
FA 5	10.0
FA 6	20.0
FA 7	10.0
deionised water	13.00

- (i) Suggest the volumes the student could use for Experiment 6.

reagent	Volume / cm <sup>3</sup>
FA 4	7.00
FA 5	20.0
FA 6	20.0
FA 7	10.0
deionised water	3.00

[1] To change  $V_{FA\ 5}$ ; keeping  $V_{FA\ 4}$ ,  $V_{FA\ 6}$  &  $V_{FA\ 7}$  all unchanged; and  $V_{FA\ 5} + V_{water} = 23\ cm^3$

(To ignore precision of all volume measurements)

[1]

- (ii) This student records a time of 140 s for Experiment 2.

The rate of reaction is directly proportional to the concentration of iron(III) ions.

Suggest how long it would take the reaction mixture proposed for Experiment 6 in (d)(i) to turn blue-black. Assume that Experiment 6 is carried out at the same temperature as Experiment 2.

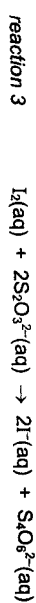
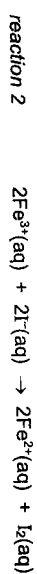
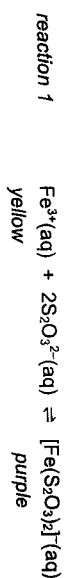
Do not carry out Experiment 6.

Since rate  $\propto [Fe^{3+}]^1$ , reaction time =  $\frac{10}{V_{FA\ 5}} \times 140 = 70\ s$

[1] to the nearest s/ 0.1 s/ 3 s.f.

reaction time = 70 s [1]

(e) When FA 4, FA 5 and FA 6 are mixed, the following three reactions occur.



When FA 5 was added to the solution prepared in step 6 of Experiment 1, the reaction mixture turned light brown and then pale yellow before the blue-black colour appeared.

The light brown colour is due to a mixture of purple  $[\text{Fe}(\text{S}_2\text{O}_3)_2]^{-}(\text{aq})$  and yellow  $\text{Fe}^{3+}(\text{aq})$  in the reaction mixture. Explain why the light brown solution turns pale yellow before the appearance of blue-black colour.

As the reaction 2 proceeds, both  $[\text{Fe}^{3+}]$  and  $[\text{S}_2\text{O}_3^{2-}]$  decreases (✓) and cause the position of equilibrium/pot of reaction 1 to shift left to form back some  $\text{Fe}^{3+}$  and  $\text{S}_2\text{O}_3^{2-}$ . (✓) Hence the solution gradually became pale yellow due to increase in  $[\text{Fe}^{3+}(\text{aq})]$ .

2(✓) [1] [1]

[Total: 15]

### 3 Qualitative Analysis

Solid FA 8 contains the polyatomic anion,  $\text{X}^{2-}$ , and one cation from the ions listed in the Qualitative Analysis Notes.

FA 9 is an aqueous solution containing a sodium salt of the polyatomic anion,  $\text{X}^{2-}$ .

FA 10 is organic solution containing one functional group.

You will perform tests to

- Identify the cation present in FA 8
- deduce the nature of FA 8
- deduce the identity of  $\text{X}^{2-}$
- identify the functional group present in FA 10

(a) (i) Perform the tests described in Table 3.1, and record your observations in the table. Test and identify any gases evolved. If there is no observable change, write no observable change.

Table 3.1

tests	observations
1 Place a spatula measure of FA 8 in a test-tube and add 1-2 cm depth of aqueous iron(II) sulfate. Shake the tube well until all FA 8 dissolves.	<ul style="list-style-type: none"> <li>• solution turns yellow/ brown/ orange-brown/ orange. (✓)</li> </ul>
2 Place a spatula measure of FA 8 in a boiling tube and add 1 cm depth of dilute nitric acid to dissolve the solid. Then add 1 cm depth of aqueous manganese(II) sulfate and 4 drops of aqueous silver nitrate to act as a catalyst. Heat cautiously to bring the mixture to boiling.	<ul style="list-style-type: none"> <li>• Colourless solution. (✓)</li> <li>• Upon heating, solution turns brown (✓) to a dark-brown/black ppt. (✓)</li> </ul>
3 To a spatula measure of FA 8 in a boiling tube, add 1-2 cm depth of aqueous sodium hydroxide. Heat cautiously.	<ul style="list-style-type: none"> <li>• No ppt. / colourless solution/ no observable change. (✓)</li> <li>• Upon heating, pungent <math>\text{NH}_3</math> (✓) gas evolved and turns damp red litmus paper blue (✓)</li> </ul>

6-7(✓) [3]: 3-5(✓) [2]: 2(✓) [1] [3]

(ii) Identify the cation in FA 8. [1]

cation:  $\text{NH}_4^+$  [1]

(iii) State, with supporting evidences, the nature (acidic, basic, amphoteric, oxidising or reducing) of FA 8. [1]

nature of FA 8: oxidising or oxidising agent [1]

evidence: FA 8 oxidises pale green  $\text{Fe}^{2+}$  in  $\text{FeSO}_4(\text{aq})$ /Test 1 to yellow/brown  $\text{Fe}^{3+}$ , and oxidises colourless  $\text{Mn}^{2+}$  in  $\text{MnSO}_4(\text{aq})$ /Test 2 to brown  $\text{Mn}^{3+}$  and dark brown/black  $\text{MnO}_2$ . [2]

(b) (i) FA 9 is an aqueous solution containing a sodium salt of the polyatomic anion,  $\text{X}^{2-}$ . In aqueous solution,  $\text{X}^{2-}$  reacts very slowly with water to produce anion P,  $\text{H}^+$  ions and oxygen gas.



Perform the tests described in Table 3.2, and record your observations in the table. Test and identify any gases evolved. If there is no observable change, write no observable change.

Table 3.2

	tests	observations
1	Test solution FA 9 with Universal Indicator paper.	UI paper turns <u>dark orange/orange-brown</u> ( $\checkmark$ ), pH <u>2/2-3/3</u> ( $\checkmark$ )
2	To 1 cm depth of FA 9 in a boiling tube, add 1 cm depth of aqueous sodium hydroxide and a piece of aluminium foil. Warm the mixture cautiously.	<u>Effervescence/Bubbles</u> ( $\checkmark$ ) of $\text{H}_2$ noted. <u>No <math>\text{NH}_3</math>/no observable change</u> ( $\checkmark$ ) with damp red litmus paper.
3	To 1 cm depth of FA 9 in a test-tube, add 1 cm depth of aqueous barium nitrate. Then add dilute nitric acid until no further change occurs.	<u>White ppt.</u> ( $\checkmark$ ) ppt. <u>insoluble in excess dilute nitric acid.</u> ( $\checkmark$ )

5-6( $\checkmark$ ) [3]: 3-4( $\checkmark$ ) [2]: 2( $\checkmark$ ) [1] [3]

(ii) Identify the anion P. Hence, use reaction 4 equation to deduce the identity of  $\text{X}^{2-}$ .

Anion P:  $\text{SO}_4^{2-}$  [1]



$\text{X}^{2-}$  is  $\text{S}_2\text{O}_8^{2-}$  [1] [2]

(c) You are provided with an organic solution FA 10 which contains one functional group.

**Care: FA 10 is flammable. Do not use Bunsen burner for heating. Use the hot water provided if heating is required.**

FA 10 gives a positive test with 2,4-dinitrophenylhydrazine.

Devise one other confirmatory test using the bench reagents provided to identify the functional group present in FA 10.

Carry out the test. Record details of the test performed and observations made in Table 3.3.

Table 3.3

Confirmatory Test	Observations
To 1 cm depth of FA 10 in a test-tube, add 1-2 cm depth of dilute $\text{H}_2\text{SO}_4$ and a few drops of $\text{KMnO}_4(\text{aq})$ . <u>Heat</u> in hot water-bath. [1]	<u>Purple <math>\text{KMnO}_4</math> decolourised.</u> [1]
To 1 cm depth of aqueous $\text{AgNO}_3$ in a test-tube, add 1 cm depth of aqueous <u><math>\text{NaOH}</math></u> . Then <u>add aqueous <math>\text{NH}_3</math></u> until the precipitate just dissolves.	Brown $\text{Ag}_2\text{O}$ ppt. dissolves to give a colourless solution of $\text{Ag}(\text{NH}_3)_2^+(\text{aq})$ .
To this mixture, add 1 cm depth of FA 10. <u>Heat</u> the mixture in the hot water-bath. [1]	A <u>silver mirror/grey ppt.</u> is formed. [1]

Functional group present in FA 10: aldehyde [1]

- If the test result is negative, accept ketone but award [0] for observations. [3]

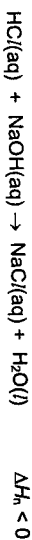
[Total: 14]

## 4 Planning

Enthalpy change of neutralisation,  $\Delta H_n$ , is the heat evolved when one mole of water is formed from the reaction of an acid and an alkali.



When aqueous hydrochloric acid,  $\text{HCl}(\text{aq})$  is mixed with aqueous sodium hydroxide,  $\text{NaOH}(\text{aq})$ , the neutralisation reaction releases heat causing a rise in the temperature of the solution.



A series of experiments can be performed where increasing volumes of  $\text{HCl}(\text{aq})$  and decreasing volumes of  $\text{NaOH}(\text{aq})$  are mixed and the temperature rise,  $\Delta T$ , for each experiment is determined.

In each of the experiments using different volumes of  $\text{HCl}(\text{aq})$  and  $\text{NaOH}(\text{aq})$ , the total volume has to be kept constant. Since the total volume of mixture remains the same, the temperature rise,  $\Delta T$ , is a direct measure of the heat liberated by the reaction. The maximum amount of heat is evolved when all the acid present is exactly neutralised by all the alkali present.

Plotting a graph of  $\Delta T$  against the volume of  $\text{HCl}(\text{aq})$  used will give 2 straight lines of best-fit.

Extrapolation of the two straight lines will produce a point of intersection from which the concentration of  $\text{HCl}(\text{aq})$  and the enthalpy change of neutralisation,  $\Delta H_n$ , between  $\text{HCl}(\text{aq})$  and  $\text{NaOH}(\text{aq})$  can be determined.

The volume of  $\text{HCl}(\text{aq})$  used should be at least  $10.00 \text{ cm}^3$  and the total volume of the reaction mixture should be kept constant at  $50.00 \text{ cm}^3$  for all experiments.

(a) Using the information given, you are required to write a plan to determine the concentration of  $\text{HCl}(\text{aq})$  and the enthalpy change of neutralisation,  $\Delta H_n$ , between  $\text{HCl}(\text{aq})$  and  $\text{NaOH}(\text{aq})$ .

You may assume that you are provided with:

- $250 \text{ cm}^3$  of  $\text{HCl}(\text{aq})$  of unknown concentration
- $250 \text{ cm}^3$  of  $1.50 \text{ mol dm}^{-3}$   $\text{NaOH}(\text{aq})$ ,
- the equipment normally found in a school or college laboratory.

In your plan you should include brief details of:

- the apparatus you would use,
- the quantities you would use, including suggested volumes of  $\text{HCl}(\text{aq})$  and  $\text{NaOH}(\text{aq})$ ,
- the procedure you would follow,
- the measurements you would make to allow a suitable  $\Delta T$  against the volume of  $\text{HCl}(\text{aq})$  graph to be drawn.

1. Fill the burette with  $\text{HCl}(\text{aq})$ .

2. Place the styrofoam cup in a  $250 \text{ cm}^3$  beaker to prevent it from tripping over. Transfer  $10.00 \text{ cm}^3$  of  $\text{HCl}(\text{aq})$  into the styrofoam cup. Measure the temperature of the  $\text{HCl}(\text{aq})$  in the cup using the  $0.2^\circ \text{C}$  interval thermometer. Record the initial temperature of  $\text{HCl}(\text{aq})$  as  $T_1$ .

3. Wash and dry the thermometer.

4. Use a  $50 \text{ cm}^3$  measuring cylinder to measure  $40.0 \text{ cm}^3$  of  $\text{NaOH}(\text{aq})$ . Measure the temperature of the  $\text{NaOH}(\text{aq})$  in the measuring cylinder using the thermometer. Record the initial temperature of  $\text{NaOH}(\text{aq})$  as  $T_2$ .

5. Add  $\text{NaOH}(\text{aq})$  from the measuring cylinder to  $\text{HCl}(\text{aq})$  in the cup. Stir the mixture using the thermometer and record the maximum temperature reached,  $T_{\text{max}}$ .

[1] uses appropriate apparatus

- burette/ $50 \text{ cm}^3$  measuring cylinder for  $\text{HCl}$
- burette/ $50 \text{ cm}^3$  measuring cylinder for  $\text{NaOH}$
- styrofoam/plastic/polystyrene cup
- thermometer

[1] measures initial temp. of  $\text{HCl}$  &  $\text{NaOH}$  before mixing (step 2 & 4).

[1] measures the maximum temp. reached after mixing (step 5).

6. Wash and dry the styrofoam cup.

7. Repeat steps 2 to 6 using  $15.00 \text{ cm}^3$ ,  $20.00 \text{ cm}^3$ ,  $25.00 \text{ cm}^3$ ,  $30.00 \text{ cm}^3$ ,  $35.00 \text{ cm}^3$  and  $40.00 \text{ cm}^3$  of  $\text{HCl}(\text{aq})$  and appropriate volumes of  $\text{NaOH}(\text{aq})$  each time, such that the total volume of the reacting mixture is  $50 \text{ cm}^3$ . (OR Repeat steps 2 to 6 using the volumes of  $\text{HCl}(\text{aq})$  and  $\text{NaOH}(\text{aq})$  stated in the table below.)

[1] uses volume of  $\text{HCl}$  between  $(10-45) \text{ cm}^3$ .

uses volume of  $\text{NaOH}$  between  $(5-40) \text{ cm}^3$ ;  
total volume =  $50 \text{ cm}^3$ .

[1] obtains min 6 data points.

8. For each reaction mixture,  $\Delta T$  is calculated based on the following:

$$\text{where } T_{\text{initial}} = \frac{(\text{Volume of } \text{HCl}(\text{aq}) \times T_1) + (\text{Volume of } \text{NaOH}(\text{aq}) \times T_2)}{50} \quad [1]$$

(c) Outline how you would use your answers from (b) to determine

(i) the concentration, in mol dm<sup>-3</sup>, of HCl(aq).

Express your results in terms of  $V_{\text{neut}}$ . It is not necessary to simplify the expression in your final answer.

$$\begin{aligned} \text{Amount of NaOH in } (50 - V_{\text{neut}}) \text{ cm}^3 \\ = \text{amount of HCl in } V_{\text{neut}} \text{ cm}^3 \\ = \left( \frac{50 - V_{\text{neut}}}{1000} \times 1.50 \right) \text{ mol} \quad [1] \end{aligned}$$

$$\begin{aligned} \text{Concentration of HCl} \\ = \frac{1000}{V_{\text{neut}}} \times \left( \frac{50 - V_{\text{neut}}}{1000} \times 1.50 \right) \text{ mol dm}^{-3} \quad [1] \end{aligned}$$

**Max: [1]** if student uses  $V_{\text{neut}}$  for  $V_{\text{NaOH}}$  and  $(50 - V_{\text{neut}})$  for  $V_{\text{HCl}}$ . [2]

(ii) the enthalpy change of neutralisation,  $\Delta H_n$ , for this reaction.



Express your answers in terms of  $\Delta T_{\text{max}}$  and  $V_{\text{neut}}$ . It is not necessary to simplify the expression in your final answer.

You should assume that the specific heat capacity of the final solution is 4.18 J g<sup>-1</sup> K<sup>-1</sup> and its density is 1.00 g cm<sup>-3</sup>.

Heat change,  $q = mc\Delta T$

$$\begin{aligned} &= (50.0 \times 1.00)(4.18)(\Delta T_{\text{max}}) \\ &= 209\Delta T_{\text{max}} \text{ J} = 0.209\Delta T_{\text{max}} \text{ kJ} \quad [1] \text{ ans. in J or kJ} \end{aligned}$$

Amount of water formed =  $n(\text{NaOH})$  reacted  
=  $n(\text{HCl})$  reacted

$$= \left( \frac{50 - V_{\text{neut}}}{1000} \times 1.50 \right) \text{ mol (ecf from (i))}$$

$$\Delta H_{\text{neut}} = - \frac{(0.209\Delta T_{\text{max}})}{\left( \frac{50 - V_{\text{neut}}}{1000} \times 1.50 \right)} \text{ kJ mol}^{-1} \quad [1] \text{ ecf} + \text{sign} + \text{units}$$

[2]

[Total: 12]

Volume of HCl(aq) / cm <sup>3</sup>	Volume of NaOH(aq) / cm <sup>3</sup>	T <sub>1</sub> / °C	T <sub>2</sub> / °C	T <sub>max</sub> / °C	T <sub>initial</sub> / °C	ΔT / °C
10.00	40.0					
15.00	35.0					
20.00	30.0					
25.00	25.0					
30.00	20.0					
35.00	15.0					
40.00	10.0					
45.00	5.0					

[6]

(b) Sketch on Fig 4.1 the graph you would expect to obtain from your results.

Indicate clearly on your sketch how you would determine:

- $V_{\text{neut}}$ , the volume of HCl(aq) needed to just completely neutralise (50 -  $V_{\text{neut}}$ ) cm<sup>3</sup> of NaOH(aq).
- $\Delta T_{\text{max}}$ , the maximum temperature rise when stoichiometric amount of HCl(aq) and NaOH(aq) reacted.

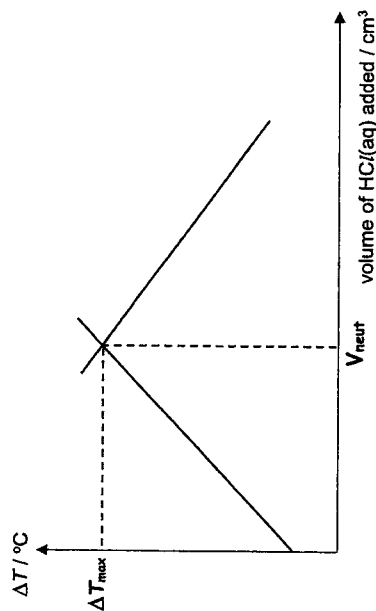


Fig 4.1

[1] gives correct graph

[1] indicates  $V_{\text{neut}}$  and  $\Delta T_{\text{max}}$  correctly

[2]

## (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 giving dark blue solution
iron(II), Fe <sup>2+</sup> (aq)	green ppt. turning brown on contact with air insoluble in excess	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

## (b) Reactions of Anions

Anion	Reaction
carbonate, CO <sub>3</sub> <sup>2-</sup>	CO <sub>2</sub> liberated by dilute acids
chloride, Cl <sup>-</sup> (aq)	gives white ppt. with Ag <sup>+</sup> (aq) (soluble in NH <sub>3</sub> (aq));
bromide, Br <sup>-</sup> (aq)	gives pale cream ppt. with Ag <sup>+</sup> (aq) (partially soluble in NH <sub>3</sub> (aq));
iodide, I <sup>-</sup> (aq)	gives yellow ppt. with Ag <sup>+</sup> (aq) (insoluble in NH <sub>3</sub> (aq));
nitrate, NO <sub>3</sub> <sup>-</sup> (aq)	NH <sub>3</sub> liberated on heating with OH <sup>-</sup> (aq) and Al foil
nitrite, NO <sub>2</sub> <sup>-</sup> (aq)	NH <sub>3</sub> liberated on heating with OH <sup>-</sup> (aq) and Al foil; NO liberated by dilute acids (colourless NO → (pale) brown NO <sub>2</sub> in air)
sulfate, SO <sub>4</sub> <sup>2-</sup> (aq)	gives white ppt. with Ba <sup>2+</sup> (aq) (insoluble in excess dilute strong acids)
sulfite, SO <sub>3</sub> <sup>2-</sup> (aq)	SO <sub>2</sub> liberated on warming with dilute acids; gives white ppt. with Ba <sup>2+</sup> (aq) (soluble in excess dilute strong acids)

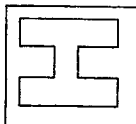
## (c) Tests for Gases

gas	Test and test results
ammonia, NH <sub>3</sub>	turns damp red litmus paper blue
carbon dioxide, CO <sub>2</sub>	gives a white ppt. with limewater (ppt. dissolves with excess CO <sub>2</sub> )
chlorine, Cl <sub>2</sub>	bleaches damp litmus paper
hydrogen, H <sub>2</sub>	"pops" with a lighted splint
oxygen, O <sub>2</sub>	relights a glowing splint
sulfur dioxide, SO <sub>2</sub>	turns acidified aqueous potassium manganate(VII) from purple to colourless

## (d) Colour of halogens

halogen	colour of element	colour in aqueous solution	colour in hexane
chlorine, Cl <sub>2</sub>	greenish yellow gas	pale yellow	pale yellow
bromine, Br <sub>2</sub>	reddish brown gas/liquid	orange	orange-red
iodine, I <sub>2</sub>	black solid/purple gas	brown	purple

Candidate Name: \_\_\_\_\_



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## 2022 Preliminary Examination Pre-University 3

### H2 CHEMISTRY

Paper 1 Multiple Choice

9729/01

21<sup>st</sup> Sep 2022

1 hour

Additional materials: Multiple Choice Answer Sheet

Data Booklet

#### READ THESE INSTRUCTIONS FIRST

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

Write in soft pencil.

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

Write your name, class and admission number in the spaces provided at the top of this page and on the Multiple Choice Answer Sheet 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 Multiple Choice Answer Sheet provided.

**Read the instructions on the Multiple Choice Answer Sheet very carefully.**

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 question paper.

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

FOR EXAMINER'S USE	
TOTAL (30 marks)	

This question paper consists of 14 printed pages and 2 blank pages.

For each question there are four possible answers, **A, B, C**, and **D**. Choose the **one** you consider to be correct.

1 Which of the following conversions have a percentage yield of 73%?

- 1 74 g of butan-1-ol ( $M_r = 74.0$ )  $\rightarrow$  52.56 g of butanal ( $M_r = 72.0$ )
  - 2 72 g of butanone ( $M_r = 72.0$ )  $\rightarrow$  54.02 g of butan-2-ol ( $M_r = 74.0$ )
  - 3 56 g of but-2-ene ( $M_r = 56.0$ )  $\rightarrow$  87.60 g of ethanoic acid ( $M_r = 60.0$ )
- A** 1 only  
**B** 1 and 2 only  
**C** 2 and 3 only  
**D** 1, 2 and 3

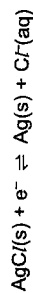
2 Ferric oxalate,  $\text{Fe}_2(\text{C}_2\text{O}_4)_3$ , is an ionic salt. A sample of  $10.0 \text{ cm}^3$  of  $0.100 \text{ mol dm}^{-3}$  ferric oxalate is titrated against  $0.100 \text{ mol dm}^{-3}$  acidified  $\text{KMnO}_4$ .

What is the volume of  $\text{KMnO}_4$  required to reach end point, and the total volume of  $\text{CO}_2$  gas evolved at r.t.p.?

	volume of $\text{KMnO}_4$	volume of gas
<b>A</b>	$4.0 \text{ cm}^3$	$72 \text{ cm}^3$
<b>B</b>	$4.0 \text{ cm}^3$	$144 \text{ cm}^3$
<b>C</b>	$12.0 \text{ cm}^3$	$72 \text{ cm}^3$
<b>D</b>	$12.0 \text{ cm}^3$	$144 \text{ cm}^3$

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

The silver chloride electrode is a type of reference electrode commonly used in electrochemical measurements. It can be represented as below.



The reduction potential of the  $\text{Co}^{3+}/\text{Co}^{2+}$  half-cell is  $+1.69 \text{ V}$  when it is measured using the  $\text{AgCl}/\text{Ag}$  reference electrode at standard conditions.

What is the reduction potential of the  $\text{AgCl}/\text{Ag}$  electrode when it is measured against the standard hydrogen electrode as reference?

- A**  $-1.89 \text{ V}$     **B**  $+0.20 \text{ V}$     **C**  $+1.49 \text{ V}$     **D**  $+1.89 \text{ V}$

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

Which of the following statements are true?

- 1  $I_2$  can reduce  $S_2O_3^{2-}$  to  $S_4O_6^{2-}$ .
  - 2 K is a stronger reducing agent than Ca.
  - 3 When  $Br_2(g)$  is bubbled into  $NaI(aq)$ , an orange solution is produced.
- A 1 only  
 B 2 only  
 C 1 and 2 only  
 D 2 and 3 only

5 The first six ionisation energies of an element, E, in  $kJ\ mol^{-1}$  are shown.

578 1817 2745 11577 14842 18379

E forms an oxide when it is heated with oxygen gas.

What is the electronic configuration of E in its oxide form?

- A  $1s^2$   
 B  $1s^2 2s^2 2p^1$   
 C  $1s^2 2s^2 2p^6$   
 D  $1s^2 2s^2 2p^6 3s^2 3p^1$

6 In which of the following pairs of compounds would the second compound have a higher boiling point than the first compound?

- 1  $CH_3CHO$ ,  $CH_3CH_2OH$
  - 2  $AlF_3$ ,  $AlCl_3$
  - 3  $CH_3CH_2CH_2CH_2CH_3$ ,  $C(CH_3)_4$
- A 1 only  
 B 1 and 2 only  
 C 1 and 3 only  
 D 2 and 3 only

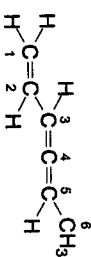
7 Information about the properties of some compounds are given below.

compound	boiling point / °C
HF	19.5
$NH_3$	-33.3
$H_2O$	100

Which statement about the hydrogen bonding in these compounds is correct?

- A HF has a higher boiling point than  $NH_3$  because each HF molecule can form more hydrogen bonds on average compared to each  $NH_3$  molecule.
- B  $H_2O$  has a higher boiling point than HF because the H–O bond dipole is greater than the H–F bond dipole.
- C  $H_2O$  has a higher boiling point than HF because hydrogen bonding between two molecules of  $H_2O$  causes it to dimerise.
- D  $NH_3$  has the lowest boiling point because it forms few hydrogen bonds on average and has the smallest bond dipole.

8 Covalent bonds involve the overlapping of orbitals.



Which statement does not describe the molecule above?

- A The  $\sigma$  bond between C2–H is formed by  $2sp^2-1s$  overlap.
- B The  $\sigma$  bond between C3–C4 is formed by  $2sp^2-2sp^2$  overlap.
- C The  $\sigma$  bond between C5–C6 is formed by  $2sp^2-2sp^3$  overlap.
- D The  $\pi$  bond between C4–C5 is formed by  $2p-2p$  overlap.

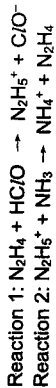


11  $20 \text{ m}^3$  of neon gas at a pressure of 30 kPa and  $30 \text{ m}^3$  of argon gas at a pressure of 50 kPa were introduced into an evacuated  $15 \text{ m}^3$  flask at a constant temperature of 300 K. The final pressure in the flask was F kPa.

What is the value of F?

	F / kPa
A	42
B	80
C	140
D	178

12 Two acid-base reactions are shown below:



Which of the following statements is incorrect?

- $\text{C/O}^-$  is the conjugate base of  $\text{HC/O}$ .
  - $\text{N}_2\text{H}_5^+$  is the Bronsted acid in Reaction 2.
  - $\text{N}_2\text{H}_4$  is the Lewis acid in Reaction 1.
- A 1 only  
 B 3 only  
 C 1 and 2 only  
 D 2 and 3 only

13 The radioactive decay of an element, H, is a first order reaction and produces element I as the product:

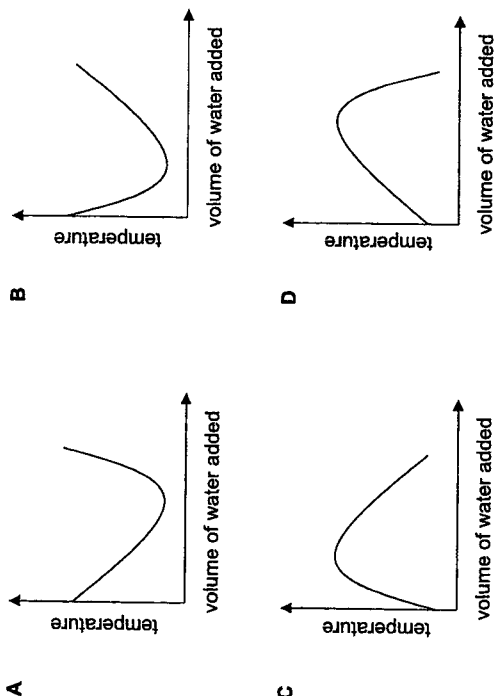


$1.00 \text{ mol}$  of H was set aside and allowed to decay. Given that it takes 8 days for  $0.75 \text{ mol}$  of I to be produced, what fraction of H remains after 40 days?

- A  $(\frac{1}{2})^1$       B  $(\frac{1}{2})^5$       C  $(\frac{1}{2})^{10}$       D  $(\frac{1}{2})^{25}$

9 When glucose is stirred into water and dissolved, strong hydrogen bonds are formed initially between the glucose and water molecules. As more water is added, these same hydrogen bonds are subsequently broken.

Assuming that the rate of energy change remains relatively constant throughout, which of the following graphs best represents the observed temperature changes?



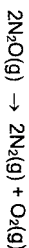
10 The  $\Delta H_c$  values of some hydrocarbons are given below.

hydrocarbon	$\Delta H_c / \text{kJ mol}^{-1}$	$M_r$
$\text{CH}_4$	-889	16.0
$\text{C}_2\text{H}_6$	-1560	30.0

What is the ratio of heat generated by  $\text{CH}_4$  to  $\text{C}_2\text{H}_6$  when the same mass of each hydrocarbon is burnt?

- A 0.57      B 0.94      C 1.07      D 1.14

- 14  $\text{N}_2\text{O}$  decomposes in the presence of gold catalyst as follows:



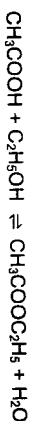
The following data is obtained from an experiment carried out at 1200 K.

time / s	0	1040	2370	4250	7460
partial pressure of $\text{N}_2\text{O}$ / kPa	25.0	20.0	15.0	10.0	5.0

Which of the following statements is **incorrect**?

- A The reaction is first order with respect to  $\text{N}_2\text{O}$ .  
 B The total pressure upon reaction completion can be determined from the above data.  
 C The values of the partial pressures of  $\text{N}_2\text{O}$  are affected by temperature.  
 D The value of rate constant of the reaction remains the same even in the absence of gold.

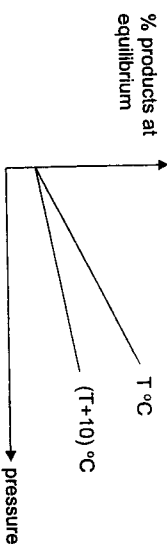
15



Which of the following conditions will be met when the above reaction has reached dynamic equilibrium?

- A The equilibrium constant  $K$  is equal to 1.  
 B The reaction between the acid and the alcohol has stopped.  
 C The concentrations of the products equal those of the reactants.  
 D The rate of production of ethyl ethanoate equals its rate of hydrolysis.

- 16 The graph below shows the percentage of products present at equilibrium over a range of temperatures and pressures.



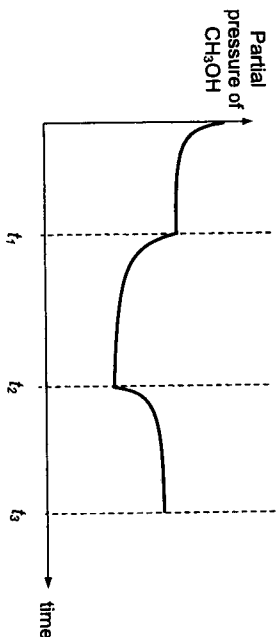
Which of the following reactions could the graph represent?

- A  $\text{C}(\text{s}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{CO}(\text{g})$   $\Delta H = -99 \text{ kJ mol}^{-1}$   
 B  $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$   $\Delta H = +20 \text{ kJ mol}^{-1}$   
 C  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$   $\Delta H = -92 \text{ kJ mol}^{-1}$   
 D  $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$   $\Delta H = +57 \text{ kJ mol}^{-1}$

- 17 A synthesis was carried out to produce methanol from hydrogen and carbon monoxide at a high temperature:



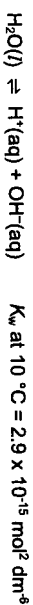
The partial pressure of  $\text{CH}_3\text{OH}(\text{g})$  was monitored over time, and changes were made to the reaction system at times  $t_1$  and  $t_2$ .



What are the possible changes made to the system at  $t_1$  and  $t_2$ ?

- A  $\text{CH}_3\text{OH}$  was removed      Temperature was increased  
 B  $\text{CO}$  was removed      Temperature was decreased  
 C Temperature was increased       $\text{CO}$  was removed  
 D Temperature was decreased       $\text{CH}_3\text{OH}$  was added

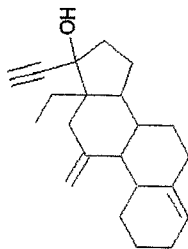
- 18 Pure water undergoes slight auto-ionisation:



Which of the following equations about water at  $10^\circ\text{C}$  is true?

- A  $\text{pH} > 7$   
 B  $\text{pH} = 7$   
 C  $\text{pH} < 7$   
 D  $[\text{H}^+] < [\text{OH}^-]$

22 Desogestrel is a medication used in birth control pills.

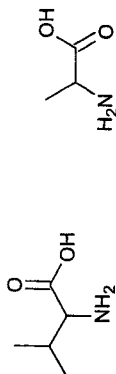


desogestrel

How many stereoisomers does desogestrel have?

- A  $2^4$       B  $2^5$       C  $2^6$       D  $2^7$

23 The structures of two amino acids are given below.



Which of the following statements about the amino acids is correct?

- A Both compounds are able to form zwitterions.  
 B Both compounds are able to react with ethanoic acid in the presence of concentrated sulfuric acid to give an amide.  
 C Both compounds are able to react with  $\text{NaBH}_4$  in methanol to give an alcohol.  
 D Both compounds are soluble in water due to the formation of intermolecular hydrogen bonding.

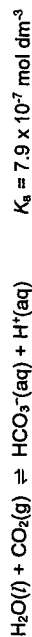
19 Trimethylamine,  $(\text{CH}_3)_3\text{N}$ , has a  $\text{p}K_b$  of 4.1.

$10.0 \text{ cm}^3$  of  $0.1 \text{ mol dm}^{-3}$   $(\text{CH}_3)_3\text{N}$  was pipetted into a conical flask and titrated against  $10.00 \text{ cm}^3$  of  $0.1 \text{ mol dm}^{-3}$   $\text{HCl}$ .

Which of the following statements is true about the pH of the reaction mixture?

	before addition of $\text{HCl}$	after adding $10.00 \text{ cm}^3$ $\text{HCl}$
A	11.5	5.6
B	11.5	9.9
C	13.8	5.6
D	13.8	9.9

20 The blood buffer system in the human body which maintains the pH of blood at 7.40 can be represented with the following equilibrium:



Which of the following statements about the blood buffer system is **not** true?

- A During vigorous exercise which produces large amounts of lactic acid in the blood, the body regulates pH by exhaling more  $\text{CO}_2$ .  
 B When a person hyperventilates (breathes in and out excessively quickly), the loss of  $\text{CO}_2$  causes the pH of blood to increase slightly.  
 C The pH of blood is 7.40 when the ratio of  $[\text{HCO}_3^-] : [\text{CO}_2]$  is 16:1.  
 D The blood buffer system is made up of  $\text{H}_2\text{CO}_3$  and  $\text{HCO}_3^-$ .

21  $\text{Ag}_2\text{CO}_3$  is a sparingly soluble salt with a  $K_{sp}$  value of  $8.2 \times 10^{-12} \text{ mol}^3 \text{ dm}^{-9}$ .

Which one of the following statements about a solution containing solid  $\text{Ag}_2\text{CO}_3$  is correct?

- A Addition of  $\text{NaCl}(\text{aq})$  causes more  $\text{Ag}_2\text{CO}_3$  solid to dissolve.  
 B Addition of sodium carbonate increases the solubility of  $\text{Ag}_2\text{CO}_3$ .  
 C Addition of  $\text{AgNO}_3$  solution decreases the  $K_{sp}$  value of  $\text{Ag}_2\text{CO}_3$ .  
 D Addition of water decreases the solubility of  $\text{Ag}_2\text{CO}_3$ .

24 Benzene,  $C_6H_6$ , is a non-polar molecule.

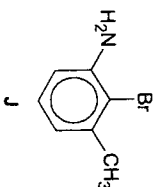
Which of the following statements are true about benzene?

- 1 Benzene is a good conductor of electricity due to its delocalised  $\pi$  electrons.
- 2 Benzene undergoes addition reactions readily due to its unsaturated C=C bonds.
- 3 The enthalpy change of hydrogenation of benzene is less exothermic than that predicted for cyclohexatriene.
- 4 The C-C bond lengths in benzene are all equivalent, and shorter than a typical alkane C-C bond length.

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

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

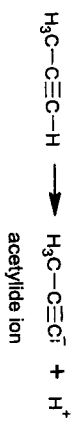
Compound J can be synthesised starting from benzene.



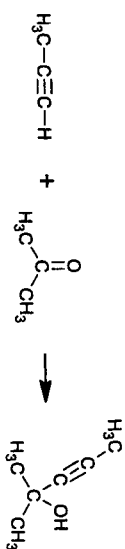
Which of the following synthetic routes will yield the optimum amount of J?

- A alkylation  $\rightarrow$  bromination  $\rightarrow$  nitration  $\rightarrow$  reduction  
 B alkylation  $\rightarrow$  nitration  $\rightarrow$  reduction  $\rightarrow$  bromination  
 C bromination  $\rightarrow$  alkylation  $\rightarrow$  nitration  $\rightarrow$  reduction  
 D bromination  $\rightarrow$  nitration  $\rightarrow$  alkylation  $\rightarrow$  reduction

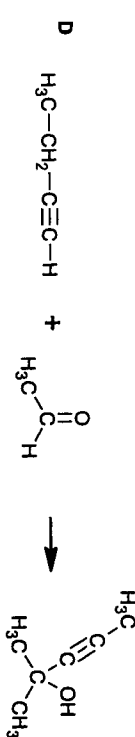
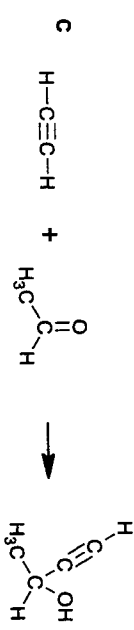
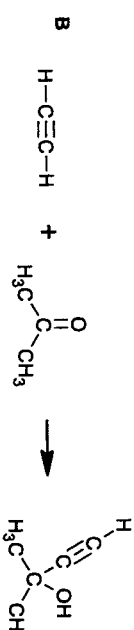
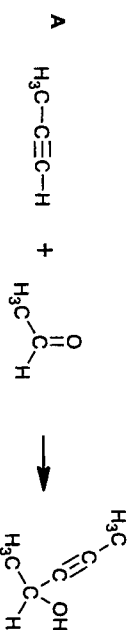
26 Alkynes can be deprotonated to form strong nucleophilic ions known as acetylides.



The acetylide ion can react with carbonyl compounds. An example of such a reaction is shown below:

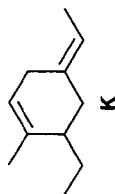


Which of the following reaction schemes does **not** show the correct corresponding product formed?



13

27 Compound **K** has the following structure:



Which of the following statements are correct when **K** is treated with hot acidified  $\text{KMnO}_4$ ?

- 1 There is only one organic product.
  - 2 The product(s) contain at least one carbonyl functional group.
  - 3 The product(s) contain at least one carboxylic acid functional group.
- A** 1 only  
**B** 1 and 2 only  
**C** 2 and 3 only  
**D** 1, 2 and 3

28 A Period 3 chloride and Period 3 oxide are dissolved in two separate portions of water to form aqueous solutions.

Both of the resulting solutions can be used to dissolve  $\text{Al}_2\text{O}_3$  but only one of the two can dissolve  $\text{SiO}_2$  slightly.

Which of the following could be the chloride and the oxide used?

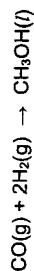
- 1  $\text{PCl}_5$   $\text{P}_4\text{O}_{10}$
  - 2  $\text{MgCl}_2$   $\text{SO}_3$
  - 3  $\text{SiCl}_4$   $\text{Na}_2\text{O}$
- A** 2 only  
**B** 3 only  
**C** 1 and 2 only  
**D** 1 and 3 only

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29 Which of the following correctly describes the complex formed when different reagents are added to solid copper(II) sulfate?

	reagent added	colour of resultant solution	identity of coloured complex ion
<b>A</b>	$\text{H}_2\text{O}$	pale blue	$[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$
<b>B</b>	$\text{H}_2\text{O}_2$ , followed by $\text{Zn}$	pink	$[\text{Cu}(\text{H}_2\text{O})_6]^{+}$
<b>C</b>	conc. $\text{HCl}$	yellow	$[\text{CuCl}_4]^{2-}$
<b>D</b>	excess $\text{NH}_3(\text{aq})$	dark blue	$[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$

30 Solid  $\text{Cr}_2\text{O}_3$  can be used as a catalyst in the synthesis of methanol.



Which of the following statements is **false** about the use of  $\text{Cr}_2\text{O}_3$  in this synthesis?

- A**  $\text{Cr}_2\text{O}_3$  functions as a catalyst by increasing the concentration of reactant molecules on its surface.
- B**  $\text{Cr}_2\text{O}_3$  lowers the activation energy by using its partially filled 3d orbitals for the adsorption of reactant molecules.
- C** The Cr atom of  $\text{Cr}_2\text{O}_3$  is able to form temporary bonds to the reactants.
- D** The oxidation state of Cr is increased after the reaction.

END OF PAPER 1

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