

RAFFLES INSTITUTION
2017 YEAR 6 PRELIMINARY EXAMINATION

HIGHER 2



CHEMISTRY

9729/01

Paper 1 Multiple Choice

25 September 2017

1 hour

Additional Materials: Multiple Choice Answer Sheet
Data Booklet

READ THESE INSTRUCTIONS FIRST

Do not open this question booklet until you are told to do so.

Write in soft pencil.

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

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

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

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

Read the instructions on the Answer Sheet very carefully.

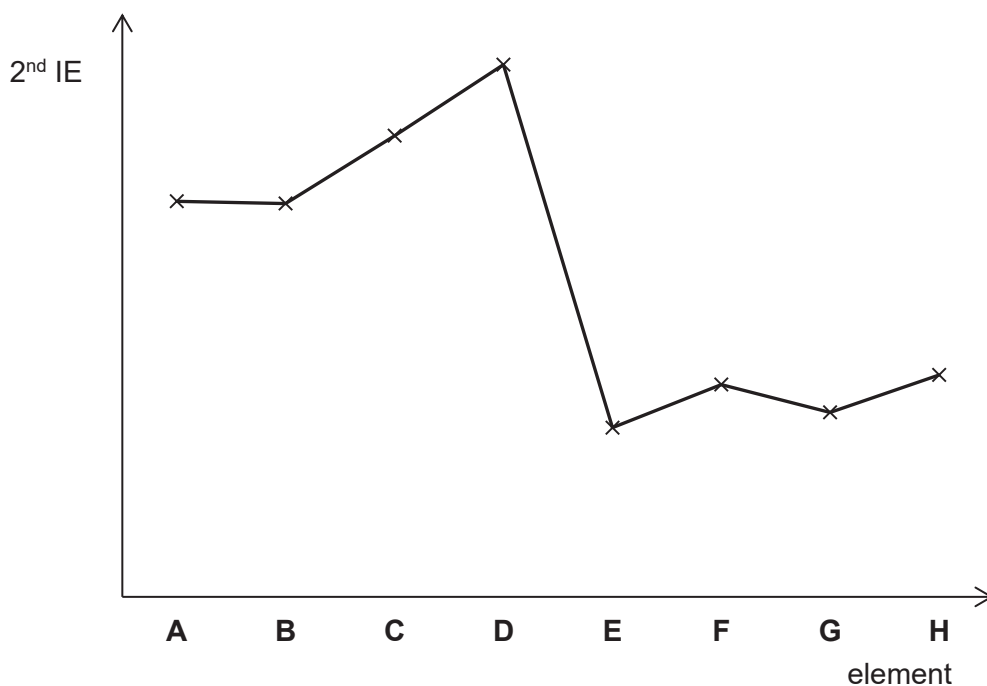
Each correct answer will score one mark. A mark will not be deducted for a wrong answer.

Any rough working should be done in this booklet.

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

This document consists of **15** printed pages.

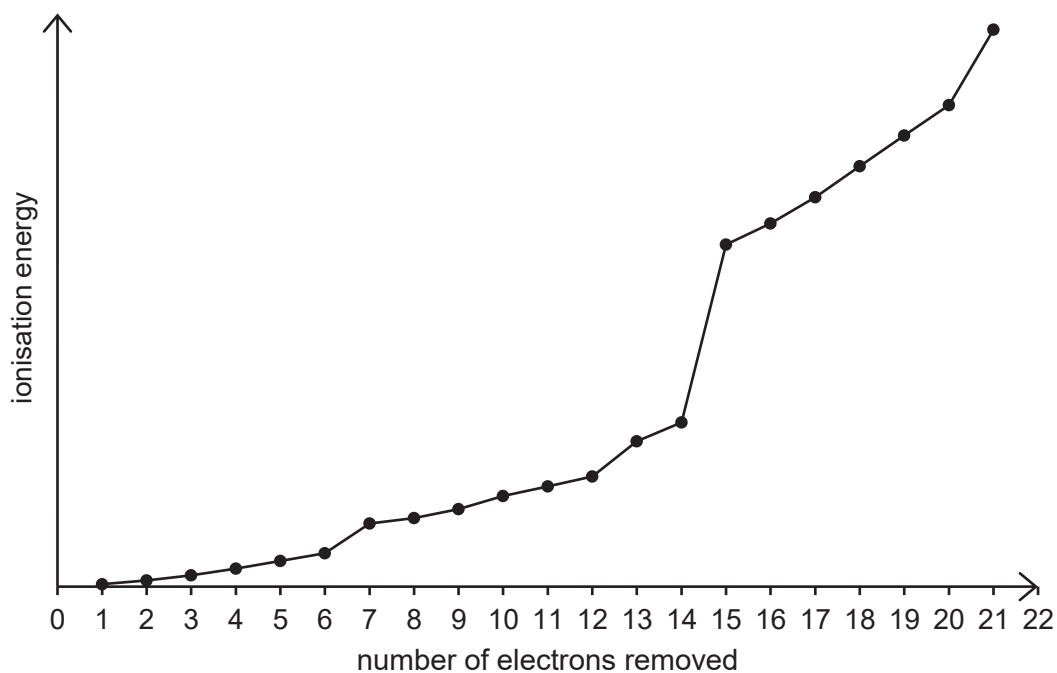
- 1 **A** to **H** are consecutive elements with atomic numbers less than 20. The graph below shows their second ionisation energies (2^{nd} IE).



Which of the following statements is correct?

- A** The 2^{nd} IE of **G** is lower than that of **F** due to the inter-electronic repulsion between its paired s electrons.
- B** **C** exists as diatomic molecules at room temperature.
- C** The compound formed between **A** and **E** has a low melting point.
- D** Element **B** is from Group 17.

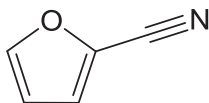
- 2 The graph below shows the successive ionisation energies of the Period 4 element, X.



Which of the following statements about X is correct?

- A X is Fe.
- B X belongs to Group 16.
- C X has 6 unpaired electrons in the ground state.
- D A stable compound, NaXO_4 , can be formed.
- 3 Which statement about ionic and covalent compounds is correct?
- A Some covalent compounds can serve as electrolytes in water.
- B Ionic compounds can conduct electricity in both the solid and liquid states.
- C Ionic bonds and covalent bonds cannot both occur in the same compound.
- D An ionic compound will have greater covalent character if the radius of the cation is large.

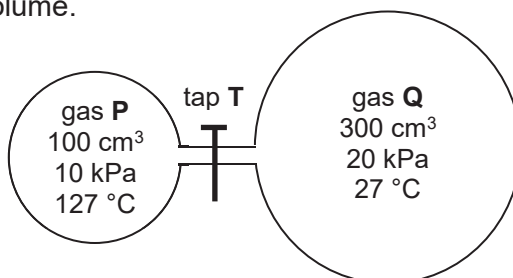
- 4 2-Furonitrile has the following structure.



Which row correctly describes the bonding and hybridisation in the above molecule?

	number of π bonds	number of sp C atoms	number of sp ² C atoms
A	3	0	5
B	4	1	4
C	4	0	5
D	2	1	4

- 5 Ideal gases **P** and **Q**, initially at different pressures and temperatures, are placed in different bulbs as shown in the diagram below. The bulbs are connected by a narrow tube of negligible volume.



When tap **T** is opened, the gases mix. What is the final pressure of the mixture if both bulbs are then maintained at 127 °C?

- | | | | |
|----------|----------|----------|----------|
| A | 22.5 kPa | B | 36.7 kPa |
| C | 73.1 kPa | D | 104 kPa |

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

Elements **X**, **Y** and **Z** are either chlorine, bromine or iodine. The following is a series of tests performed to determine the identities of the elements.

When **X**₂ is added to separate solutions containing **Y**⁻ and **Z**⁻ ions, no reaction occurs.

When **Y**₂ is added to a solution containing **Z**⁻ ions, no reaction occurs.

Which of the following statements are correct?

- 1 **X** is iodine.
- 2 The reaction between **Z**₂(aq) and **Y**⁻(aq) will occur spontaneously.
- 3 When a limiting amount of **KMnO**₄ is added to **X**⁻(aq), and the mixture shaken with hexane, the organic layer turns violet.

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

7 Which of the following statements about the Period 3 elements sodium to chlorine, and their compounds, is correct?

- 1 The ionic radius decreases across the period.
- 2 The maximum oxidation state of the elements in their oxides increases across the period.
- 3 The boiling points of the elements decreases in the order phosphorus > sulfur > chlorine.

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

8 The relative atomic mass of iridium, which consists of the isotopes ¹⁹¹Ir and ¹⁹³Ir, is 192.2. What is the percentage of ¹⁹³Ir atoms in the mixture?

- | | | | |
|----------|------|----------|------|
| A | 40 % | B | 45 % |
| C | 55 % | D | 60 % |

- 9 In 2016, several high profile tennis players were banned for consuming the performance-enhancing drug Meldonium.

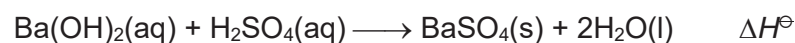


What is the empirical formula of Meldonium?

- | | |
|-------------------------|----------------------------|
| A $C_3HN_2O_2$ | B C_3H_7NO |
| C $C_3H_8N_2O_2$ | D $C_6H_{14}N_2O_2$ |
- 10 When 30 cm^3 of 1.0 mol dm^{-3} $KOH(aq)$ is neutralised with an equal volume of 1.0 mol dm^{-3} $HCl(aq)$, the temperature of the mixture rose by $6.8 \text{ }^\circ\text{C}$.

What would be the temperature change if 15 cm^3 of 2.0 mol dm^{-3} $KOH(aq)$ is reacted with an equal volume of 2.0 mol dm^{-3} $HCl(aq)$?

- | | | | |
|---------------------------------------|---------------------------------------|--|--|
| A $3.4 \text{ }^\circ\text{C}$ | B $6.8 \text{ }^\circ\text{C}$ | C $13.6 \text{ }^\circ\text{C}$ | D $27.2 \text{ }^\circ\text{C}$ |
|---------------------------------------|---------------------------------------|--|--|
- 11 When aqueous $Ba(OH)_2$ reacts with dilute sulfuric acid, the following reaction takes place.



ΔH^\ominus can be calculated using only three of the following enthalpy changes.

Which one of the following is **not** used in the calculation of ΔH^\ominus ?

- | | |
|----------|---|
| A | lattice energy of $BaSO_4$ |
| B | standard enthalpy changes of hydration of Ba^{2+} and SO_4^{2-} |
| C | standard enthalpy change of neutralisation of HCl with $NaOH$ |
| D | standard enthalpy change of solution of $Ba(OH)_2$ |

- 12** The age of rock samples can be calculated using Uranium-Lead dating. ^{235}U is an unstable isotope which decays into ^{207}Pb . This nuclear reaction obeys first-order kinetics with a half-life of 710 million years.

The decay can be summarised by the following equation:

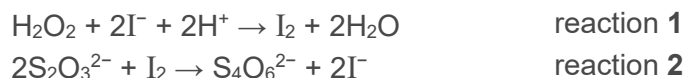


A rock sample had a $^{235}\text{U} : ^{207}\text{Pb}$ ratio = 1 : 7.

Assuming that all the ^{207}Pb detected was formed from the decay of ^{235}U , what is the age of the rock sample?

- | | | | |
|----------|--------------------|----------|--------------------|
| A | 710 million years | B | 1420 million years |
| C | 2130 million years | D | 2840 million years |
- 13** The initial rate of the reaction between H_2O_2 and acidified KI solution can be studied by the “clock” method, using a small but constant amount of $\text{Na}_2\text{S}_2\text{O}_3$.

The equations for the reactions are as follows.



Reaction 2 takes place at a much higher rate than reaction 1.

When the $\text{Na}_2\text{S}_2\text{O}_3$ is used up, the free I_2 produced will form a deep blue complex with starch.

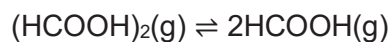
The rate equation for reaction 1 was found to be:

$$\text{rate} = k[\text{I}^-][\text{H}_2\text{O}_2]$$

Assuming no other reactions occur, which of the following statements are correct if a large excess of $\text{S}_2\text{O}_3^{2-}$ were used instead?

- | | |
|----------|--|
| 1 | The mixture will not turn blue-black. |
| 2 | The reaction becomes overall pseudo-first order. |
| 3 | As the reactions proceed, the $[\text{I}^-]$ will remain effectively constant. |
- | | | | |
|----------|--------------|----------|-----------------|
| A | 1 only | B | 2 and 3 only |
| C | 1 and 3 only | D | 1, 2 and 3 only |

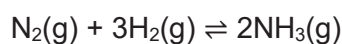
- 14 0.40 dm³ of gaseous (HCOOH)₂ was allowed to dissociate under constant pressure of 1 atm at 300 °C in a gas syringe according to the equation below.



When equilibrium was achieved, the total volume of the mixture increased to 0.60 dm³.

What is the K_p for the reaction at 300 °C?

- A 0.0170 atm B 1.33 atm
 C 800 atm D 135 000 atm
- 15 The K_p values for the Haber Process were determined at different temperatures.

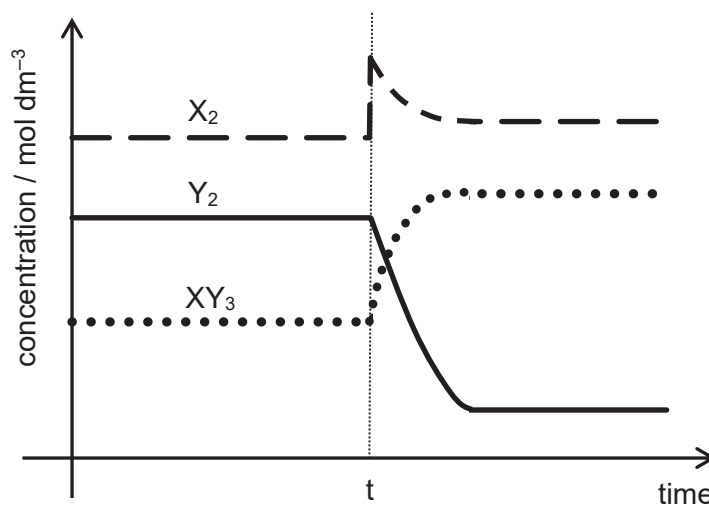
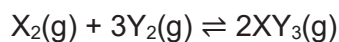


Temperature / °C	K_p
300	4.34×10^{-3}
500	1.45×10^{-5}

Which statement about the standard Gibbs free energy change of the reaction, ΔG^\ominus , is correct?

- A ΔG^\ominus is equal to 0.
 B ΔG^\ominus becomes more positive with increasing temperature.
 C ΔG^\ominus becomes less positive with increasing temperature.
 D No conclusion can be drawn about ΔG^\ominus .

- 16 The concentrations of X_2 , Y_2 and XY_3 in the following gaseous equilibrium were monitored with time.



Which of the following shows the correct changes in rates **immediately after** the change at time, t ?

	forward reaction rate	backward reaction rate
A	increases	unchanged
B	increases	decreases
C	unchanged	decreases
D	decreases	increases

- 17 Which of the following pairs would give a buffer solution of pH 4.1 when the two solutions are mixed? (pK_a of $C_6H_5COOH = 4.22$)

- 1 50 cm^3 of 1 mol dm^{-3} of C_6H_5COOH and 50 cm^3 of 1 mol dm^{-3} of $NaOH$
- 2 175 cm^3 of 1 mol dm^{-3} of C_6H_5COOH and 75 cm^3 of 1 mol dm^{-3} of $NaOH$
- 3 30 cm^3 of 1 mol dm^{-3} of C_6H_5COONa and 40 cm^3 of 1 mol dm^{-3} of C_6H_5COOH

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

18 Which of the following correctly lists 0.10 mol dm^{-3} aqueous solutions of $\text{Cr}(\text{NO}_3)_3$, KCN and NaNO_3 in order of decreasing pH?

- A NaNO_3 , KCN, $\text{Cr}(\text{NO}_3)_3$
 B $\text{Cr}(\text{NO}_3)_3$, NaNO_3 , KCN
 C NaNO_3 , $\text{Cr}(\text{NO}_3)_3$, KCN
 D KCN, NaNO_3 , $\text{Cr}(\text{NO}_3)_3$

19 The following tests were performed on an aqueous solution containing chloride and iodide ions.

Step	Test	Observations
1	Add excess $\text{AgNO}_3(\text{aq})$.	A mixture of white and yellow precipitates was formed.
2	To the mixture from step 1, add excess $\text{NH}_3(\text{aq})$.	The white precipitate dissolved to form a colourless solution. The yellow precipitate was insoluble.
3	Filter the mixture from step 2.	Filtrate was a colourless solution. Residue was a yellow solid.
4	Add KI(s) to filtrate.	

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

- A The K_{sp} for AgCl is higher than that for AgI .
 B In step 2, the addition of $\text{NH}_3(\text{aq})$ results in complexation and momentarily decreases the ionic product of AgCl .
 C In the filtrate from step 3, the ionic product of AgI is less than the K_{sp} of AgI .
 D In step 4, a yellow precipitate was formed.

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

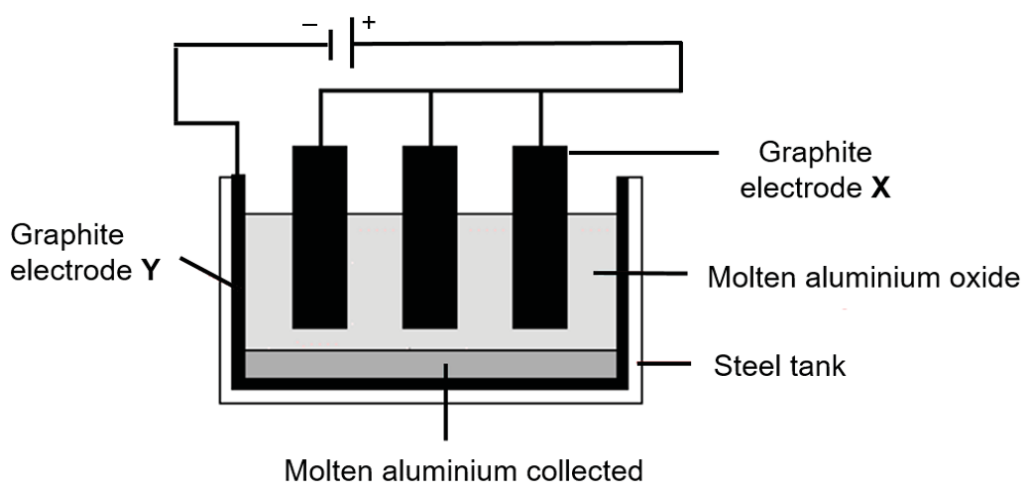
The colours of vanadium-containing ions in aqueous solution are given in the table below.

Species	VO_2^+	VO^{2+}	V^{3+}	V^{2+}
Colour	yellow	blue	green	violet

What is the final colour of the solution when excess aqueous hydrochloric acid is added to a solution containing V^{2+} ions?

- A yellow B blue C green D violet

- 21 Aluminium is extracted from its ore by electrolysis.



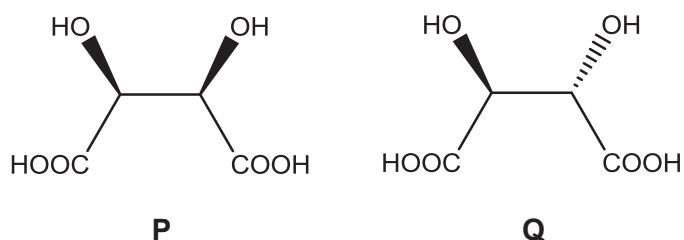
Which of the following statements is correct?

- 1 Oxygen gas is produced.
 - 2 Aluminium ions migrate to electrode X.
 - 3 Electrons move from electrode X to electrode Y.
- A 1 and 2 only B 1 and 3 only
 C 2 and 3 only D 1 only

- 22 What is the electronic configuration of copper in the $[\text{CuCl}_2]^-$ complex ion?

- A $[\text{Ar}] 3d^9$
 B $[\text{Ar}] 3d^{10}$
 C $[\text{Ar}] 3d^9 4s^1$
 D $[\text{Ar}] 3d^9 4s^2$

- 23 Tartaric acid occurs naturally in many plants, most notably in grapes. **P** and **Q** are two stereoisomers of tartaric acid.



Which of the following statements is correct?

- A** Both **P** and **Q** have a plane of symmetry.
- B** **P** and **Q** are cis-trans isomers.
- C** **P** and **Q** are a pair of enantiomers.
- D** An equimolar mixture of **P** and **Q** will rotate plane-polarised light.
- 24 The enzyme chymotrypsin digested tetrapeptide **P** at the carboxylic acid end of the amino acid phenylalanine (Phe).

tetrapeptide **P**: Val–Lys–Phe–Arg

Amino acid	M_r
Val	117
Lys	146
Phe	165
Arg	174

What are the M_r of the two fragments obtained?

	M_r of fragment 1	M_r of fragment 2
A	428	174
B	392	174
C	339	263
D	321	245

- 25 An enantiomer which rotates plane polarised light in a clockwise direction is known as the (+) form. The other enantiomer, which rotates plane polarised light in an anticlockwise direction, is known as the (–) form.

(+)-2-Chlorobutane undergoes two separate reactions as shown below.

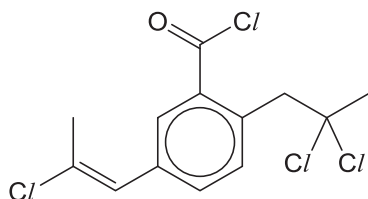
Reaction 1: When (+)-2-chlorobutane is warmed with NaI in a suitable solvent, (–)-2-iodobutane is produced.

Reaction 2: When (+)-2-chlorobutane is warmed with aqueous NaOH, a racemic mixture of butan-2-ol is produced.

Which of the following statements are correct?

- | | | | |
|---|--|---|--------------|
| 1 | Reaction 1 proceeds via a single-step reaction. | | |
| 2 | Reaction 2 proceeds via both S_N1 and S_N2 mechanisms. | | |
| 3 | The rates of both reactions are dependent on the concentrations of the nucleophiles. | | |
| A | 1 only | B | 1 and 3 only |
| C | 2 and 3 only | D | 1 and 2 only |

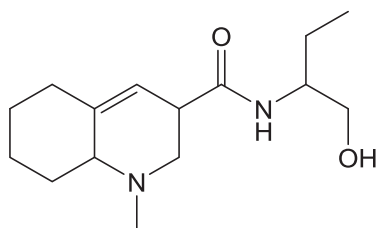
- 26 The following compound is heated with water for a prolonged duration.



Which of the following is a possible product?

- | | | | |
|---|--|---|--|
| A | | B | |
| C | | D | |

- 27 Compound **X** has the following structure.

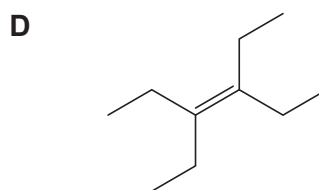
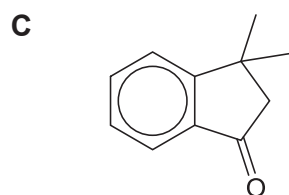
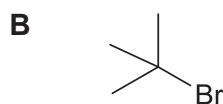
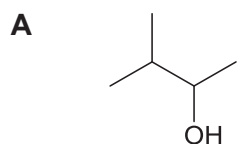


Compound **X** undergoes a complete reaction with reagent **Y**.

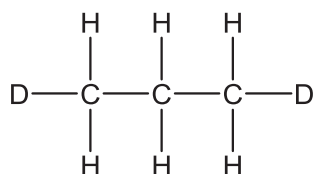
The product of this reaction has the same number of chiral centres as compound **X**.

Which of the following could be reagent **Y**?

- | | | | |
|----------|--------------------|----------|-----------------------------------|
| A | LiAlH ₄ | B | H ₂ , Ni, heat |
| C | HBr | D | cold KMnO ₄ , NaOH(aq) |
- 28 An organic compound, **Z**, is converted into a carboxylic acid using either a one-step or two-step synthesis. Which of the following **cannot** be **Z**?



- 29 Deuterium, D, is a heavy isotope of hydrogen. 1,3-Dideuteriopropene is reacted with limiting chlorine under UV light, so that monochlorination takes place.

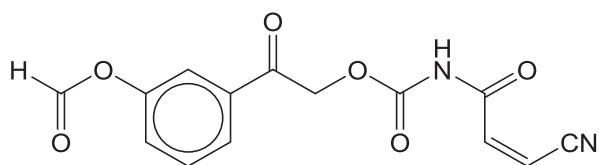


1,3-dideuteriopropene

Assuming that a C–D bond is broken as easily as a C–H bond, what proportion of the monochlorinated products will contain a chiral centre?

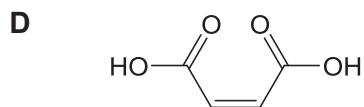
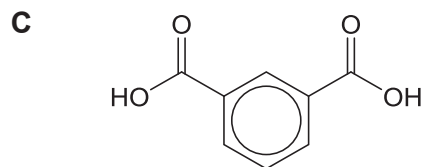
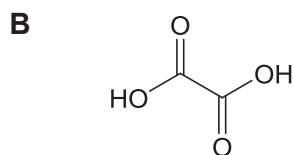
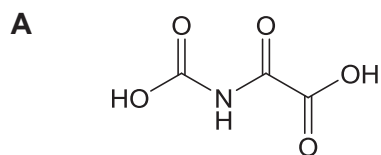
- | | | | | | | | |
|----------|-----|----------|-----|----------|-----|----------|-----|
| A | 33% | B | 40% | C | 50% | D | 66% |
|----------|-----|----------|-----|----------|-----|----------|-----|

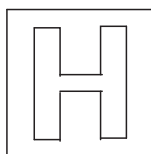
- 30 Compound **S** is heated under reflux with acidified potassium dichromate(VI).



compound **S**

What is a possible product from the reaction?





**RAFFLES INSTITUTION
2017 YEAR 6 PRELIMINARY EXAMINATION**

Higher 2



CANDIDATE
NAME

CLASS

INDEX NUMBER

CHEMISTRY

9729/02

Paper 2 Structured Questions

**11 September 2017
2 hours**

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, class and index number in the spaces provided at the top of this page.

Write in dark blue or black pen.

You may use a HB pencil for any diagrams or graphs.

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

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

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

A Data Booklet is provided. Do not write anything in it.

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

For Examiner's Use	
1	/ 9
2	/ 11
3	/ 12
4	/ 13
5	/ 23
6	/ 7
Total	/ 75

This document consists of **25** printed pages.

- 1 (a) Draw a fully labelled diagram to show how you would measure the *standard electrode potential* of a $\text{Zn}^{2+}(\text{aq})/\text{Zn}(\text{s})$ half-cell.

[3]

- (b) The button cell used in watches is based on the following half-cells:



- (i) Write an overall equation for the reaction taking place in the button cell during use.

.....[1]

- (ii) State which species is oxidised and which is reduced in this cell during use.

species being oxidised:

species being reduced: [1]

(iii) Calculate the standard cell potential, $E_{\text{cell}}^{\ominus}$, for the above button cell.

[1]

(iv) Use your answer to part (b)(iii) to calculate the standard Gibbs free energy change, ΔG^{\ominus} , for the reaction in this cell.

[1]

(v) Predict the effect on the value of E_{cell} if water is added to the $\text{Ag}_2\text{O}/\text{Ag}$ half-cell. Explain your answer.

.....
.....
.....
.....
.....[2]

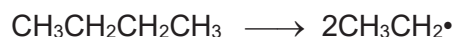
[Total: 9]

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

Hydrocarbon cracking is a process whereby a hydrocarbon is broken down into smaller, more useful alkanes and alkenes.

Many chemical reactions that take place during the cracking process involve free radicals. In the initiation step, a C–C bond is broken rather than a C–H bond.

For example,



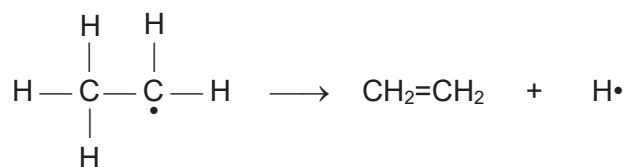
(a) (i) Explain what is meant by a *free radical*.

.....[1]

(ii) Suggest a reason why the initiation step involves breaking a C–C bond, rather than a C–H bond.

.....[1]

(b) One of the reactions which forms ethene is shown below.



Using curly arrows, show clearly the movement of electrons in the above reaction. [1]

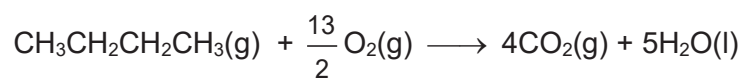
(c) (i) Write a balanced equation to show the cracking of gaseous butane to form ethene as the only organic product.

.....[1]

(ii) Determine the enthalpy change of reaction for your answer in (c)(i).

[1]

- (d) Using the information provided below and your answer to (c)(ii), determine the enthalpy change of combustion of butane by drawing an energy cycle.



- Enthalpy change of formation of $\text{CH}_2=\text{CH}_2(\text{g})$ $+52.5 \text{ kJ mol}^{-1}$
- Enthalpy change of combustion of $\text{H}_2(\text{g})$ $-285.8 \text{ kJ mol}^{-1}$
- Enthalpy change of combustion of $\text{C}(\text{s})$ $-393.5 \text{ kJ mol}^{-1}$

[3]

- (e) With the aid of a sketch of the Boltzmann distribution curve, explain how an increase in temperature increases the rate of a chemical reaction.

.....

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.....

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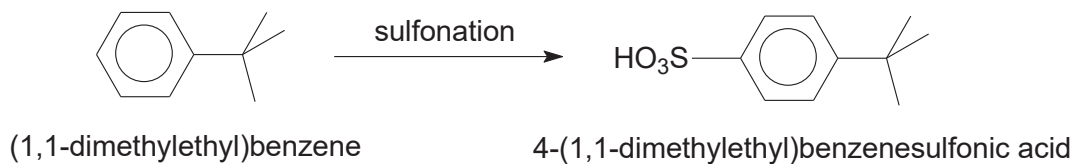
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.....

..... [3]

[Total: 11]

When (1,1-dimethylethyl)benzene undergoes sulfonation, the organic product obtained is almost entirely 4-(1,1-dimethylethyl)benzenesulfonic acid.



- (b) (i)** Explain whether (1,1-dimethylethyl)benzene undergoes sulfonation at a slower or faster rate than benzene.

.....

.....

.....

.....[1]

- (ii)** Explain why 2-(1,1-dimethylethyl)benzenesulfonic acid is not produced in the above sulfonation reaction.

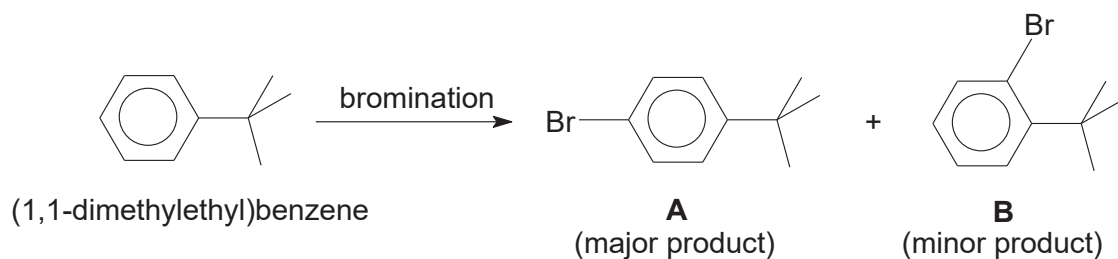
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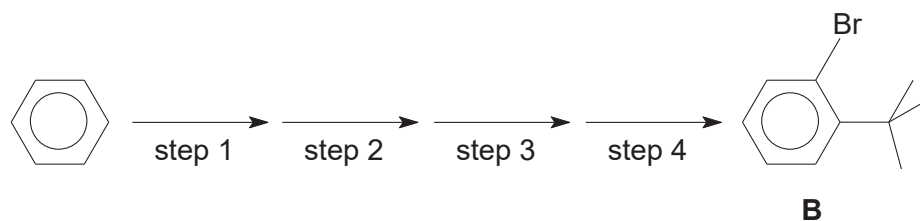
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.....[1]

When (1,1-dimethylethyl)benzene undergoes bromination, two organic products are obtained. The major organic product is compound **A** while the minor organic product is compound **B**.



(c) When benzene undergoes a four-step reaction pathway, it is converted to compound **B** *only*. This is because each step produces only one organic product.



Using the fact that the sulfonation reaction can be reversed, suggest reagents and conditions for each of the four steps shown above.

step 1:

step 2:

step 3:

step 4:

[3]

(d) Compounds **C** and **D** are isomers of (1,1-dimethylethyl)benzene.

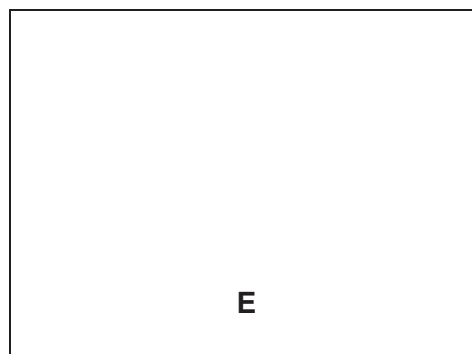
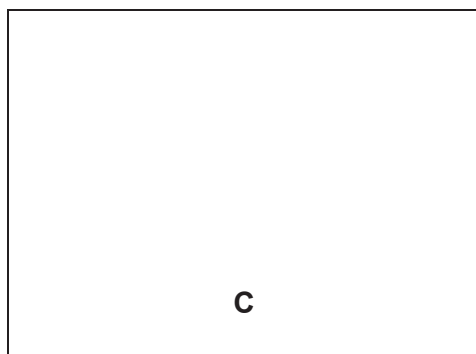
(i) Compound **C** does not display *cis-trans* isomerism nor enantiomerism.

When **C** reacts with chlorine in the presence of ultraviolet light, four monochlorinated constitutional isomers are formed.

When one of these monochlorinated isomers is treated with aluminium chloride, compound **E**, $C_{10}H_{12}$, is the only organic product obtained.

When **E** is heated under reflux with acidified potassium manganate(VII), benzene-1,2,3-tricarboxylic acid is the only organic product obtained.

Suggest a suitable structure each for compounds **C** and **E**.



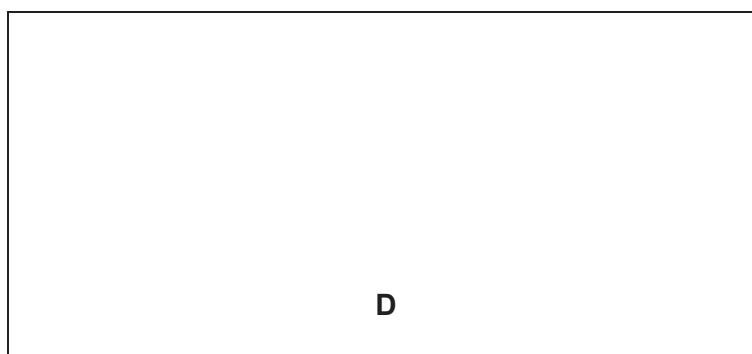
[2]

(ii) Compound **D** displays *cis-trans* isomerism but not enantiomerism.

One mole of **D** reacts with four moles of bromine in the dark.

When **D** is heated under reflux with acidified potassium manganate(VII), ethanoic acid is the only organic product obtained.

Draw a skeletal formula to show the stereoisomer of **D** in which all the carbon-carbon double bonds in the molecule are in the *cis* arrangement.

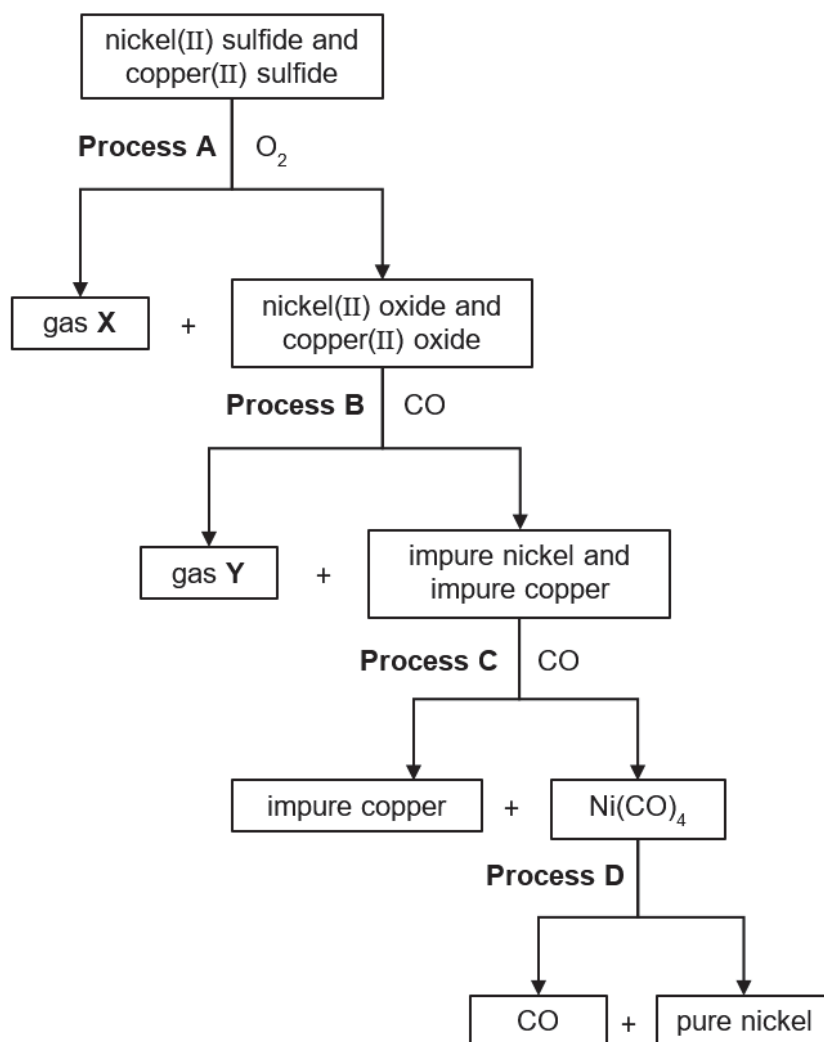


[1]

[Total: 12]

- 4 Nickel is a transition element in the d-block of the Periodic Table. It is commonly used as a catalyst and as an alloying ingredient.

The flow diagram below shows part of the process of extraction and purification of nickel from its ore.



- (a) Identify the following two gases produced from **Process A** and **Process B**:

gas X:

gas Y:

[1]

- (b) State the role of carbon monoxide in each of the following processes:

Process B:

Process C:

[1]

The reaction taking place in **Process C** can be represented by the equation below.



The standard entropies, S^\ominus , of the substances involved in this reaction are given below.

	Ni(s)	CO(g)	Ni(CO) ₄ (g)
$S^\ominus / \text{J mol}^{-1} \text{K}^{-1}$	+29.9	+197.7	+410.6

(c) (i) Calculate the standard entropy change, ΔS_r^\ominus , for the above reaction.

[1]

(ii) Comment on the sign of ΔS_r^\ominus calculated in (c)(i).

.....

 [1]

(d) Determine the temperature below which the above reaction is spontaneous.

[2]

- (e) The purification of nickel is carried out via **Processes C** and **D**.

With the aid of your answer in (d) and given that the boiling point of $\text{Ni}(\text{CO})_4$ is 43°C , suggest suitable temperatures for these two processes and explain your answers.

Process C:

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.....

.....

.....

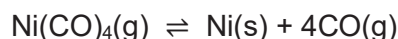
Process D:

.....

.....

..... [2]

- (f) The equilibrium constant, K_p , for the decomposition reaction given below is 1.01 atm^3 at $T \text{ K}$.



In a study, some $\text{Ni}(\text{CO})_4(\text{g})$ was placed in a 2 dm^3 container at $T \text{ K}$ and the decomposition reaction was allowed to take place until equilibrium was reached. The partial pressure of $\text{CO}(\text{g})$ at equilibrium was found to be 1.50 atm .

- (i) Calculate the partial pressure of $\text{Ni}(\text{CO})_4$ at equilibrium.

[1]

- (ii) Hence calculate the initial pressure of $\text{Ni}(\text{CO})_4$ in the container.

[1]

Nickel forms many compounds including nickel(II) carbonate and nickel(II) nitrate. Nickel(II) carbonate undergoes thermal decomposition to give similar products as the carbonates of Group 2 elements.

- (g) (i)** Describe and explain the trend in the thermal stabilities of the carbonates of Group 2 elements.

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.....[2]

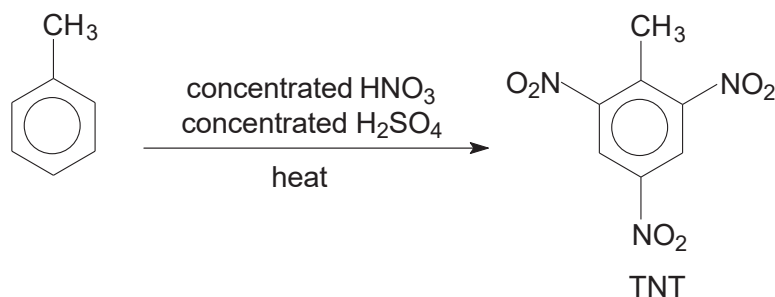
- (ii)** By quoting relevant data from the *Data Booklet*, state whether nickel(II) carbonate would decompose at a higher or lower temperature than calcium carbonate.

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

[Total: 13]

5 This question explores the characteristics of explosives.

- (a) 2,4,6-Trinitrotoluene, commonly known as TNT, is an explosive invented in 1863 and it is still widely used in the military. It can be produced from methylbenzene as shown below.



In this reaction, concentrated H_2SO_4 acts as a Brønsted-Lowry acid.

- (i) Define *Brønsted-Lowry acid*.

.....[1]

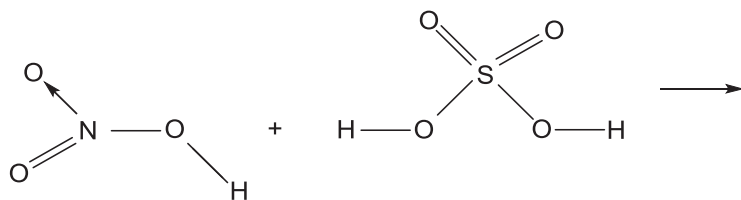
- (ii) In the reaction above, concentrated HNO_3 reacts with concentrated H_2SO_4 to generate NO_2^+ . The mechanism involves the following two steps.

- In step 1, a lone pair of electrons from the oxygen atom of the O—H group in HNO_3 is donated to a hydrogen atom in H_2SO_4 to form H_2NO_3^+ .
- In step 2, H_2O is lost from H_2NO_3^+ to produce NO_2^+ .

Complete the diagram below to suggest a mechanism to show how NO_2^+ is formed. Show the following:

- all charges and relevant lone pairs;
- displayed formulae of all compounds;
- and the movement of electron pairs by using curly arrows.

Step 1:



Step 2:

[3]

(b) The heat liberated in an explosion raises the temperature of the gaseous products.

(i) In an explosion, explosives produce different products. The products of explosion of solid TNT, $C_7H_5N_3O_6$, are determined according to the Kistiakowsky-Wilson Rules:

1. Hydrogen atoms are converted to steam.
2. If any oxygen remains, then carbon is converted to carbon monoxide.
3. Any excess carbon remains as elemental carbon.
4. All the nitrogen is converted to nitrogen gas.

By using the Kistiakowsky-Wilson Rules, construct a balanced equation, including state symbols, for the explosion of TNT.

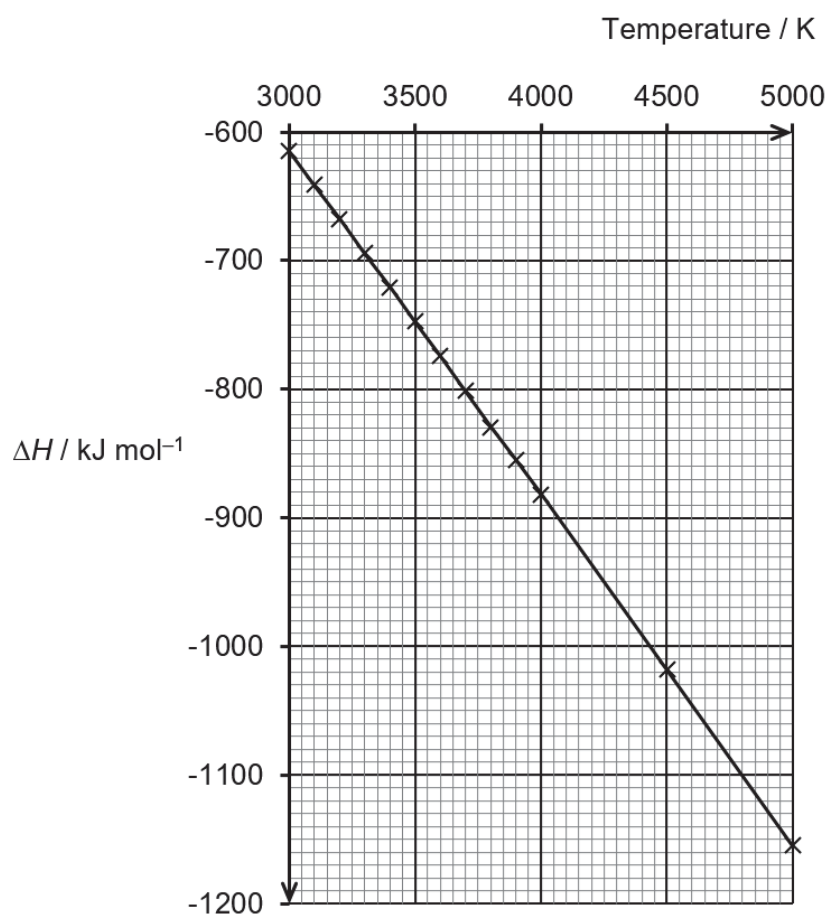
..... [1]

(ii) By using relevant enthalpy change of formation data below, calculate the enthalpy change of explosion of TNT.

Substance	$\Delta H_f / \text{kJ mol}^{-1}$
TNT	-63.2
water	-285.8
steam	-241.8
carbon dioxide	-393.5
carbon monoxide	-110.5

[2]

- (iii) The graph below shows the enthalpy change of explosion of TNT, ΔH , at various temperatures.



Based on the value obtained from (b)(ii), estimate the temperature of explosion of TNT.

Temperature of explosion of TNT = K [1]

- (c) The amount of heat liberated during an explosion of TNT can be increased by the addition of a metal.

- (i) Complete the following table.

Metal	Estimated cost per gram	Enthalpy change of explosion of metal, ΔH / kJ mol ⁻¹	Heat released on explosion of metal / kJ g ⁻¹
Aluminium	\$0.238	-834.3	
Magnesium	\$0.160	-602.6	
Zinc	\$0.109	-353.2	

By also considering the cost of each metal, suggest the most **suitable** metal that could be used to raise the amount of heat liberated during an explosion of TNT. Explain your choice.

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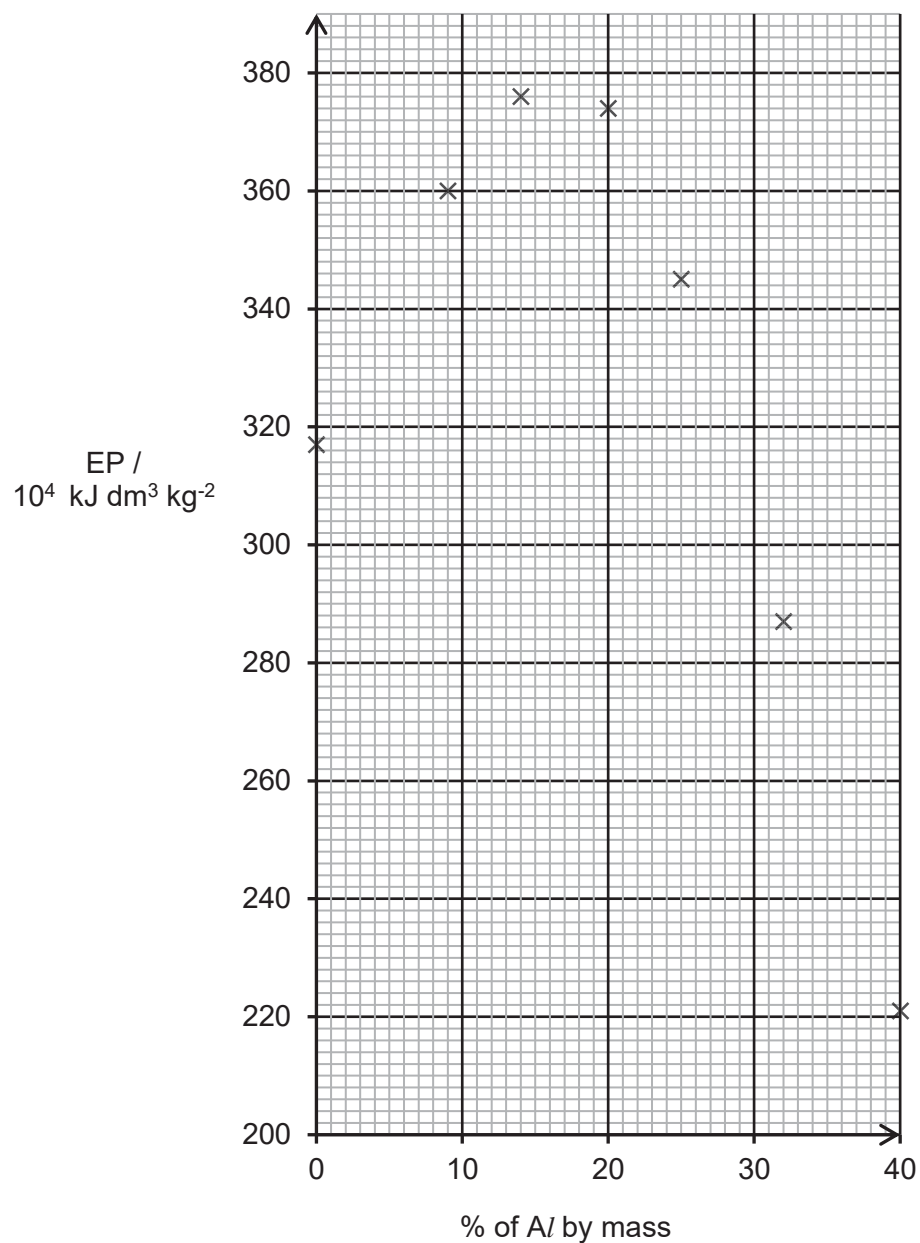
.....

.....[3]

The Explosive Power (EP) of a substance can be expressed as:

$$\text{EP} = \frac{\text{Heat released on explosion}}{(\text{kJ kg}^{-1})} \times \frac{\text{Volume of gases evolved on explosion}}{(\text{dm}^3 \text{ kg}^{-1})}$$

Adding a suitable amount of aluminium to TNT increases its EP as shown below.



- (ii) By drawing a suitable graph above, determine the percentage of Al by mass that gives rise to the maximum EP and the corresponding maximum EP.

% of Al by mass = %

Maximum EP = $\text{kJ dm}^3 \text{ kg}^{-2}$

[2]

(iii) 1 kg of aluminised TNT releases 586 dm³ of gases at its maximum EP.

Calculate the amount of heat released in an explosion of 1 kg of aluminised TNT at its maximum EP. Express your answer in kJ kg⁻¹.

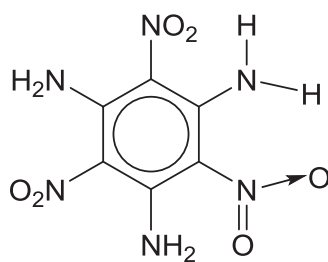
[1]

(iv) 1 kg of TNT, C₇H₅N₃O₆, and 1 kg of aluminised TNT were separately exploded.

By referring to your answer in (c)(iii) and that in (b)(ii) on page 16, calculate the difference in the amount of heat released. Express your answer in kJ kg⁻¹.

[2]

- (d) TATB, $C_6H_6N_6O_6$, is a powerful explosive with the following structure. It was evaluated for use in the military in the 1960s.



TATB

- (i) Write down the name of TATB according to the IUPAC nomenclature for organic compounds.

.....[1]

- (ii) On the diagram above, illustrate one intramolecular hydrogen bond between the $-NO_2$ and the $-NH_2$ groups in one molecule of TATB. [1]

- (iii) The carbon–nitrogen (C–N) bond lengths of some compounds are shown below:

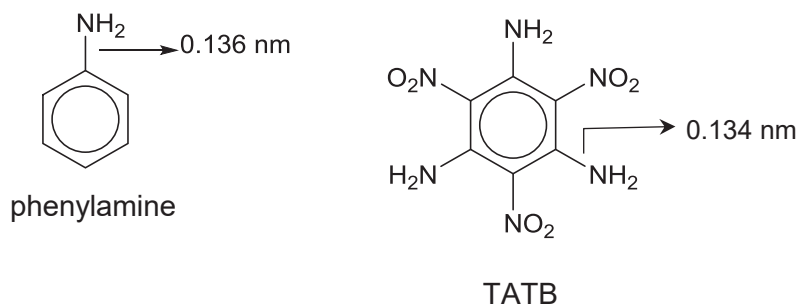
Compound	C–N bond length / nm
methylamine	0.147
nitrobenzene	0.147
phenylamine	0.136

Explain why the C–N bond in phenylamine is shorter than the C–N bond in nitrobenzene.

.....

[1]

(iv) The C–N bond lengths of phenylamine and TATB are shown below:

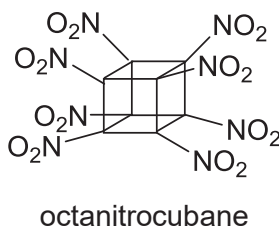


Suggest a reason why the indicated C–N bond in TATB is shorter than the C–N bond in phenylamine.

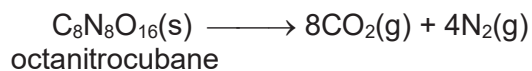
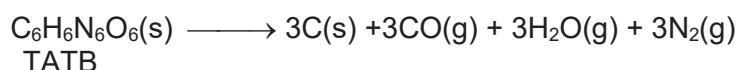
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[1]

(e) There is a continuing search for more powerful materials which can be used as potential explosives and propellants in the future. Octanitrocubane, C₈N₈O₁₆, may be one such example.



TATB and octanitrocubane explode to give the products as shown below.



Some data of TATB and octanitrocubane are given below.

Explosive	M_r	Heat released on explosion / kJ kg ⁻¹	Density / g cm ⁻³
TATB	258.0	3498	1.80
octanitrocubane	464.0	7648	2.10

- (i) Using the relationship given on page 19,

$$\text{EP} = \frac{\text{Heat released on explosion (kJ kg}^{-1}\text{)}}{\text{Volume of gases evolved on explosion (dm}^3\text{ kg}^{-1}\text{)}} \times$$

calculate $\frac{\text{EP of TATB}}{\text{EP of octanitrocubane}}$ at constant temperature and pressure.

[2]

- (ii) By referring to the information given, suggest one advantage (other than EP) for using octanitrocubane as an explosive in the future.

.....

[1]

[Total: 23]

- 6 (a) Aluminium hydroxide is a sparingly soluble salt with a K_{sp} value of 3.3×10^{-34} .

In an experiment, solid sodium hydroxide is gradually added to a solution containing $1.00 \times 10^{-20} \text{ mol dm}^{-3}$ of aluminium chloride.

Calculate the pH of the solution when aluminium hydroxide starts to precipitate.

[2]

- (b) People who suffer from excessive sweating often use antiperspirants which help to reduce sweating by direct action on the sweat glands. Aerosol antiperspirants contain a compressed gas, such as butane, which transports the active ingredients out of the bottle when the valve is open.

- (i) A 150 cm^3 bottle of antiperspirant contains 1.10 g of butane. Calculate the pressure in the bottle at room temperature.

[1]

- (ii) When spraying the aerosol antiperspirant, a cooling sensation is felt on the skin.

By considering the intermolecular forces between the butane molecules, briefly explain why the release of butane from the can (a region of high pressure) onto the skin (a region of low pressure) gives rise to the cooling sensation.

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.....[2]

- (c) Aluminum chlorohydrate, $Al_2(OH)_5Cl$, is the main active ingredient in many antiperspirants.

Studies show that the sweat pores are blocked when aluminum chlorohydrate mixes with sweat.

- (i) When mixed with water, $Al_2(OH)_5Cl$ dissociates completely to form Cl^- and $Al_2(OH)_5^+$ ions. The $Al_2(OH)_5^+$ ion undergoes hydrolysis to form a mildly acidic solution. Aluminium hydroxide is also formed in the process.

Write an equation for the hydrolysis of $Al_2(OH)_5^+$.

.....[1]

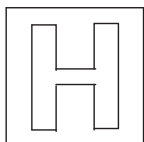
- (ii) Using the information above, describe how aluminium chlorohydrate is able to function as an antiperspirant.

.....

.....

.....[1]

[Total: 7]



**RAFFLES INSTITUTION
2017 YEAR 6 PRELIMINARY EXAMINATION**

Higher 2



CHEMISTRY

Paper 3 Free Response

9729/03

15 September 2017

2 hours

Candidates answer on separate paper.

Additional Materials: Answer Paper
 Data Booklet

READ THESE INSTRUCTIONS FIRST

Do not open this question booklet until you are told to do so.

Write your name, class and 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 soft pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Section A

Answer **all** questions.

Section B

Answer **one** question.

Begin each question on a fresh sheet of paper.

A Data Booklet is provided. Do not write anything in it.
You are reminded of the need for good English and clear presentation in your answers.

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

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

This document consists of **13** printed pages and **1** blank page.

Section A

Answer **all** questionsBegin **each** question on a **fresh sheet** of paper.

- 1 Iron is a transition metal found in mineral ores where it exists in either the +2 or +3 oxidation state.

Potassium is a Group 1 metal which is found in the same Period as iron. However, they differ significantly in their chemical and physical properties.

- (a) (i) Explain briefly why iron can be found in variable oxidation states in various compounds, but potassium exists in only one stable oxidation state in its compounds. [2]

- (ii) Explain why iron has a significantly higher melting point (1535 °C) than potassium (63.5 °C). [2]

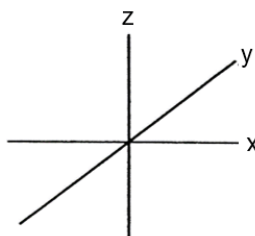
- (b) Iron, like other transition elements, displays a strong tendency to form complexes with ligands such as H_2O and CN^- .

- (i) Explain how CN^- is able to act as a ligand. [1]

In a free, gas-phase transition metal ion, the d orbitals all have the same energy. When the ion is in an octahedral complex, the orbitals are split into two energy levels.

- (ii) Using the Cartesian axes like those shown below, draw separate labelled diagrams of

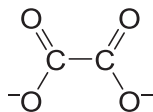
- (I) one of the d orbitals at the **lower** energy level in an octahedral complex,
(II) one of the d orbitals at the **higher** energy level in an octahedral complex.



[2]

- (iii) Using your diagrams in (b)(ii), explain why the d subshell of a transition metal ion is split into two energy levels in an octahedral complex. [2]
- (iv) How does this splitting help to explain why transition metal complexes are often coloured? Use a fully labelled diagram to illustrate your answer for an octahedral complex. [3]
- (c) An example of a complex of iron is the hexacyanoferrate(III) ion, $[\text{Fe}(\text{CN})_6]^{3-}$. Its potassium salt $\text{K}_3[\text{Fe}(\text{CN})_6]$ can be synthesised from the following steps.
- Step 1** Pale green aqueous FeSO_4 is boiled with an excess of KCN, producing a yellow solution which contains $[\text{Fe}(\text{CN})_6]^{4-}$ ions.
- Step 2** The yellow solution is acidified, then chlorine is bubbled into the solution forming a red solution.
- Step 3** The red solution is evaporated to give dark red crystals containing $[\text{Fe}(\text{CN})_6]^{3-}$ ions.
- (i) The complex ion $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ is responsible for the green colour of aqueous FeSO_4 .
- Write an appropriate equation to account for the colour change in **Step 1** and state the type of reaction that has occurred. [2]
- (ii) By considering your answer in (b)(iv), suggest why $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{Fe}(\text{CN})_6]^{4-}$ have different colours. [1]
- (iii) By using relevant data from the *Data Booklet*, predict whether iodine can be used instead of chlorine to carry out the reaction in **Step 2**. [1]

- (d) The ethanedioate anion, $\text{C}_2\text{O}_4^{2-}$, has the following structure and is commonly used as a ligand to form complexes with iron.

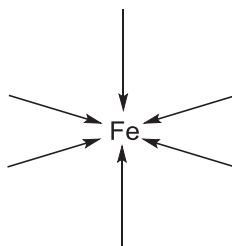


The reaction of iron(III) chloride with potassium ethanedioate, $\text{K}_2\text{C}_2\text{O}_4$, produces a salt, **Y**, which has the following composition by mass.

K, 27.9%; Fe, 13.3%; Cl, 16.9%; C, 11.4%; O, 30.5%

One formula unit of **Y** contains a cation and an iron-containing complex anion in a 3:1 ratio.

- (i) Determine the empirical formula of the salt **Y**. [2]
- (ii) Suggest the chemical formula of the complex anion in **Y**. [1]
- (iii) Copy the following diagram onto your writing paper.



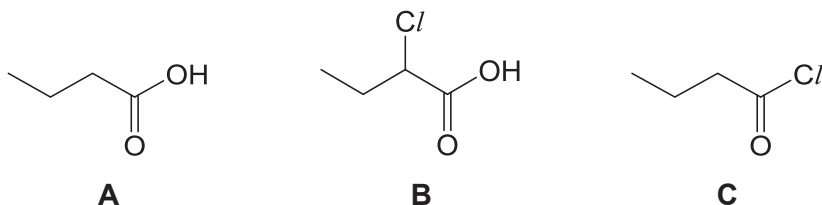
Complete the diagram to suggest the structure for this complex anion. [1]

[Total: 20]

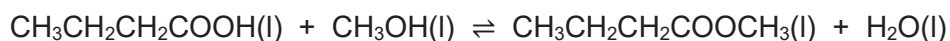
2 This question discusses the chemistry of carboxylic acids and its derivatives.

- (a) When 1 mole of each of the following three compounds was dissolved in 1 dm³ of water, acidic solutions of different pH were obtained.

Arrange the three compounds in order of increasing pH of their aqueous solutions and explain your reasoning. [3]



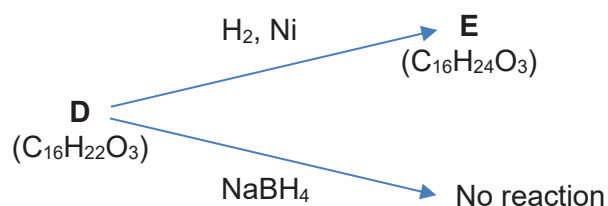
- (b) Butanoic acid undergoes esterification with methanol to produce methyl butanoate which gives the distinct aroma of apples in certain perfumes.



- (i) Write an expression for the equilibrium constant for the above reaction, K_c . [1]
- (ii) Given that $K_c = 4.15$ at 298 K, calculate the amount of ester present at equilibrium, when two moles of butanoic acid are reacted with two moles of methanol. [1]
- (iii) State Le Chatelier's Principle and use it to predict the effect on the yield of the ester when water is removed. [2]

(c) Compound **D** is an ester with the molecular formula, $C_{16}H_{22}O_3$.

When **D** was treated with different reducing agents, the following observations were made.



E exhibits enantiomerism whereas **D** does not. **D** reacts fully with aqueous bromine in the ratio 1:2.

On heating with acidified potassium manganate(VII), **D** gives 3 organic products, **F**, $C_8H_6O_5$, **G**, $C_4H_{10}O$ and **H**, C_3H_6O .

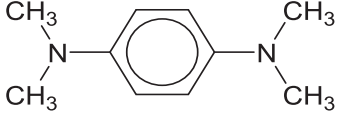
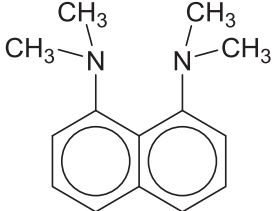
- 1 mole of **F** reacts with 2 moles of $SOCl_2$.
- Effervescence is observed when a small piece of sodium metal is added to **G**.
- **H** gives an orange precipitate, **J**, with 2,4-dinitrophenylhydrazine.

Suggest structures for **D** – **H** and **J**, and explain the observations described above.
[13]

[Total: 20]

3 This question discusses the chemistry of phenylamines and its derivatives.

(a) TMPD and DMAN are *Lewis bases*. The following table compares their pK_b values.

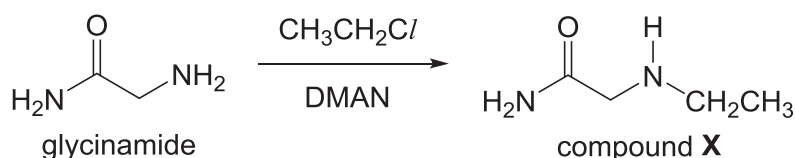
Base	Structure	pK_{b1}	pK_{b2}
TMPD		7.7	11.7
DMAN		1.7	23.0

(i) Explain what is meant by *Lewis base*. [1]

(ii) Draw the displayed formula for the conjugate acid of DMAN and use it to explain why the pK_{b1} of DMAN is *so much less* than the pK_{b1} of TMPD. [2]

(iii) By discussing its property as a *Lewis base*, explain why the pK_{b2} of DMAN is *so much greater* than the pK_{b2} of TMPD. [1]

(b) In an experiment, glycineamide reacted with chloroethane, in the presence of DMAN, to form compound **X**.



(i) The first step of the mechanism involves a S_N2 reaction between glycineamide and chloroethane. DMAN acts as a base in the second step to liberate compound **X**.

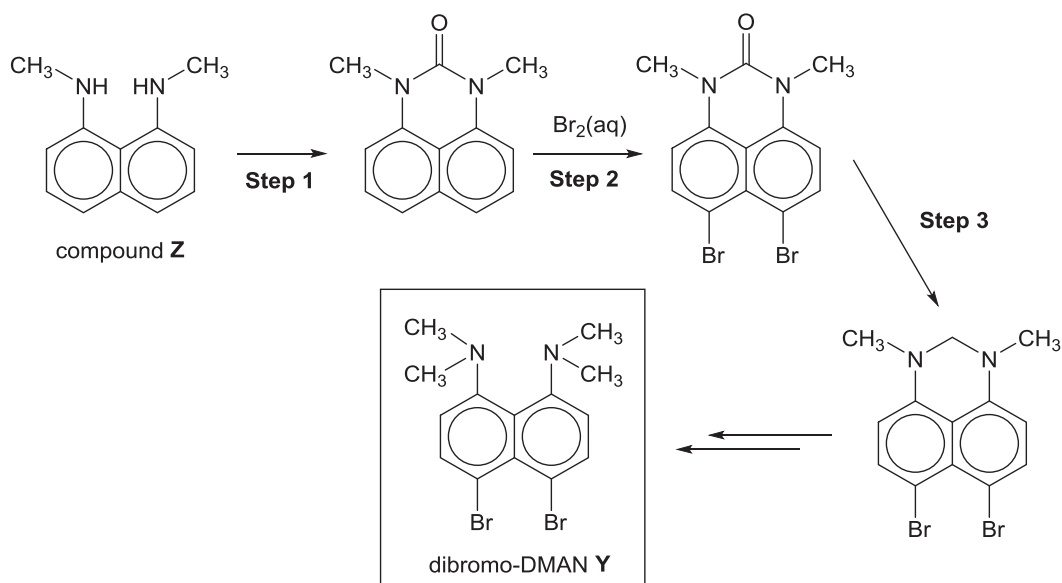
Draw a mechanism for the reaction to form compound **X**. You may abbreviate glycineamide as $R-NH_2$. Show relevant lone pairs and dipoles, using curly arrows to indicate the movement of electron pairs. [4]

- (ii) DMAN is chosen for this reaction because it is a *non-nucleophilic base*.

Suggest a reason why DMAN is unable to act as a nucleophile, but is still able to act as a base. [2]

- (iii) The nitrogen atom on the $-\text{CONH}_2$ group of glycnamide does not react even in the presence of large excess of chloroethane. Explain why. [1]

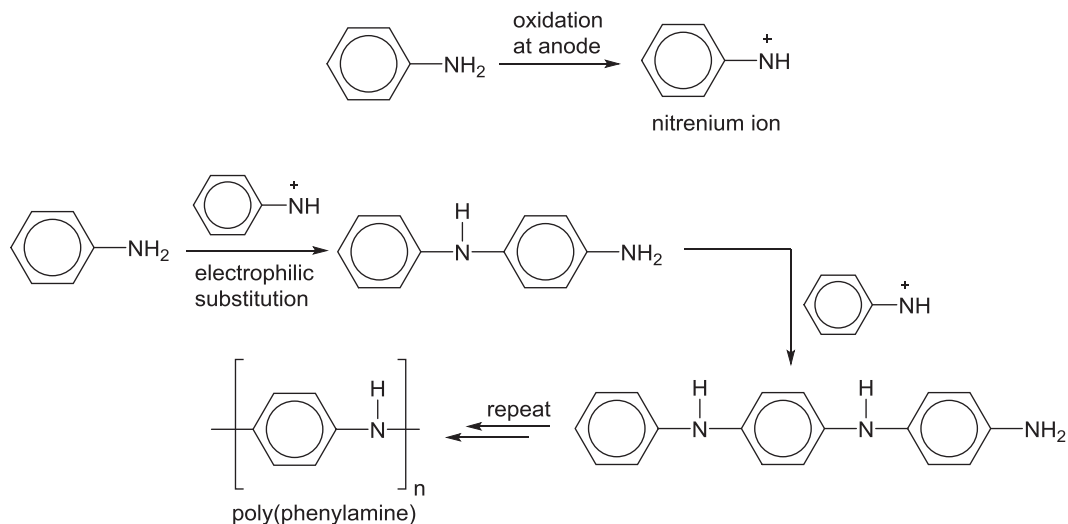
- (c) The following reaction scheme shows how dibromo-DMAN **Y** can be prepared from compound **Z**.



- (i) Suggest reagents and conditions to carry out **steps 1** and **3**. [2]
- (ii) Draw the structure of the product formed in the reaction between compound **Z** and $\text{Br}_2(\text{aq})$. Hence explain why **step 1** is necessary in the synthesis of dibromo-DMAN **Y**. [2]

- (d) Poly(phenylamine) has captured the attention of the scientific community due to its high electrical conductivity.

Recent methods to prepare poly(phenylamine) involve the use of electrochemical oxidation at the anode followed by electrophilic substitution of another phenylamine molecule.



- (i) Suggest a reason why poly(phenylamine) has high electrical conductivity. [1]
- (ii) Write the half-equation for the oxidation of phenylamine to the nitrenium ion, given that it occurs in acidic medium. [1]
- (iii) During the oxidation, a current of 2.0 A was passed through for 5 min. Calculate the amount, in moles, of nitrenium ions produced in that time. [2]
- (iv) Use your answer from (d)(iii) to calculate the number of repeat units in the polymer assuming all the nitrenium ions produced polymerised into one poly(phenylamine) chain. Give your answer to three significant figures. [1]

[Total: 20]

Section B

Answer **one** question from this section.

- 4 (a) PH_3 is part of a series of Group 15 compounds with the formula XH_3 .

The boiling points of some XH_3 compounds are given below.

	NH_3	PH_3	AsH_3	SbH_3
Boiling point / $^\circ\text{C}$	-34.5	-87.5	-62.4	-18.4

Describe and explain the trend in their boiling points. [3]

- (b) Describe the reactions, if any, of the oxides P_4O_{10} and Al_2O_3 with water. Include the approximate pH value of any resulting solutions, and write equations, with state symbols, for any reactions that occur. [3]

- (c) Phosphorus halides can be used to convert alcohols to halogenoalkanes in the absence of water.

When ethanol is reacted with phosphorus pentachloride, phosphorus oxychloride, POCl_3 , is produced as one of the products.

- (i) Explain why this reaction must be carried out in the absence of water. [1]

- (ii) Write a balanced equation for this reaction and state any observations. [2]

- (iii) Draw a dot-cross diagram to show the bonding in POCl_3 and predict its shape. Explain your answer using the Valence Shell Electron Pair Repulsion theory. [2]

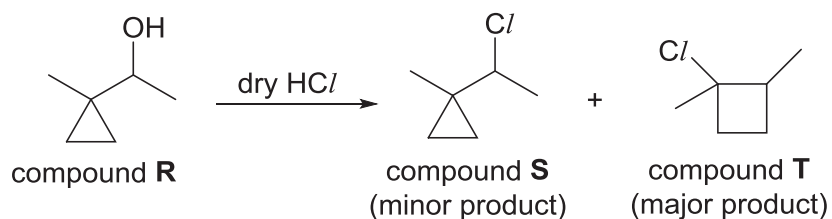
- (d) The conversion of alcohols to halogenoalkanes can also be achieved by using hydrogen halides.

When ethanol is reacted separately with dry HCl and HBr , $\text{CH}_3\text{CH}_2\text{Cl}$ and $\text{CH}_3\text{CH}_2\text{Br}$ are produced respectively.

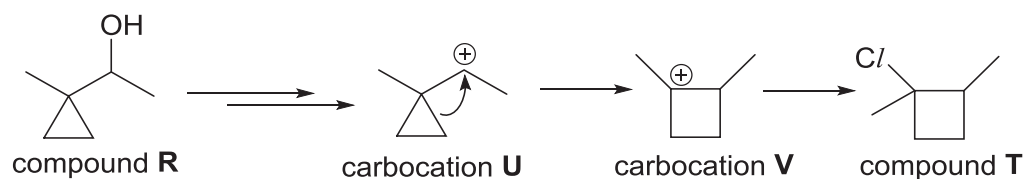
- (i) Suggest a simple chemical test to distinguish between these two halogenoalkanes. [2]

- (ii) Suggest and explain how the rate of hydrolysis for $\text{CH}_3\text{CH}_2\text{Br}$ and $\text{CH}_3\text{CH}_2\text{Cl}$ differ. [2]

When compound **R** was treated with dry HCl , compound **T** was obtained as the major product instead of the expected compound **S**.

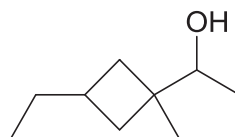


The simplified mechanism for the formation of compound **T** is shown below. A carbocation rearrangement occurs converting **U** to **V**.



(iii) By considering the information above, explain fully why compound **T** was obtained as the major product. [4]

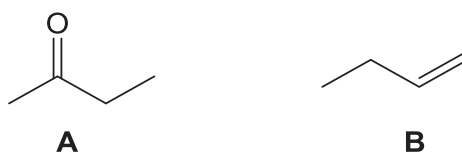
(iv) Suggest the structure of the major chloroalkane formed if the following alcohol was used instead of compound **R**.



[1]

[Total: 20]

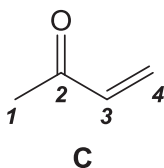
- 5 Two four-carbon containing organic compounds are shown below.



Although both compounds contain unsaturated bonds, C=O or C=C, the reactions they undergo are different.

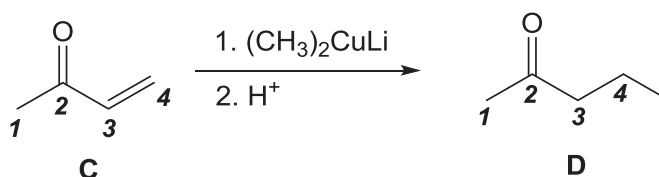
- **A** reacts with cold HCN with a trace amount of NaCN but **B** does not.
 - On the other hand, **B** reacts with dry HBr but **A** does not.
- (a) (i) Name the type of reaction undergone by **A** with cold HCN with a trace amount of NaCN, and draw the structure of the product formed in the reaction. [2]
- (ii) Explain why the C=O group in **A** reacts with HCN but the C=C group in **B** does not. [2]
- (iii) Describe the mechanism undergone by compound **B** when it reacts with dry HBr. In your answer, draw the structure of the major product as well as any relevant lone pairs, dipole charges and indicate the movement of electron pairs with curly arrows. [3]
- (iv) Explain why the resultant mixture formed in (a)(iii) is optically inactive. Support your answer with three-dimensional diagrams. [2]

Compound **C** is a four-carbon organic compound that contains both C=O and C=C double bonds.



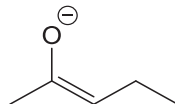
The close proximity of C=O to C=C polarises the C=C bond, causing C4 to also be electron deficient. This causes C4 to be susceptible to attacks from nucleophilic reagents such as the Gilman reagent.

(CH₃)₂CuLi is an example of a Gilman reagent which reacts with **C** in the following reaction.



- (b) (i) The reaction between **C** and the Gilman reagent proceeds via the following two steps.

- In the slow step, the nucleophile $:\text{CH}_3^-$ attacks the $\text{C}=\text{C}$ to give a reactive intermediate with a negative charge on O as shown below.



- The reactive intermediate then reacts with an H^+ ion to give **D**.

Use the information provided to describe the mechanism for this reaction. Show any relevant lone pairs and indicate the movement of electron pairs with curly arrows. [3]

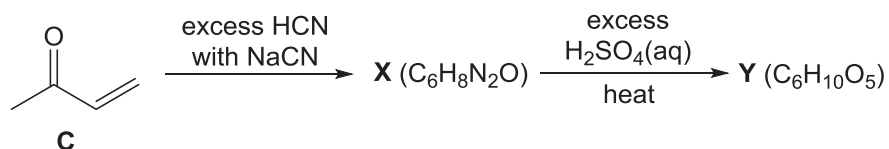
- (ii) Given that the enthalpy change of the Gilman reaction is exothermic, draw the energy profile diagram for the reaction.

On the diagram, label

- the axes,
- the enthalpy change of reaction, ΔH^\ominus ,
- the activation energies.

[3]

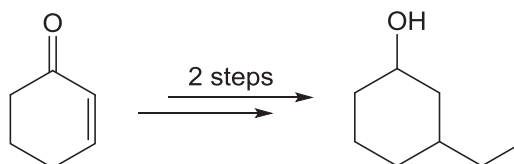
- (iii) Compound **C** was used as the starting material for the following synthesis.



Draw the structures of **X** and **Y**.

[2]

- (iv) Suggest a 2-step synthesis for the following transformation. Your answer should include the reagents and conditions, and the structure of the reaction intermediate. One of your steps should include the use of an appropriate Gilman reagent.



[3]

[Total: 20]

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2017 Year 6 Preliminary Examinations Paper 1 Suggested Solutions

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

Q1(D)

Since there is sharp decrease in 2nd IE between elements D & E, the electron removed from E(g) is in an electron shell that is further from the nucleus than that from D(g).

D⁺ has noble gas configuration. D has 1 valence electron, hence it is from Group 1. Counting backwards, B is from Group 17.

Q2(C)

X is actually Cr. It has an electronic configuration of [Ar] 3d⁵ 4s¹. Since the 4s and 3d electrons are similar in energy, there is only a gentle increase for the first six ionisation energies. There is a slightly larger jump between the 6th and 7th IE because the 7th electron is removed from the 3p subshell which is marginally over in energy.

B is incorrect because if X belonged to Group 16, there will be a large jump between the 6th and 7th IE.

vanO₄ cannot be formed because X would have a +7 oxidation state which is not energetically feasible since only the 4s and 3d electrons can be used in bonding.

Cr has six unpaired electrons as shown in the electron-n-box diagram: [Ar] $\uparrow\uparrow\uparrow\uparrow\uparrow\uparrow$
_{4s} _{3d}

Q3(A)

Covalent compounds like pure HCl(g) can dissociate in water to form ions which can serve as mobile charge carriers. HCl(g) → H⁺(aq) + Cl⁻(g)

C is incorrect because in ionic compounds like ammonium chloride, there are N-H covalent bonds within the NH₄⁺ cation.

Q4(B)

All the 4 C in the ring are sp² hybridised. The C in the -C≡N group is sp hybridised. Each C=C contains one π bond and the -C≡N group contains 2 π bonds.

3 is incorrect because sulfur, which exist as S₈ molecules, has more electrons than the P₄ and C₂ molecules, has the strongest instantaneous dipole-induced dipole interactions and the highest boiling point.

Q8(D)

Let abundance of ¹⁰³Ir be x.

$$(193)x + (191)(1-x) = 192.2$$

$$x = 0.6 = 60\%$$

Q9(B)

Counting atoms, the molecular formula of Meldolum is C₈H₁₄N₂O₂, hence empirical formula is C₄H₇N₁O.

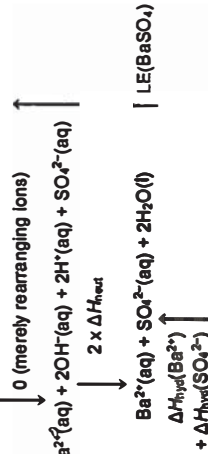
Q10(C)

In the second reaction, the same number of moles of reactants were used, therefore the same amount of heat, q, will be evolved.

However the total volume of solution was halved, therefore there is half the mass of solution to heat up, and the temperature increase will hence be doubled according to the equation q = mcΔT

Q11(D)

The ionic equation for the neutralisation of HCl with NaOH is H⁺(aq) + OH⁻(aq) → H₂O(l). Hence they have the same enthalpy change.



Q12(C)

Assuming that the initial amount of ²³⁵U is 1 mol,

Number of half lives	²³⁵ U	²⁰⁷ Pb	²³⁵ U : ²⁰⁷ Pb
0	1 mol	0 mol	1 : 0
1	0.5 mol	0.5 mol	1 : 1
2	0.25 mol	0.75 mol	1 : 3
3	0.125 mol	0.875 mol	1 : 7

Age of sample = 3 x 710 = 2130 million years

Q13(D)

Mixture 1 will not turn blue-black as all the I₂ from reaction 1 will be immediately converted back to I⁻ in reaction 2.

Due to thi, [I⁻] will remain constant. Hence rate = k[I₂O₂] where k' = k[I⁻]. Reaction is pseudo-first order

Q14(B)

Since reaction was carried out at constant pressure, (partial) volume of gas is proportional to the number of moles of a gas.

Only in this case may you construct an ICE table using partial volumes.

	(HCOOH)(g)	⇌	2HCOOH(g)
Initial vol / dm ³	0.4		0
Change vol / dm ³	-x		+2x
Eqm vol / dm ³	0.4 - x		2x

$$0.4 - x + 2x = 0.6$$

$$x = 0.2 \text{ dm}^3$$

$$\text{Partial pressure of (HCOOH)}_2 = 0.2/0.6 \times 1 \text{ atm}$$

$$= 0.333 \text{ atm}$$

$$\text{Partial pressure of HCOOH(g)} = 0.4/0.6 \times 1 \text{ atm}$$

$$= 0.667 \text{ atm}$$

$$K_p = \frac{P^2_{\text{HCOOH}}}{P_{\text{(HCOOH)}_2}} = \frac{0.667^2}{0.333} = 1.33 \text{ atm}$$

Q15(B)

As temperature increases, K_p decreases, showing that position of equilibrium had shifted to the left. Forward reaction thus becomes less feasible and ΔG^o becomes more positive.

At equilibrium, ΔG = 0, but ΔG^o ≠ 0

Q16(A)



From the graph, immediately after the change at time, t, [X₂] increased but [Y₂] and [XY₃] remained constant.

Forward reaction rate = k_f[X₂][Y₂]³ increases

Backward reaction rate = k_b[XY₃]² remains unchanged (k_f and k_b are the rate constants of the forward and backward reactions respectively.)

Q17(A)
An acidic buffer comprises a mixture of a weak acid and its conjugate base.

1 C_6H_5COOH and $NaOH$ react according to the following equation:

Ant/mole	$C_6H_5COOH + NaOH \rightarrow C_6H_5COO^-Na^+ + H_2O$
Initial	$\frac{50}{1000}^{(1)}$ 0
Change	$-\frac{50}{1000}^{(1)}$ $-\frac{50}{1000}^{(1)}$
Final	0 $\frac{50}{1000}^{(1)}$

Resultant solution = 0.1 dm³ of 0.05 = 0.5 mol dm⁻³ $C_6H_5COO^-Na^+$ (aq) which is not a buffer solution.

2 C_6H_5COOH and $NaOH$ react according to the following equation:

Ant/mole	$C_6H_5COOH + NaOH \rightarrow C_6H_5COO^-Na^+ + H_2O$
Initial	$\frac{175}{1000}^{(1)}$ $\frac{75}{1000}^{(1)}$ 0
Change	$-\frac{75}{1000}^{(1)}$ $-\frac{75}{1000}^{(1)}$ $\frac{75}{1000}^{(1)}$
Final	$\frac{100}{1000}^{(1)}$ 0 $\frac{75}{1000}^{(1)}$

Resultant solution contains a 0.25 dm³ mixture of C_6H_5COOH (weak acid) and $C_6H_5COO^-$ (conjugate base), which is a buffer solution.

$$pH = pK_a + \lg \frac{[C_6H_5COO^-]}{[C_6H_5COOH]}$$

$$= 4.22 + \lg \frac{(0.075/0.25)}{(0.10/0.25)} = 4.1$$

3 Resultant solution contains a 0.070 dm³ mixture of C_6H_5COOH (weak acid) and $C_6H_5COO^-$ (conjugate base), which is a buffer solution.

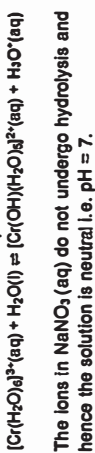
$$pH = pK_a + \lg \frac{[C_6H_5COO^-]}{[C_6H_5COOH]}$$

$$= 4.22 + \lg \frac{\frac{30(1)}{1000} / 0.070}{\frac{40(1)}{1000} / 0.070} = 4.1$$

Q18(D)
KCN contains CN^- which is the conjugate base of the weak acid HCN. Hence, CN^- undergoes hydrolysis in water to give an alkaline solution i.e. $pH > 7$:



$Cr(NO_3)_3$ contains Cr^{3+} which exists as $[Cr(H_2O)_6]^{3+}$ in aqueous solution. It undergoes hydrolysis in water to form an acidic solution i.e. $pH < 7$:



In decreasing pH: KCN, $NaNO_3$, $Cr(NO_3)_3$.

Q19(C)

Step	Reactions
1	$Ag^+(aq) + Cr^+(aq) \rightleftharpoons AgCl(s)$ (white ppt) $Ag^+(aq) + I^-(aq) \rightleftharpoons AgI(s)$ (yellow ppt) White $AgCl$ dissolved in excess $NH_3(aq)$ to form the colourless $[Ag(NH_3)_2]^+(aq)$. $Ag^+(aq) + Cr^+(aq) \rightleftharpoons AgCl(s)$ -- (1) $Ag^+(aq) + 2NH_3(aq) \rightleftharpoons [Ag(NH_3)_2]^+(aq)$. -- (2) Yellow AgI remained insoluble.
2	Residue contains the yellow ppt of $AgI(s)$.
3	Filtrate contains $[Ag(NH_3)_2]^+(aq)$, $Ag^+(aq)$, $Cr^+(aq)$, $2NH_3(aq)$ and $I^-(aq)$.
4	$I^-(aq)$ from KI reacts with $Ag^+(aq)$ in the filtrate to form the yellow ppt of AgI .

A Correct statement. In step 2, the formation of the complex reduces $[Ag^+(aq)]$ momentarily. The decrease in $[Ag^+(aq)]$ causes the ionic product of $AgCl$ to fall below its K_{sp} , the position of equilibrium (1) shifts left to produce more $Ag^+(aq)$, causing $AgCl$ to dissolve.
However, the decrease in $[Ag^+(aq)]$ does not cause the ionic product of AgI to fall below its K_{sp} . The $K_{sp}(AgI)$ is more easily exceeded than $K_{sp}(AgCl)$ i.e. $K_{sp}(AgCl) > K_{sp}(AgI)$

B Correct statement. See reactions described in step 2 and explanation of option A.

C Incorrect statement. Before filtration in step 3, AgI ppt is present and exists in equilibrium with its aqueous ions i.e. ionic product $(AgI) = K_{sp}(AgI)$. $[Ag^+]$ did not change during filtration and hence ionic product (AgI) is still equal to $K_{sp}(AgI)$.

D Correct statement. See reactions described in step 4.

Q20(C)

Relevant data from data booklet:

$V^{3+} + e^- \rightleftharpoons V^{2+}$	-0.26
$VO_3^- + 2H^+ + e^- \rightleftharpoons VO_2^+ + H_2O$	+0.34
$VO_3^- + 2H^+ + e^- \rightleftharpoons VO_2^+ + H_2O$	+1.00
$VO_3^- + 4H^+ + e^- \rightleftharpoons VO_2^+ + 2H_2O$	+1.00
$2H^+ + 2e^- \rightleftharpoons H_2$	0.00
$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$	+1.36
$O_3 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	+1.23

Consider whether H^+ , Cr^+ and H_2O will react with V^{2+} .

Reaction $Cr^+ + V^{2+}$	Remarks
No reaction. Both species can only be oxidised.	
$H_2O + V^{2+}$	No reaction. Both species can only be oxidised.
$H^+ + V^{2+}$	$2V^{2+} + 2H^+ \rightarrow H_2 + 2V^{3+}$ $E_{cell}^{\circ} = 0.00 - (-0.26) = +0.26V > 0$ V i.e. reaction is spontaneous and solution turns green.

Since excess $HCl(aq)$ is added, check whether V^{2+} can be oxidised by H^+ , Cr^+ and H_2O .

Reaction	Remarks
$Cr^+ + V^{2+}$	No reaction. Both species can only be oxidised.
$H_2O + V^{2+}$	No reaction. Both species can only be oxidised.
$H^+ + V^{2+}$	$2V^{2+} + 2H_2O \rightarrow H_2 + 2VO^{2+} + 2H^+$ $E_{cell}^{\circ} = 0.00 - (+0.34) = -0.34V < 0$ V i.e. reaction is non-spontaneous and solution remains green.

Q21(B)

Electrons move from

- negative terminal of the battery to electrode Y, and
 - electrode X to the positive terminal of the battery.
- Overall, electrons move from electrode X to electrode Y. (Option 3 is correct)

Electrode Y is the negative electrode i.e. the cathode, cations (i.e. Al^{3+}) migrate here and reduction takes place. (Option 2 is incorrect)

Electrode X is the positive electrode i.e. the anode, anions (i.e. OH^-) migrate here and oxidation takes place. OH^- is oxidised to $O_2(g)$. (Option 1 is correct)

Q22(B)

Let the oxidation state of Cu in $[CuCl_2]^-$ be x.
 $x + 2(-1) = -1 \Rightarrow x = +1$

electronic configuration of Cu = $[Ar] 3d^{10} 4s^1$
electronic configuration of Cu^+ = $[Ar] 3d^{10}$

Q23(D)

	Incorrect	plane of symmetry	no plane of symmetry
A			
B	Incorrect One condition for cis-trans isomerism is the presence of restricted rotation about a double bond or ring structure. The carbon atoms on P and Q bearing the -OH groups are connected by a single bond and can rotate freely i.e. there is no restricted rotation in P and Q.		
C	Incorrect Enantiomers are non-superimposable mirror images. The mirror image of Q is shown below and is clearly not P.		
D	Correct P has 2 chiral centres but contains an internal plane of symmetry i.e. P is a meso compound and does not rotate plane-polarised light. Q has 2 chiral centres and no internal plane of symmetry i.e. Q is optically active and rotates plane-polarised light. Hence, an equimolar mixture of P and Q will rotate plane-polarised light.		

Q24(B)

By convention, a polypeptide chain is drawn from the amino end (N-terminus) at the left end to the carboxyl end (C-terminus) at the right end.



Since chymotrypsin digested P at the carboxylic acid end of Phe, then the two fragments obtained are Val—Lys—Phe and Arg.

M _r of Val—Lys—Phe	M _r of Arg
117 + 146 + 165 - 2(18) = 392	174
1 H ₂ O (M _r = 18) is lost when 2 amino acids form a peptide. 2 H ₂ O are lost when 2 amino acids form 2 peptide linkages	
$\begin{array}{c} \text{H} & & \text{H} \\ & & \\ \text{H}-\text{C}-\text{O}-\text{H} & + & \text{H}-\text{C}-\text{O}-\text{H} \\ & & \\ \text{H} & & \text{H} \end{array} \rightarrow \begin{array}{c} \text{H} & & \text{H} \\ & & \\ \text{H}-\text{C}-\text{O}-\text{C}-\text{N}-\text{H} \\ & & \\ \text{H} & & \text{H} \end{array} + \text{H}_2\text{O}$	

Q25(A)

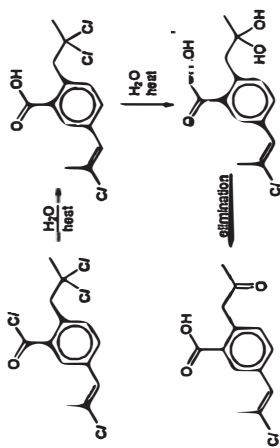
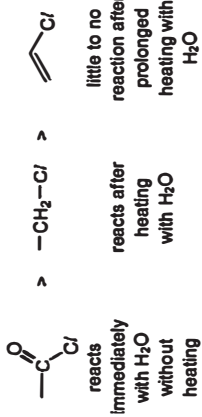
In reaction 1, there is inversion of configuration i.e. bimolecular nucleophilic substitution, S_N2, took place. rate = k[(+)-2-chlorobutane][nucleophile]

In reaction 2, a racemic mixture was obtained i.e. bimolecular nucleophilic substitution, S_N1, took place. rate = k[(+)-2-chlorobutane]

Correct. Reaction 1 proceeds via S _N 2 mechanism which has only 1 step.
Incorrect. If both S _N 1 and S _N 2 occurred i.e. some of the (+)-2-chlorobutane undergo inversion while some undergo racemisation, the resultant solution will be optically active. Hence, reaction 2 proceeds via S _N 1 mechanism only.
Incorrect. See rate equations given above.

Q26(C)

Ease of nucleophilic substitution with water:

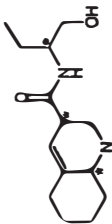


The final step is an elimination reaction which occurs when a carbon atom contains more than 1 -OH group (see Carboxylic Acids and Derivatives tutorial).



Q27(A)

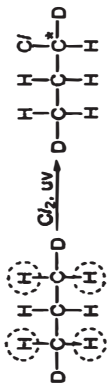
Compound X contains 3 chiral centres.



A	3 chiral centres after reaction with LiAlH ₄ .
B	4 chiral centres after reaction with H ₂ , Ni, heat.
C	4 chiral centres after reaction with HBr.
D	5 chiral centres after reaction with cold, KMnO ₄ , NaOH(aq).

Q29(C)

Monosubstitution of any of the 4 circled hydrogens will give a product with one chiral centre.



Since the C-D bond is broken as easily as a C-H bond, the C¹ radical can substitute any of the 8 atoms (8 H's and 2 D's)

Proportion of monochlorinated products with a chiral centre = (4/8) x 100 = 50%

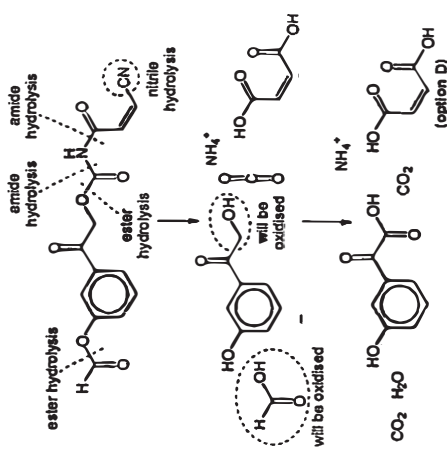
Q30(D)

When heated under reflux with acidified K₂Cr₂O₇(aq), the following reactions can happen:

- strong oxidation of 1° or 2° alcohols
- strong oxidation of aldehydes
- acidic hydrolysis of esters, amides or nitriles

The following reactions do not happen with acidified K₂Cr₂O₇(aq):

- oxidation of C=C
- oxidation of side chain of benzene



Q28(D)

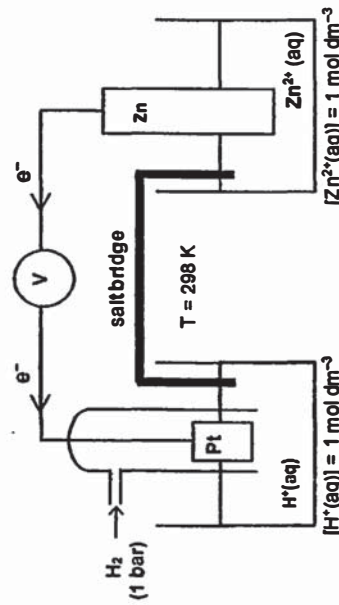
A	1. I ₂ , NaOH, heat 2. HCl(aq)
B	ethanolic KCN, heat HCl(aq), heat
C	KMnO ₄ , H ₂ SO ₄ (aq), heat
D	KMnO ₄ (aq), H ₂ SO ₄ , heat HCN, trace KCN, heat HCl(aq), heat

Note: There are alternative answers.

Please revisit Carboxylic Acids & Derivatives if you do not understand why the above reaction takes place.

Note: All alternative answers require at least 3 steps.

1(a)



Examiners Comments

- Many students omitted the salt bridge or did not state the standard conditions.
- Note that standard conditions are 298 K (or 25 °C) and 1 bar (not 1 atm).
- Some students used 1 mol dm³ H₂SO₄ as the electrolyte. Note that [H⁺] must be 1 mol dm³ so [H₂SO₄] will have to be 0.5 mol dm³.
- Also, the electrode in the S.H.E. must be made of Pt, not graphite.

1(b)(i)



Examiners Comments

- Most students obtained full marks for this question.

1b(ii)

Species being oxidised: Zn
Species being reduced: Ag₂O

Examiners Comments

- Ag₂O is insoluble in water and does not dissociate to form aqueous ions. In order to properly describe what happened to Ag₂O, candidates should use accurate description. In this case, silver changed oxidation state from +1 to 0, and Ag₂O is reduced to Ag i.e. describe the compound as being reduced (or oxidised), while the element changes oxidation state.
- A common mistake was to write Ag or Ag⁺ as the species being reduced.

1b(iii)

$$E_{\text{cell}}^{\ominus} = +0.34 - (-0.76) = +1.10 \text{ V}$$

Examiners Comments

- Most students obtained full marks for this question.
- Please remember to always express your answer to 3 s.f., even in this case.

1b(iv)

$$\begin{aligned} \Delta G^{\ominus} &= -nFE_{\text{cell}}^{\ominus} \\ &= -2 \times 96500 \times 1.10 \\ &= -212300 \text{ J mol}^{-1} \\ &= -212 \text{ kJ mol}^{-1} \end{aligned}$$

Examiners Comments

- Many students were unable to do this question because they forgot the formula or recalled the formula wrongly.
- Other common mistakes were due to incorrect or unconventional units. The following units are incorrect: kJ, J, or C V mol⁻¹.
- Note that the joule can be expressed in terms of C V (or even other SI units) but in this context, the use of the formula gives ΔG[⊖] in J mol⁻¹.

1b(v)

When water was added, the concentration of OH⁻ decreased. Therefore, the equilibrium position shifts right and E(Ag₂O/Ag) increases. Thus, E_{cell} will increase.

Examiners Comments

- Many students lost marks here because they did not explain how the addition of water caused the equilibrium position to shift, or incorrectly stated that the addition of water increased the concentration of water.
- Since water is a solvent here, its concentration is a constant. Only aqueous ions will change in concentration. In this case, only OH⁻ in the Ag₂O/Ag half-cell will decrease in concentration.
- Some students also stated that Zn²⁺ concentration will decrease, but Zn²⁺ is not present in the Ag₂O/Ag half-cell.

2(a)(i)

A free radical is a species containing an unpaired electron.

Examiners Comments

- Incorrect answers include:

Wrong terms	Why it was not accepted
atom	Free radicals can contain multiple atoms, e.g. •OH
ion	Free radicals are typically uncharged.
free electron	This means that the species contains a total of one electron.

- A common wrong answer was "A free radical is an unpaired electron." Free radicals are not electrons!
- Please learn your definitions well.

2(a)(ii)

$$\text{BE}(\text{C}-\text{H}) = 410 \text{ kJ mol}^{-1} \quad \text{BE}(\text{C}-\text{C}) = 350 \text{ kJ mol}^{-1}$$

A C–C bond is weaker than a C–H bond and is hence easier to break.

Examiners Comments

- Many students had the misconception that only non-polar bonds can undergo homolytic fission. This is not true.
- Many students incorrectly explained that the C–C bond has to break in order to produce smaller molecules. That reasoning is flawed. It is because the C–C bond is weaker than a C–H bond that cracking occurs in nature to produce smaller molecules. The cause-effect relationship is incorrect for those students.

3(a)(i)

Measure the pH of the benzenesulfonic acid solution and the value should be 1.

Examiners Comments

- Majority of the students did not suggest a measurable indicator of a strong acid.
- Students are to show understanding that strong acids undergo complete dissociation and state the expected pH value of 1 ($[H^+] = [\text{benzenesulfonic acid}] = 1 \text{ mol dm}^{-3}$), verifying that benzenesulfonic acid is a strong acid.
- A handful of students misinterpreted the question and suggested how to verify that benzenesulfonic acid is a stronger acid than benzoic acid, cyclohexanol and phenol.

3(a)(ii)

The acidity of the given compounds increases in the following order:



Cyclohexanol is the least acidic because its conjugate base is destabilised by the electron-donating effect of the cyclohexyl group, which intensifies the negative charge on the oxygen in the conjugate base.

Phenol is more acidic than cyclohexanol because the phenoxide ion is stabilised by the dispersal of the negative charge into the benzene ring. In the phenoxide ion, the p orbital of the oxygen overlaps with the pi electron cloud of the benzene ring. This allows a lone pair of electrons of oxygen and hence the negative charge on oxygen to be delocalised into the benzene ring.

Benzoic acid is more acidic than phenol because the benzoate ion is more greatly resonance-stabilised than the phenoxide ion. In this case, the negative charge of the benzoate ion is dispersed by delocalisation over two highly electronegative oxygen atoms, resulting in benzoate ion being a resonance hybrid of two equivalent resonance structures.

Examiners Comments

- This question was unexpectedly poorly attempted and many students are unable to provide clear explanations. Please revise these basic concepts and explanations thoroughly.
- Majority of the students missed out on crucial key points required for this answer or did not provide explanation for all 3 compounds.
- There should be comparison of the relative stabilities of conjugate bases. Between alkoxide and phenoxide as well as between phenoxide and benzoate.
- Clear reference to the compound (acid) / conjugate base should be made when appropriate. For example, 'electron-donating cyclohexyl group intensifies the negative charge on the oxygen in the conjugate base, it is destabilised and it is least acidic' is an unclear statement. No credit will be awarded. It is the *alkoxide ion* that is destabilised and the *cyclohexanol* that is least acidic.
- Students are to note that the negative charge of the benzoate ion is not delocalised into the benzene ring.
- The explanation for the stability of the benzoate ion was lacking for many candidates. Please revise this again.
- Many students are unclear about the use of the words "disperse" and "delocalise". They are not interchangeable. Please clarify with your tutors if you are unsure.

3(b)(i)

(1,1-dimethylethyl)benzene undergoes sulfonation at a faster rate than benzene because the electron-donating 1,1-dimethylethyl group increases the electron density in the benzene ring and enables it to attract the SO_3 electrophile more strongly than the unsubstituted benzene ring.

Examiners Comments

- Generally well done.
- A proper answer should mention that the alkyl group is electron-donating and its effect on the electron density in the benzene ring.
- Students may also explain in terms of how the electron-donating 1,1-dimethylethyl group helps to disperse the positive charge in the intermediate carbocation and leads to the stabilisation of the carbocation.

3(b)(ii)

The given sulfonation reaction does not produce 2-(1,1-dimethylethyl)sulfonic acid because the bulky 1,1-dimethylethyl substituent group sterically hinders the approach of the bulky SO_3 electrophile to the 2-position of the benzene ring.

Examiners Comments

- Generally well done.
- Some students incorrectly identified the electrophile. Note that it is stated in the question that sulfur trioxide, SO_3 , is the electrophile involved in the sulfonation reaction.

3(c)

Step 1: $(CH_3)_2CBr^+$, $FeBr_3$

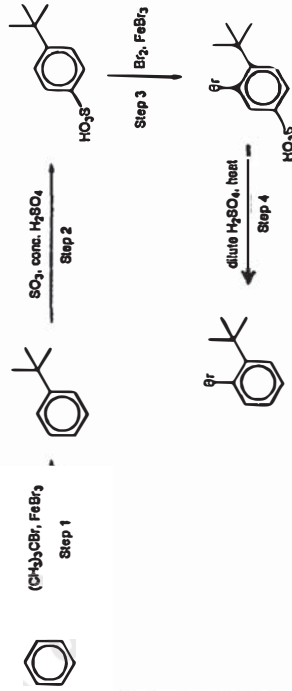
Step 2: SO_3 , conc. H_2SO_4

Step 3: Br_2 , $FeBr_3$

Step 4: dilute H_2SO_4 , heat

Examiners Comments

- Many students who did not do well for this part did not understand that the question provided information about how sulfonation and desulfonation can be used. Please read the question again to see if you can pick up on those clues. Such questions which require students to make use of information provided are not uncommon.
- Many students incorrectly believe that the use of $Br_2(aq)$ in step 3 will cause bromination of the benzene ring. This only works for benzene rings attached to highly activating substituents. Such compounds include phenol and phenylamine. Alkyl groups are weakly activating and still require the use of $FeBr_3$ as a Lewis acid catalyst.



- Step 1: Friedel-Crafts alkylation (electrophilic substitution) of benzene. Reagent needed is an alkyl halide and a Lewis acid catalyst.

3d(ii)

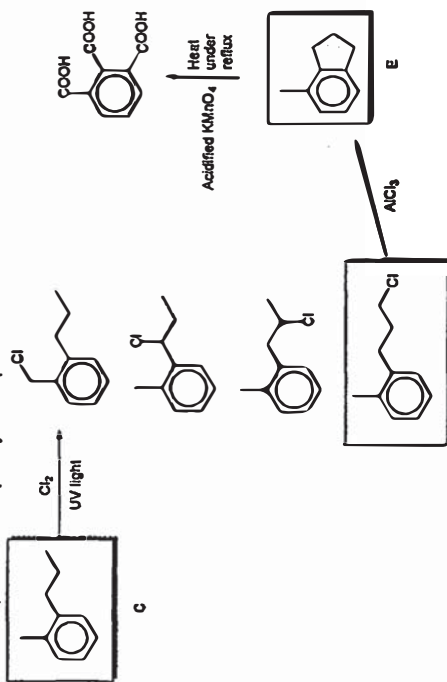
- Step 2: Sulfonation reaction. Refer to question stem, for reagents and conditions. Note that (aq) state symbol should not be written for conc. H_2SO_4 . Also, organic product obtained is entirely 4-(1,1-dimethylethyl)benzenesulfonic acid.
- Step 3: Bromination. Lewis acid catalyst is required for bromination of an alkylbenzene. Refer to question stem, since the 4-position on the benzene ring is occupied by the $-\text{SO}_3\text{H}$ substituent, the substitution will take place at the 2-position.
- Step 4: Reverse sulfonation. Refer to question stem, for reagents and conditions.

3d(i)



Examiners Comments

This question was poorly attempted.



- Many wrong answers stem from the lack of understanding of what constitutional isomers are. Constitutional isomers have the same molecular formula but different structural formula i.e. different arrangement of atoms. Compound C (with 4 sets of equivalent H on the alkyl side chains) undergoes free-radical substitution to form the 4 monochlorinated constitutional isomers.
- One of these isomers undergoes intramolecular Friedel-Crafts alkylation (electrophilic substitution), in the presence of Lewis acid catalyst, AlCl_3 , to form Compound H as the only product. Compound E undergoes side chain oxidation when heated with acidified KMnO_4 to give benzene-1,2,3-tricarboxylic acid is the only organic product.
- A handful of students drew structures that did not match the molecular formula.

D:



Examiners Comments

- Since compound D displays cis-trans isomerism, it is likely that C=C bonds are present. There are 4 C=C bonds present since one mole of compound D undergoes electrophilic addition reaction with 4 moles of Br_2 in the dark. When compound D undergoes oxidative cleavage when heated with acidified KMnO_4 , ethanoic acid is the only organic product obtained; CO_2 and H_2O are the other products.
- The question required students to draw the skeletal formula (where C & H atoms are not explicitly shown) of the cis isomer (where H atoms are located on the same side of the C=C). Many students did not adhere to these instructions.

4(a)

Gas X: SO_2
Gas Y: CO_2

Examiners Comments

- SO_3 was not accepted since it can only be formed significantly when SO_2 reacts with O_2 in the presence of V_2O_5 catalyst (Contact Process).
- Sulfur was also not accepted as it will not be a gas.

4(b)

Process B: CO acts as a reducing agent.
Process C: CO acts as a ligand/Lewis base.

Examiners Comments

- Since CO is oxidised to CO_2 , it must have reduced the oxides of Ni and Cu, thus it is a reducing agent in process B.
- In process C, CO binds to Ni as a ligand or Lewis base, where the electron pair on C in CO is donated to the empty d-orbitals of Ni. The answer "base" is too vague and was not accepted. Candidates are required to appreciate that there is an electron pair donated from C in CO to Ni, thus, the Lewis definition of a base has to be illustrated.

4(c)(i)

$$\Delta S^\ominus = +410.6 - 29.9 - (4)(+197.7) = -410.1 = -410 \text{ J K}^{-1} \text{ mol}^{-1}$$

Examiners Comments

- Correct value with correct units were required for this mark.
- Generally well-done.

4(c)(ii)

The sign of ΔS^\ominus is negative because the reaction leads to a decrease in the number of gaseous particles in the system such that the system becomes less disordered than before.

Examiners Comments

- The explanation has to be based on the sign of entropy obtained in part (c)(i). Thus, no credit was given if part (c)(ii) was blank since there will be no reference for the explanation.
- Note that this reaction is not a "phase change" from solid Ni to form $\text{Ni}(\text{CO})_4$ gas as phase change has to be for the same compound.

4(d)

Assume ΔH° and ΔS° do not vary with temperature.

For the given reaction to be thermodynamically feasible, $\Delta G^\circ < 0$

$$\Delta H^\circ - T\Delta S^\circ < 0$$

$$-160.9 - T(-410.1/1000) < 0$$

$$T < 392 \text{ K}$$

Hence the temperature below which the reaction is feasible is 392 K.

Examiners Comments

Some careless mistakes involved students forgetting to change ΔH° to J mol^{-1} or ΔS° to $\text{kJ mol}^{-1} \text{K}^{-1}$ in the use of the formula.

4(e)

Temperature for Process C: 60 °C or 333 K

This ensures that the reaction is spontaneous and the $\text{Ni}(\text{CO})_4$ formed is a gas and can be separated from the solid copper and also other solid impurities.

Process D is carried out 200 °C or 473 K

This ensures that the decomposition of $\text{Ni}(\text{CO})_4$ to produce Ni and CO is spontaneous. Hence pure Ni can be obtained and CO gas obtained can be separated and recycled.

Examiners Comments

For Process C:

- Accept any value within the range:
 - 43 °C < temperature < 119 °C, or
 - 316 K < temperature < 392 K
- Students should give a specific value and not specify a range of temperatures since question asked for a temperature value.
- Many students did not make use of the boiling point of 43°C and state that $\text{Ni}(\text{CO})_4$ had to be gaseous to enable it to be separated by from the mixture. Answers that just stated that the mixture must be boiled for $\text{Ni}(\text{CO})_4$ to be separated were not given credit since it is just repeating the question about boiling.
- Temperature cannot be equal to 119°C since it would be at equilibrium.

For Process D:

- Accept any value above 119 °C or 392 K
- Students should give a specific value and not specify a range of temperatures since question asked for a temperature value.
- Temperature cannot be equal to 119°C since it would be at equilibrium.

4(f)(i)

$$K_p = \frac{P_{\text{CO}}^4}{P_{\text{NiCO}_4}} \Rightarrow 1.01 = (1.50)^4 / P_{\text{NiCO}_4}$$

$$P_{\text{NiCO}_4} = 5.012 = 5.01 \text{ atm}$$

4(f)(ii)

Initial pressure of $\text{Ni}(\text{CO})_4 = 5.012 + (1.50/4) = 5.387 = 5.39 \text{ atm}$

4(g)(i)

Down the group, the ionic radius of the Group 2 cations increases. This causes the charge density and hence the polarising power of the Group 2 cations to decrease down the group.

Consequently, the extent of distortion of the electron cloud of the CO_3^{2-} anion and the extent of weakening of covalent bonds within the CO_3^{2-} anion decrease down the group.

Therefore, the amount of heat required to break the covalent bonds within the CO_3^{2-} anion increases causing the decomposition temperature to increase down the group. Hence the thermal stability of the Group II carbonates increases down the group.

Examiners Comments

- Students who made use of "atomic radius" or "size of element" increase was not given any credit. Charge density results from ions which are charged species, not atoms or elements which are not charged.
- Note that it is also incorrect to state that the cation distorts the CO bond as bonds can only be "polarised" or "weakened", not "distorted".
- A handful of students were confused between "thermal decomposition" and "melting". For melting, it is the ionic bonds (or electrostatic forces of attraction) between M^{2+} and CO_3^{2-} that is broken and it would depend on lattice energy which is in turn dependant on ionic radii. Hence, melting point would decrease down the group. However, thermal decomposition involves the breaking of covalent bonds within the carbonate anion which depends on the charge density of the cation. Since covalent bonds are weakened less with decreasing charge density of cation, the thermal decomposition temperature would increase down the group and thermal stability would likewise increase.

4(g)(ii)

Ionic radius: Ca^{2+} , 0.099 nm; Ni^{2+} , 0.069 nm
Hence NiCO_3 decomposes at a lower temperature than CaCO_3

Examiners Comments

- It is required that values from the *Data Booklet* has to be quoted.
- As this is NOT a redox reaction, it is inappropriate to quote E° values.

Question 5

This is a data response question. In general, students are expected to read all instructions and refer to the data given carefully. Whatever concepts chosen to answer the question must be driven by the data given. It is important to ensure the consistent use of accurate terminologies in explaining concepts.

5(a)(i)

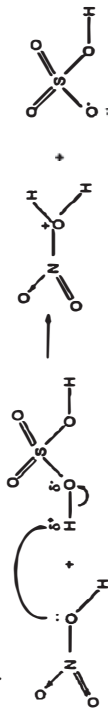
Proton donor.

Examiners Comments

- Some students gave the definition of a Lewis acid instead and failed to mention the donation of H^+ .
- The preferred and more accepted term is "donor" rather than "donator".

5(a)(ii)

Step 1:



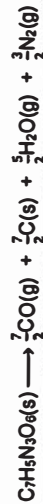
Step 2:



Examiners Comments

- Generally quite well done. Most students illustrated their understanding of arrow pushing by carefully following the instructions given. Some students, however, failed to assign the positive charge on the species (H_2NO_3^+ and NO_2^+) correctly.
- A large number of students did not indicate the partial charges on the O-H bond.

5(b)(i)



Examiners Comments

- Students must follow the instructions given to write the balanced equation. If they have done this conscientiously, there would have been no need to include O_2 , CO_2 and water in their equation.
- A number of students forgot to give the required state symbols.

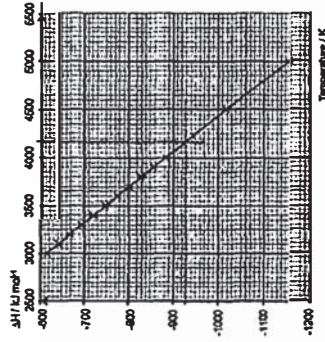
5(b)(ii)

$$\Delta H = \left[\frac{7}{2} \times (-110.5) + \frac{5}{2} \times (-241.8) \right] - (-63.2) = -928 \text{ kJ mol}^{-1}$$

Examiners Comments

- Many students failed to take into consideration that the enthalpy change of explosion should be calculated for 1 mol of TNT. Some, on the other hand, carelessly chose irrelevant data, like those of ΔH_f (water) and ΔH_f (CO_2).
- A small number expressed the balanced equation using "TNT" instead of the actual chemical formula " $\text{C}_7\text{H}_5\text{N}_3\text{O}_6$ ". This is not acceptable.

5(b)(iii)



Temperature of explosion of TNT = 4176 K

Examiners Comments

- Students should be more careful in reading the data point from the graph correctly. Many incorrectly estimated the required value.
- Students should also have realised at this point that if they were unable to read their calculated value in (b)(ii) from the given graph, they should have gone back and check their working for (b)(ii).
- Any extrapolation or plotting of points beyond the given grid is not acceptable because there are no data points that supports the extrapolation.

5(c)(i)

Elements	Estimated cost per gram	Enthalpy change of explosion of metal, ΔH / kJ mol^{-1}	Heat released on explosion of metal / kJ g^{-1}
Aluminium	\$0.238	-834.3	30.9
Magnesium	\$0.160	-602.6	24.8
Zinc	\$0.109	-353.2	5.4

For every \$1 spent on the element, amount of heat produced (in kJ g^{-1}):

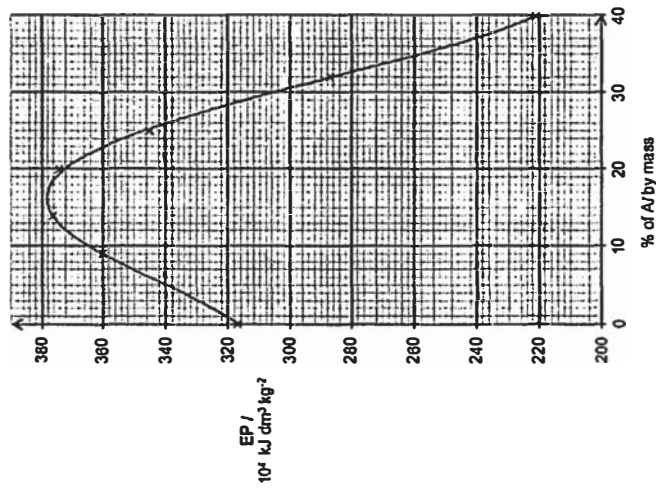
Al	Mg	Zn
$\frac{30.9}{0.238} = 130 \text{ kJ g}^{-1}$	$\frac{24.8}{0.160} = 155 \text{ kJ g}^{-1}$	$\frac{5.4}{0.109} = 49.5 \text{ kJ g}^{-1}$

Magnesium produces the most amount of heat energy per gram per dollar.

Examiners Comments

- "Heat released" is a magnitude – no sign is required.
- Any sensible answers comparing the cost of using all three metals were accepted.
- There were some students who consistently revealed their difficulties in handling and understanding data with unusual units. It is important to review the skills needed in unit analysis.

5(c)(ii)



% by mass of Al = 16 %

$$\text{Maximum EP} = 378 \times 10^4 \text{ kJ dm}^3 \text{ kg}^{-2}$$

Examiners Comments

- Students who drew two straight lines and extrapolated to find the maximum point did not understand the question. In so doing, their graph would have resulted in several anomalous points.
- Many students erroneously left out the first or the last data point when drawing their graph.
- Students should be more careful in reading the data point from their drawn graph correctly.
- Students also did not pay attention to the axis label given on the graph and hence presented the maximum EP without " $\times 10^4$ ".

5(c)(iii)

$$\text{Heat released on explosion} = \frac{380 \times 10^4}{586} = 6484 \text{ kJ kg}^{-1} = 6480 \text{ kJ kg}^{-1} \text{ (3sf)}$$

Examiners Comments

- Generally well done.

5(c)(iv)

$$M_r \text{ of TNT} = 227.0$$

$$\text{Heat released on explosion of 1 kg of TNT} = \frac{928}{227} \times 1000 = 4088 \text{ kJ kg}^{-1}$$

$$\text{Increase in amount of heat released} = 6484 - 4088 = 2396 = 2400 \text{ kJ kg}^{-1} \text{ (3sf)}$$

Examiners Comments

- Students made careless mistakes (e.g. wrong M_r , forgot to convert 1 g to 1 in their calculation of amount of TNT in 1 kg).

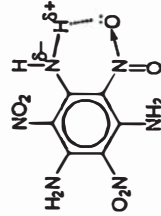
5(d)(i)

1,3,5-triamino-2,4,6-trinitrobenzene
(or 2,4,6-triamino-1,3,5-trinitrobenzene)

Examiners Comments

- This was very poorly done. Students did not pay attention to the details in their answer, e.g. the appropriate use of "-," indication of "tri" in front of each substituent, the incorrect use of "amine" instead of "amino" when identifying $-\text{NH}_2$ as a substituent, the incorrect usage of brackets "()" etc.
- The answer was also partially hinted in the given abbreviation i.e. TATB for 1,3,5-triamino-2,4,6-trinitrobenzene.

5(d)(ii)



Examiners Comments

- The two partial charges and the lone pair of electrons on O were commonly left out in their answers.
- Some students chose to use other $-\text{NH}_2$ and $-\text{NO}_2$ groups to illustrate hydrogen bonding. In so doing, they would not have been able to illustrate the partial charges and lone pair of electrons on the individual H and O atoms.

5(d)(iii)

The lone pair of electrons on nitrogen of the $-\text{NH}_2$ group is delocalised into the π electron cloud of the benzene ring, giving the carbon-nitrogen bond a partial double bond character.

Examiners Comments

- Students attempted to answer the questions by comparing the effectiveness of the overlap between different hybrid orbitals. That would have led to a wrong conclusion. This is a classic example of the need to use appropriate concepts to account for the data given.
- Keywords such as "lone pair of electrons on N" and "delocalisation" were missing.

5(d)(iv)

The presence of the electron withdrawing $-\text{NO}_2$ group in TATB causes the lone pair of electrons on the $-\text{NH}_2$ group to be more extensively delocalised into the benzene ring, resulting in greater partial double bond character in the carbon-nitrogen ($-\text{NH}_2$) bond.

Examiners Comments

- This was badly done. Students were able to identify the difference between the two compounds, i.e. the presence of $-\text{NO}_2$ groups, but failed to clearly mention the effect this group has on the benzene ring and the adjacent $-\text{NH}_2$ group and how that effect results in a much shorter bond indicated in the question.

6(e)(i)

At constant temperature and pressure,

$$EP \text{ of TATB} \propto 3498 \times 9 \times \frac{1000}{255}$$

$$EP \text{ of octanitrocubane} \propto 7648 \times 12 \times \frac{1000}{464}$$

$$\frac{EP \text{ of TATB}}{EP \text{ of octanitrocubane}} = \frac{3498 \times 9 \times \frac{1000}{255.0}}{7648 \times 12 \times \frac{1000}{464.0}} = 0.617$$

Examiners Comments

- This is an example to illustrate the importance of manipulating with unit analysis carefully. The volume of gases evolved is proportional to the amount of gases produced (in mol) at constant temperature and pressure.

6(e)(ii)

Advantage:

High density, can pack more explosive material per unit volume such that 1cm³ of octanitrocubane releases more energy than TATB of the same volume.

Examiners Comments

- Both compounds are solids and there is no issue with transportation of solids unlike the example in Common Test 2 which required a comparison between gases and liquids used in fuel cells. Students who merely highlighted higher density as an advantage without making a reference to the packing of explosive material, resulting in a higher amount of energy released per unit volume etc. were not awarded the mark.
- A mere mention of "pollutants" without specifying which compound was being referred to also did not receive any credit.

6(e)(i)

Let the required concentration of [OH⁻] be y mol dm⁻³.



$$\text{Ionic product} = [Al^{3+}][OH^-]^3 = (10^{-20})(y)^3$$

When precipitation starts to occur, ionic product = K_{sp}

$$(10^{-20})(y)^3 = 3.3 \times 10^{-34}$$

$$y = [OH^-] = 3.208 \times 10^{-5} \text{ mol dm}^{-3}$$

$$pOH = -\lg(3.208 \times 10^{-5}) = 4.49$$

$$pH = 14 - 4.49 = 9.51$$

Aluminium hydroxide starts to precipitate at pH 9.5.

Examiners Comments

- Most common mistake is thinking that Al(OH)₃ is the source of both ions, and thus thinking that IP = x(3x)³ where x is conc of Al(OH)₃ dissolved. Such an approach only works if Al(OH)₃ was used as the only source of both ions in solution. In this question, both Al³⁺ and OH⁻ came from different sources, and do not follow a 1:3 ratio. To set up the correct "IP = K_{sp}" equation, always use the actual and total concentrations of each ion in the IP expression from all sources. This works for common ion effect questions as well as questions like this one.
- Many students also lost marks from carelessness.

6(b)(i)

$$pV = nRT$$

$$p(150 \times 10^{-4}) = \left(\frac{1.10}{4(12) + 10(1)} \right) (8.31)(273 + 20)$$

$$p = 3.08 \times 10^5 \text{ Pa}$$

Examiners Comments

- Generally well done for students who attempted this question.
- Common mistakes include: not knowing the correct temperature for room temperature (20°C, not 25°C) and incorrect conversion of cm³ to m³; it is 10⁻⁶ from + (100 × 100 × 100)
- Careless mistakes are also very common here.

6(b)(ii)

When butane is released from a high pressure region to a low pressure region, the gas expands / volume increases. The molecules move apart and energy from the surroundings is absorbed to overcome the intermolecular forces of attraction.

Examiners Comments

- It is important to describe what happens to the molecules (that they are moving apart), and the molecular description is required, to link to breaking of IMF. Vague descriptions of expansion may not be given full credit, as expansion could come about due to different processes. Some students also write that "molecules expand" which would be incorrect, as that physically means molecules individually getting bigger.
- Some students discussed using pV=nRT, which would be irrelevant, since consideration of IMF means that the gas is non-ideal. Also, even for an ideal gas, decreasing p will be brought about by decreasing T, only in constant volume, which is not happening in this context. Even with constant volume, it is difficult to do the opposite, i.e. decreasing T by decreasing p (you need to engineer some physical means to slow down the molecules and reduce their impact on container walls, but that means cooling too) in terms of cause and effect, it makes more sense to decrease p by decreasing T, and not the other way around. In any case, these approaches are all irrelevant in a non constant volume, non ideal gas context.
- Some students also discuss work done by ideal gas in expanding (they should complete this argument by stating work done against constant external pressure), or adiabatic expansion (which is the same as work done in expansion). While this does take place, it does not address the question which requires addressing effect of IMF. Thus these students miss the point.

6(c)(i)



Examiners Comments

- Generally poorly done. Students need to develop the skills/approach to write equations for unfamiliar reactions. The approach is as follows:
 - Identify all starting materials and products. Question may give clues.
 - Balance elements that occur in smaller numbers of compounds first.
 - Balance charge with charge particles/ions that are sensible (eg H⁺ in acidic conditions)
 - Balance O and H last (as they occur in many compounds) usually with H₂O. Also, compounds like O₂ and H₂ occur as products in specific types of reactions, eg acid-metal, redox, decomposition reactions.
- As the question already stated that aluminium hydroxide, a compound all students should be familiar with as Al(OH)₃ is the product, students should write the formula in the equation first, and start balancing from there.

6(c)(II)

Aluminum chlorohydrate reacts with sweat / moisture on the skin to form the Insoluble $Al(OH)_3$ which clogs/blocks/obstructs the sweat pores.

Examiners Comments

- Students need to specifically state that the product is a solid that would block the pores. Any vague references/statements such as "it blocks the pores" where "it" could refer to the starting material, does not give credit, as the question stem already informs the student that the antiperspirant works by blocking pores.
- Quite a few students also suggest that the antiperspirant works by absorbing water in the reaction; Students need to read questions carefully for context and clues. In this question, it is stated that the sweat pores can be blocked. It also does not make practical sense for an antiperspirant to work by absorbing water, as large volumes of water can be released in sweat but only a small amount of antiperspirant can be applied.

2017 H2 Chemistry Preliminary Examinations Paper 3 Suggested Solutions

- 1 (a) (i) Due to the similarity in energy between the 3d electrons and the 4s electrons, both 3d and 4s electrons are available for bond formation / Fe can use different number of these electrons in bond formation when they form compounds, and hence Fe has a tendency to exist in variable oxidation states.

Due to the large energy difference between the 3p and 4s subshell of potassium, a lot more energy is needed to remove the 2nd electron. Hence potassium only exists in one stable oxidation state.

Examiner's Comments

- Most students recognised the fact that Fe has 3d and 4s electrons/orbitals that are similar in energy.
- However, a significant number of students just mentioned that only the 4s electrons of K can be used for bonding, without discussing why this is so, thus they were only able to get 1 mark out of 2.
- The mention of partially filled d orbitals is irrelevant here as this is not a requirement for variable oxidation state. One example is Cu which has a fully filled d orbital, yet is able to exist commonly as Cu⁺ and Cu²⁺.
- Students who just discussed about Fe having low-lying d orbitals or being able to expand octet were not awarded any credit.

- (ii) Fe has a significantly higher melting point than K due to its stronger metallic bonding. This is because both the 3d and 4s electrons of Fe can be contributed to the 'sea' of delocalised electrons in the metallic lattice, due to the small energy difference between these electrons. For K, only the one valence 4s electron can be contributed to the 'sea' of delocalised electrons.

Alternative answer:

Since Fe contributes both its 3d and 4s electrons to the delocalised electron cloud in the metallic lattice, the iron cations in the lattice are smaller and more highly charged, resulting in stronger electrostatic attraction between these cations and the delocalised electrons / stronger metallic bonding than in the case of potassium ions.

Examiner's Comments

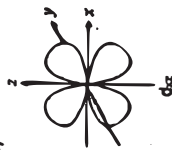
- Generally well done. Note that both Fe and K are metals and it is important to discuss about the relative strength of metallic bonding which is due to the number of delocalised electrons or the charge density of the cations.
- Students who only mentioned that Fe has more delocalised electrons without stating that both the 4s and 3d electrons can be delocalised were only given partial credit, since the availability of 4s and 3d electrons for delocalisation is the main reason why transition metals have higher melting point than main group ones.

- (b) (i) Lone pair of electrons on C of CN⁻ is able to form coordinate bond to vacant low-lying orbitals of the central metal atom/ion.

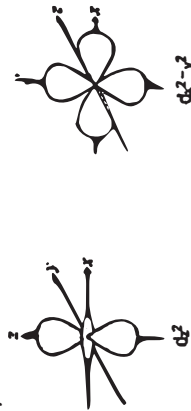
Examiner's Comments

- Generally well done. Note that the lone pair of electrons that is commonly donated to the metal ion is on C and not N, since C is less electronegative than N, thus more willing to donate its lone pair of electrons.

(ii) (i)



(ii)



Examiner's Comments

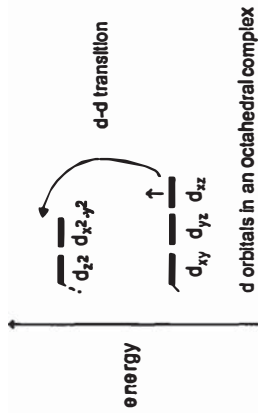
- All 3 axes must be shown since the question mentions using the Cartesian coordinates as shown. No credit was awarded if any one axis was missing.
- The orbitals drawn must also be clearly indicated as higher or lower energy together with the type of orbitals (d_{xy}, d_{xz} etc) drawn.

- (iii) The d-orbitals which lie on the axis experience greater repulsion from lone pairs on ligands while the d-orbitals with lobes between the axes experience less repulsion from lone pairs on ligands.

Examiner's Comments

- Generally well done. It is important to compare the different degree of repulsion for the both types of orbitals (those which lie between the axis or along the axis) with the incoming ligands which approach along the axis to be awarded the full credit.

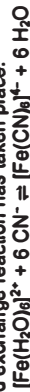
- (iv) Since the 3d orbitals in the transition metal ion are partially filled, electrons from the lower-energy d orbitals can absorb visible light energy and get promoted to the higher-energy d orbitals. The colour observed is the complement of colour absorbed.



Examiner's Comments

- For the diagram, all the d-orbitals have to be labelled, either on the diagram or in the explanation.
- The energy axis or energy gap must be annotated on the diagram.
- A significant number of students lost marks for failing to state in the explanation that the d orbitals had to be partially filled in order for d-d transition to occur.
- It is important to state clearly that it is the electrons that absorb light energy to be promoted. Students who mentioned that the complex or the orbitals that absorbed light energy was not given any credit.

- (c) (i) A ligand exchange reaction has taken place.



Examiner's Comments

- Ligand exchange/ligand displacement were acceptable as possible answers.
- A handful of students who wrote the charge on the complex incorrectly were not given credit.
- Note that in the question, it was already stated that the complex was $[\text{Fe}(\text{CN})_6]^{4-}$, thus ALL 6 H_2O ligands had to be exchanged for CN^- ligands and not only one of them.

- (ii) The complexes contain different ligands, namely H_2O and CN^- , and the ligands split the d orbitals of Fe^{2+} to different extent (or with different energy gaps between d orbitals), thus different wavelengths of light are absorbed to promote the electrons from the lower energy d-orbitals to the higher energy d-orbitals in the two complexes, hence leading to different colours observed.

Examiner's Comments

- Students who only mentioned that a different wavelength of light was absorbed without explaining why were not awarded any credit for their answers.

- (iii) $E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} = +0.54 - (+0.36) = +0.18 \text{ V} > 0$.
The oxidation of yellow $[\text{Fe}(\text{CN})_6]^{4-}$ to red $[\text{Fe}(\text{CN})_6]^{3-}$ by I_2 is spontaneous. Therefore, I_2 can be used.

Examiner's Comments

- It was important to calculate the E_{cell}° for the reaction AND conclude that it was spontaneous before concluding that I_2 can be used. A positive E_{cell}° calculation is not sufficient to substantiate the possibility for the use of I_2 if there is no link provided that the reaction is spontaneous/feasible.
- A significant number of students used +0.77 instead of +0.36 and came to the incorrect conclusion that I_2 cannot be used. Note that the complex involved is $[\text{Fe}(\text{CN})_6]^{4-}$ and not $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$. The value of +0.77 which is for $\text{Fe}^{3+}/\text{Fe}^{2+}$ is for the aqua complex.

- (d) (i) Assuming 100g sample of Y,

	K	Fe	Cl	C	O
Am / mol	27.9 / 39.1	13.3 / 55.8	16.9 / 35.5	11.4 / 12.0	30.5 / 16.0
Mol ratio	3	1	2	4	8

Empirical formula = $\text{K}_3\text{FeCl}_2\text{C}_4\text{O}_8$

Examiner's Comments

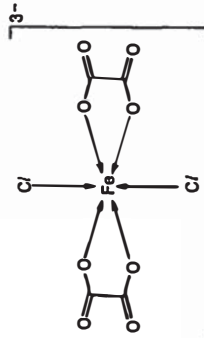
- Generally well done.

- (ii) Chemical formula of complex anion = $[\text{FeCl}_2(\text{C}_2\text{O}_4)_2]^{3-}$

Examiner's Comments

- It is a requirement to group the C and O atoms together into the $\text{C}_2\text{O}_4^{2-}$ ligand which is already given in the question.
- The question asked for the anion. Thus, the answer $\text{K}_3\text{Fe}(\text{C}_2\text{O}_4)_2\text{Cl}_2$ was not given any credit.

- (iii)



Examiner's Comments

- The $\text{C}_2\text{O}_4^{2-}$ ligand is bidentate and uses both the negatively charged oxygen atoms to bond to the Fe ion.
- Some students who drew charges on the oxygen and Cl atoms and ALSO indicated the charge on the outside were not given any credit as the charges will not balance. Indicate EITHER overall charge outside the complex OR on the relevant atoms (negative charge on the 4 oxygen atoms, negative charge on the Cl atoms and 3+ charge on the Fe atom).



C undergoes hydrolysis to form HCl. The HCl produced dissolves in water and dissociates completely (or mention strong acid), producing a solution with the highest $[\text{H}^+]$ and hence the pH of an aqueous solution of C is the lowest.

Both A and B are weak acids that dissociate partially. The presence of the electron-withdrawing $-\text{Cl}$ group helps to further disperse the negative charge of the carboxylate ion of B, hence making it more stable relative to the carboxylate ion of A. \therefore B is a stronger acid than A and will dissociate to a greater extent forming a solution of lower pH than A.

Order of increasing pH of their aqueous solutions: $\text{C} < \text{B} < \text{A}$.

Examiner's Comments

- Many students were unable to appreciate that acid chlorides, when added to water, undergo hydrolysis. Hence they assumed that C was a neutral compound. Instead, by observing that there was no O-H bond present in the structural formula.
- The $-\text{Cl}$ group (NOT C-*group*) has an electron-withdrawing effect via induction and not resonance. Some students were confused and claimed that there was greater delocalisation instead.
- Students were careless in the arrangement of the organic compounds in the required order. Some arranged the compounds in order of increasing acidity or in decreasing order of pH instead. Some students used the mathematical symbols " $<$ " and " $>$ " wrongly. No marks were awarded in such cases.
- Their answers were also poorly phrased lacking the essential key phrases or randomly joining words they have previously encountered in the notes without paying attention to the overall meaning they convey. E.g. "stabilising the negative charge when it should be "dispersing the negative charge" and "stabilising the carboxylate ion" separately.
- The following terms all seem to refer to a species which is "capable of donating H^+ to varying extent" when compared to other species but they do not necessarily convey the meaning of a species which "dissociates completely to produce H^+ ": "highly acidic", "strongly acidic", "stronger acid" \neq "strong acid".
- Students used the term "it" loosely and hence gave ambiguous answers, leaving the markers baffled as to what "it" is.



Examiner's Comments

- When writing the K_c expression, it is important to check the state symbols of the given equation. Some students omitted $[\text{H}_2\text{O}]$ in the expression, thinking that H_2O was used as a solvent in the question. Such a mistake would have been avoided if students checked the state symbols and realized that all the species in the equation were in liquid form. Hence, water is not a solvent and is not in excess.

(ii)

	acid	alcohol	\rightleftharpoons	ester	+	water
Initial amount / mol	2.00	2.00				
Change / mol	$-x$	$-x$		$+x$		$+x$
Eqm amount / mol	$2.00 - x$	$2.00 - x$		x		x

$$\frac{\left(\frac{x}{V}\right)\left(\frac{x}{V}\right)}{\left(\frac{2-x}{V}\right)\left(\frac{2-x}{V}\right)} = 4.15$$

$$\left(\frac{x}{2-x}\right)^2 = 4.15$$

Amount of ester, $x = 1.34$ mol

Examiner's Comments

- No ecf were awarded to this part when (b)(i) was wrong.
- This question was very badly done. Many students failed to consider the changes in the amount of both products and reactants as equilibrium took place, i.e. did not consider ICE table.
- The wrong answers were all greater than 2 moles. Students should have realised that it was impossible to obtain more than 2 moles of ester when equilibrium is reached. This is a reaction that does not go to completion, i.e. %yield will be less than 100%. (Or in another words, the answer must be less than 2 moles!)
- Some students were still using the wrong units such as "moles". There is no plural term when using the symbols to represent units. It is just like how we do not write "gs" to represent grams or "cms" to represent centimetres, please DO NOT write "moles".

- (iii) When a system at equilibrium is subjected to a change (or stress), the system will react to counteract the change (or stress) imposed so as to re-establish the equilibrium.

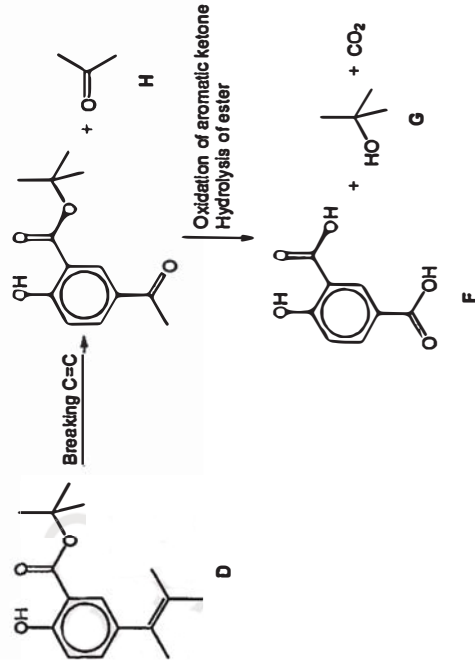
When water is removed, equilibrium position shifts to the right, i.e. forward reaction is favoured, to produce more water, hence the yield of the ester also increases.

Examiner's Comments

- Students did not read the question carefully and omitted the first part where they had to "state Le Chatelier's Principle". Hence 1 mark was lost.
- Those who attempted to state LCP gave incomplete answers, failing to recognise key phrases such as "re-establish the equilibrium", which means the system must first be at equilibrium before a change it made to it.
- Students were able to suggest that the forward reaction will be favoured when water is removed. However some students failed to comment on how the yield of ester will be affected. No marks were awarded for such cases.

Evidence	Conclusion / Explanation
Reduction of D with H_2 and Ni gives E, $C_{16}H_{24}O_3$.	\Rightarrow D has either a <u>C=C</u> , <u>aldehyde</u> or <u>ketone</u> .
D is not reduced by $NaBH_4$.	\Rightarrow D does not have <u>aldehyde</u> or <u>ketone</u> group. \therefore D has 1 <u>C=C</u> bond.
E exhibits enantiomerism whereas D does not.	\Rightarrow E has at least 1 <u>chiral carbon</u> while D does not have any <u>chiral carbon</u> .
$D + 2 Br_2(aq) \rightarrow rxn$ ($C_{16}H_{22}O_3$)	<u>Electrophilic addition of C=C</u> occurred.
$D \xrightarrow[\text{heat}]{KMnO_4/H^+}$ ($C_{16}H_{22}O_3$)	<u>Electrophilic substitution of phenol</u> occurred \Rightarrow <u>One</u> Br is substituted on either <u>2- or 4-position</u> with respect to <u>-OH</u> .
$D \xrightarrow[\text{heat}]{KMnO_4/H^+}$ ($C_{16}H_{22}O_3$)	<u>Oxidative cleavage of C=C</u> occurred. <u>Oxidation of side chain on benzene ring</u> (1 mol of CO_2 is formed from oxidising 1 mol of D)
$D \xrightarrow[\text{heat}]{KMnO_4/H^+}$ ($C_{16}H_{22}O_3$)	<u>Hydrolysis of ester</u> occurred. \Rightarrow G is a <u>3° alcohol</u> as it is not oxidised by acidified $KMnO_4$.
$F + 2 SOCl_2 \rightarrow rxn$ ($C_8H_{10}O_5$)	<u>Substitution</u> occurred. (no mark if electrophilic substitution mentioned) \Rightarrow F has 2 <u>-COOH</u> which are converted to <u>2 -COCl</u> .
$G \xrightarrow{Na}$ effervescence ($C_4H_{10}O$)	<u>Acid-metal reaction / Redox reaction</u> occurred. \Rightarrow Effervescence is due to <u>$H_2(g)$</u> \Rightarrow G is an <u>alcohol</u> .
$H \xrightarrow{2,4-DNPH}$ orange ppt ($C_8H_{10}O$)	<u>Condensation</u> occurred. \Rightarrow H is a <u>ketone</u> .

D	E
F	G
H	J



Examiner's Comments

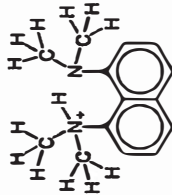
- This question was poorly attempted.
- In explaining the observations, students were required to state the type of reaction that took place and the structural features (i.e. functional groups) of the compounds which they could identify from such a reaction. The type of reaction that took place was commonly left out. No marks were awarded for partial answers.
- Observations such as "effervescence" needs to be explained too. Many did not mention that it was due to the production of H_2 .
- If reacting ratios or molecular formula were provided, students need to also comment on the number of such functional groups present to undergo the reaction.
- In presenting the answers for this question, the use of mindmap is not encouraged. Students who drew mindmaps presented their work in a messy manner as they tried to squeeze in information in any empty space they can find on the writing paper and often times, leaving out crucial information. Certain pieces of evidence need to be considered together but were drawn far apart in their mindmaps. They seemed to be confused by their own work too, as they were unable to piece the information together to come up with the correct structures in the end.
- Please be reminded that students will be penalised if the markers are unable to comprehend their messy presentation or illegible handwriting.

- (a) (i) A Lewis base is an electron-pair donor.

Examiner's Comments

- A common incorrect answer is that it is an electron-donor or that it donates electrons. A Lewis base is defined as an electron-pair donor.
- Some students use the definition of Bronsted-Lowry base (proton acceptor) instead.

- (a) (ii)



Intramolecular H-bond stabilises the conjugate acid of DMAN. Such stabilising effect is absent in the conjugate acid of TMPD.

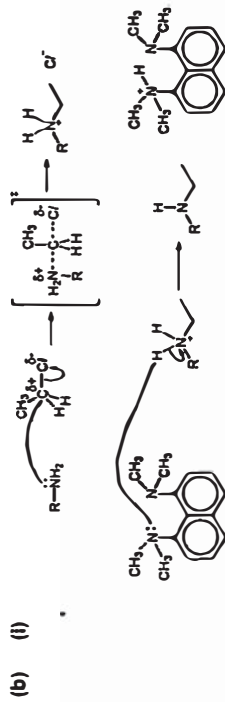
Examiner's Comments

- Many students did not draw the correct structure for the conjugate acid of DMAN. DMAN is a diacidic base i.e. it can accept $2 H^+$. When asked for the conjugate acid of DMAN, it is the structure after DMAN accepted $1 H^+$ (recall that a conjugate acid base pair differ by 1 proton). Many students drew the structure obtained when DMAN has accepted $2 H^+$ which is incorrect. This affected their ability to explain using the structure since their structure was already incorrect.
- Even more students either did not see or did not understand the meaning of the term "displayed formula". It requires students to show all atoms and all bonds between the atoms.
- There are past year A-level questions where Cambridge examiners required students to draw the displayed formula so that it provides a strong hint to the next part of the question. This question aimed to replicate this experience for students. The drawing of the displayed formula guides students to see the intramolecular hydrogen-bonding which exists in the conjugate acid of DMAN.
- A common incorrect answer was to talk about the delocalisation of the lone pair of electrons on the N atoms of DMAN into the benzene ring, reducing the availability of the lone pair of electrons to form dative bonds to protons. Students need to realise that the same can be said for TMPD, meaning that the difference in basicity cannot be because of this similar factor.
- Students need to be more cautious in their choice of words. Many students wrote "DMAN has intramolecular hydrogen bonding and is stabilised..." when they really meant that the conjugate acid of DMAN has intramolecular hydrogen bonding. Such comments discussing students' loose use of language is prevalent for this cohort. Please learn and improve.

- (a) (iii) The lone pair of electrons on N in the conjugate acid of DMAN is involved in the intramolecular hydrogen bond and is significantly less available to form a dative bond with a proton.

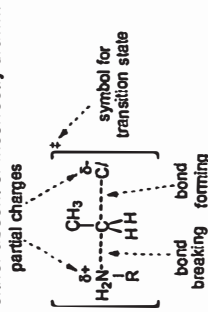
Examiner's Comments

- Students who saw the intramolecular hydrogen bonding in the previous part generally scored here as well.
- A common incorrect answer provided was that it is difficult to add a proton to a positively charged species i.e. protonated DMAN. However, once again, the protonated TMPD faces the same situation as well.



Examiner's Comments

- As stated in the question, this reaction has 2 steps: step 1 involves an S_N2 reaction between $R-NH_2$ and CH_3CH_2Cl while step 2 involves DMAN liberating the product. Many candidates ignored the information given about step 2 and drew other mechanisms. No marks were awarded.
- The S_N2 mechanism in step 1 was very poorly drawn. Please take note of the following:
 - 2 curly arrows (1 from lone pair on N of RNH_2 to δ^+ of chloroethane, 1 for the breaking of the C-Cl bond in chloroethane)
 - The transition state was either absent or incorrectly drawn.



- Of the students who indicated the partial charges in the transition state, many of them labelled the partial charge on N incorrectly. The thought process for deciding partial charges on transition state is as follows:
 - the N on the nucleophile, $R-NH_2$ has no net charge.
 - the N on the product of step 1 has a positive charge.
 - in the transition state, the charge on N is "growing" from 0 to 1^+ . Hence, N in the transition state has a δ^+ charge.
 A similar train of thought can be applied to decide the partial charge on Cl in the transition state.
- Unless otherwise stated, structural formula must be used when drawing mechanisms. Many students used "DMAN" in step 2 and were not given credit for that step.

- (b) (ii) Nitrogen atoms of DMAN are sterically hindered by the methyl groups making it difficult to approach electrophilic carbon. However, the lone pairs are available to coordinate to the small H^+ ion.

Examiner's Comments

- This is a 2 part question which requires the discussion of 2 main points:
 - why DMAN is unable to act as a nucleophile (steric hindrance from groups around N atom of DMAN),
 - why DMAN is able to act as a base (small H^+ ion is unaffected by the steric hindrance).
- In general, question 3 revealed students' inability to explain concepts clearly and make reference to the correct object in their answers.
 - It is the N atom of DMAN which is sterically hindered. Many students simply said "DMAN is sterically hindered". There are sites on DMAN which are not hindered.
 - When discussing the idea of sterically hindered, students should succinctly mention what groups are causing the steric hindrance. A small number of candidates mentioned the methyl groups and large benzene ring causing the steric hindrance.
 - The main reason why DMAN can still act as a base is due to the small size of H^+ and this must be emphasized.

- (b) (iii) Lone pair on N is unavailable to attack the electrophilic carbon on chloroethane because it is delocalised into the $C=O$ bond.

Examiner's Comments

- This question contrasts the 2 N atoms on DMAN: the primary amine acts as a nucleophile to attack chloroethane, but the N on ethanamide is unable to act as a nucleophile.
- A good number of students did not realize this and gave irrelevant conclusions such as "the amide is neutral" or "the C-N bond in the amide has partial double bond character". While the second statement is a true statement, this reaction does not involve the breaking of the C-N bond of amide! Students who were unsure also gave very vague answers such as "the lone pair on N is involved in resonance stabilisation". This answer is too vague and does not discuss why the lone pair is unavailable. In general, if students feel that the answer involves the idea of "resonance", they should describe it in terms of delocalisation before concluding that resonance is present.

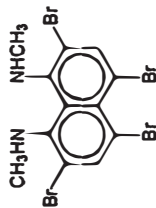
- (c) (i) Step 1: $COCl_2$, Step 3: $LiAlH_4$ in dry ether

Examiner's Comments

- Students who recognize that an amide was formed in Step 1 generally got the correct answer. Amides are formed from the reaction between acyl chlorides and an amine. Many students incorrectly thought that an amide can be formed from the reaction between a carboxylic acid and amine. This is generally not possible.
- Some students gave $COCl_2$ as the answer along with unnecessary conditions which caused $COCl_2$ to fail as a reagent. No BOD was given and no marks were awarded. Common wrong answers included:
 - $COCl_2$ in ethanol (ethanol reacts with $COCl_2$, just like how acyl chlorides react with H_2O)
 - $COCl_2(aq)$ (H_2O reacts with $COCl_2$, just like how acyl chlorides react with H_2O)
- Step 2 involved the reduction of the amide, which can only be achieved using $LiAlH_4$ in dry ether. Many students are not familiar with this reagent even though it is required by the syllabus.

- A common wrong answer involved the use of NaBH_4 , NaBH_4 can only reduce aldehydes and ketones, not amides. Finally, H_2 , Ni , heat reduces aldehydes, ketones, nitriles and alkenes, not amides.

- (c) (ii) The reaction between compound Z and $\text{Br}_2(\text{aq})$ results in the formation of the tetrabrominated DMAN, instead of the dibrominated DMAN.



Step 1 converts the highly activating $-\text{NHCH}_3$ group to the less activating amide group, which reduces the electron density of the benzene ring, allowing only disubstitution to occur.

Examiner's Comments

- To answer this question, students need to see the similarity between in phenylamine and compound Z. For phenylamine, the amine group ($-\text{NH}_2$) activates the benzene ring strongly, which allows the benzene ring to undergo tribromination at the 2-, 4-, and 6-positions. Similarly, the $-\text{NH}(\text{CH}_3)$ is also highly activating, allowing substitution of benzene ring at the 2- and 4- positions of each benzene ring.
- Students need to explain how the formation of the amide causes the disubstitution instead of tetrasubstitution. This is actually due to the lone pair on N delocalising into the $\text{C}=\text{O}$, reducing the activating ability of the substituent, reducing the electron density of the benzene ring. This is very similar to what students were taught under *Organic Nitrogen Compounds* where phenylamine needs to be first reacted with an acyl chloride so that monobromination of the benzene ring takes place instead of tribromination.
- Common incorrect answers include:
 - "The amide group is electron-withdrawing / deactivating". This is not true. The amide group is still electron-donating and activating but less so compared to the original $-\text{NH}_2(\text{CH}_3)$ group.
 - "The amide group is more sterically hindered". This is not true. The steric hindrance is very similar as the $\text{C}=\text{O}$ is on the N atoms, away from the benzene rings which undergo substitution.

- (d) (i) There is extensive delocalisation of the lone pairs of electrons on the N atoms and benzene ring throughout the entire polymer. These delocalised electrons can flow when a potential difference is applied, allowing it to conduct electricity.

Examiner's Comments

- This question is simple, with many students showing some understanding of what the answer should be.
- However, most students did not score the mark as their description was vague and unclear. In such questions, where particular compound is given and you are asked to explain a property of the compound, students need to make sure they discuss what specific features of the compound allowed for such a property.
- Many vague answers simply mentioned that there are electrons which can act as mobile charge carriers. The source of these electrons must be clear stated.



Examiner's Comments

- This part was surprisingly poorly attempted. The aim of the question was to test whether students can balance simple half equations which involve the following steps (for acidic medium):
 - Balance the elements apart from O and H
 - Balance O using H_2O
 - Balance H using H^+
 - Balance charges using electrons
- In this context, the first step would be to add 1 H^+ to the right side of the equation (since N is already balanced and there are no O's to balance). The left side of the equation has no net charge, but the right side has at $2+$ charge. So, we add 2 e^- to the right side to balance the charges.

- (d) (iii) $Q = It = n_e F \Rightarrow 2.0 (5 \times 60) = n_e (96500)$
 $n_e = 0.006217 = 0.00622 \text{ mol}$

amount of nitrenium ions = $0.00622 \times \frac{1}{2} = 0.00311 \text{ mol}$

Examiner's Comments

- Many students did well for this part as there was ecf from (d)(i).
 - Those who did not do well were not familiar with the formula, $Q = It = n_e F$.
- (d) (iv) Number of nitrenium ions = $0.00311 \times 6.02 \times 10^{23} = 1.87 \times 10^{21}$

Since all 1.87×10^{21} nitrenium ions polymerised into 1 poly(phenylamine) chain, the number of repeat units is also 1.87×10^{21} .

Examiner's Comments

- The question required students to understand that the nitrenium ions would all combined into one poly(phenylamine) chain. The number of repeat units in the polymer chain would correspond to the number of nitrenium ions generated, which can be calculated from the number of moles of nitrenium ion generated i.e. no. of repeat units = no. of nitrenium ions = (no of mol of nitrenium ions) x (Avogadro's constant).

- (a) Boiling points generally increase from PH_3 to SbH_3 due to an increase in the number of electrons OR the electron cloud size for each molecule and hence an increase in strength of instantaneous dipole-induced dipole interactions between the molecules.

NH_3 has an exceptionally high boiling point / a boiling point higher than PH_3 due to inter-molecular hydrogen bonding.

Examiner's Comments

- Some students had difficulty interpreting the trend. This question tested students' ability to describe and explain why the boiling point of NH_3 is unusually high, as well as the trend of increasing boiling points among the other three XH_3 compounds. There were quite a number of inaccurate answers alluding to the fact that XH_3 molecules form permanent-dipole induced dipole interaction. This will not account for the trend of increasing boiling points from PH_3 to SbH_3 . This trend of increasing boiling point from PH_3 to SbH_3 must have been caused by stronger instantaneous dipole-induced dipole interaction between the molecules.
- Terms, like *instantaneous dipole-induced dipole* and *hydrogen bonding* should be spelt out in full.

- (b) P_4O_{10} reacts with water to form an acidic solution with pH 2 (or 3).
 A_2O_3 does not react with water / not soluble in water.



Examiner's Comments

- Some students were not sure of the state of P_4O_{10} .
- Quite a number of students mistakenly assumed that Al_2O_3 hydrolyses in water to give an acidic solution. Such a reaction is not possible for Al_2O_3 due to the high lattice energy of Al_2O_3 .

- (c) (i) PCl_5 reacts/hydrolyses with water and is no longer present for reaction with ethanol.

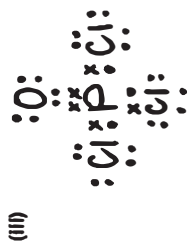
Examiner's Comments

- Some students made a wrong guess that the hydrolysis of POCl_3 was responsible for the need of an anhydrous reaction condition.



Examiner's Comments

- This question should just involve simple inspection and balancing of the equation.
- The observation stated must be a result of the equation written. It is unacceptable to state that white fumes are observed when no HCl is given out, based on the equation written.
- The chemical formulae written should show no ambiguity in terms of structure.



Tetrahedral. POCl_3 has 4 regions of electron density around P with no lone pairs on P.

Examiner's Comments

- There were still some students who forgot to include the lone pairs of electrons on oxygen and chlorine. Those who chose to represent their answers in the form of a Lewis structure were penalised.
- Students must learn to make their answers concise, focusing on the regions of electron density or the number of bond pairs and lone pairs, rather than explaining the basis of the VSEPR Theory.
- Some students failed to read the question carefully and wasted time suggesting / explaining about the bond angle which was not required.

- (d) (i) Test
 Add $\text{NaOH}(\text{aq})$ to each sample in a test-tube and heat each mixture.
 Cool each mixture and acidify with dilute HNO_3 .
 Then add $\text{AgNO}_3(\text{aq})$.

Observation

For a $\text{CH}_3\text{CH}_2\text{Cl}$, a white precipitate of AgCl is observed.
 For a $\text{CH}_3\text{CH}_2\text{Br}$, a cream (or pale yellow) precipitate of AgBr is observed.

Examiner's Comments

- Students must realise that adding $\text{AgNO}_3(\text{aq})$ directly to organic compounds such as $\text{CH}_3\text{CH}_2\text{Cl}$ and $\text{CH}_3\text{CH}_2\text{Br}$ without prior hydrolysis will not yield any AgCl or AgBr precipitate. On the other hand, if HNO_3 is not added to neutralise the NaOH , Ag_2O will be formed instead.
- A handful of students still made the mistake of carrying out a distinguishing test using reflux. It is not possible to carry out reflux when test tubes are used in distinguishing tests.

- (ii) Br is larger and more diffuse than Cl and so the overlap of orbitals for C-Br is less effective than for C-Cl. Hence C-Br bond is weaker than C-Cl bond and $\text{CH}_3\text{CH}_2\text{Br}$ undergoes hydrolysis at a faster rate compared to $\text{CH}_3\text{CH}_2\text{Cl}$.

Examiner's Comments

- Some students mistakenly suggested that $\text{CH}_3\text{CH}_2\text{Cl}$ undergoes hydrolysis more rapidly than $\text{CH}_3\text{CH}_2\text{Br}$ due to the fact that Cl is more electronegative than Br, causing the electron deficient carbon to be more susceptible to nucleophilic attack by OH^- . This is a misconception.
- It is important for students to recognise and understand that the rate of hydrolysis of halogenoalkanes is determined by the strengths of the C-X bonds.

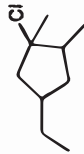
- (iii) The conversion of a 3-membered ring to a 4-membered ring in step 3 allows the bond angle in the ring to expand from 60° to 90° which is closer to the bond angle of 109.5° on a sp^3 carbon / which reduces the repulsion between bonding pairs of electrons.

The secondary carbocation in U is converted to the more stable tertiary carbocation in V due to the presence of a greater number of electron-donating alkyl groups which disperse the positive charge to a greater extent.

Examiner's Comments

- This question was not very well done.
- This question, which provides minimal guidance, aims to give leeway for students to "explain fully" why compound T was formed as the major product, in their answers, students should demonstrate their understanding on the various factors that could have contributed to this phenomenon. A large proportion of students failed to realise that ring strain has an impact on the carbocation rearrangement. Those who realised that were not able to explain it clearly.
- Students are strongly advised against using shortcuts in their answers, writing symbols like 1° , 2° or 3° carbocations. Instead, they should spell out, in full, the types of carbocations formed, e.g. tertiary carbocation.

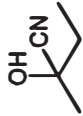
(iv)



Examiner's Comments

- Some students were careless and gave structures with a particular carbon having 5 covalent bonds.

- (a) (i) Nucleophilic addition



Examiner's Comments

- Most candidates were able to answer this question correctly. However, candidates are reminded to be careful in showing the correct bonding to the correct atoms, i.e. C of CN and O of OH. Ambiguous bonding resulted in loss of marks.

- (ii) In compound A, the carbonyl C in C=O is electron-deficient (or electrophilic) as it is bonded to highly electronegative O atom, attracting CN^- nucleophiles.
In compound B, C=C does not contain an electron-deficient site as there is no electronegativity difference between the two C atoms, hence C=C do not attract CN^- nucleophiles.

Examiner's Comments

- Candidates will only be awarded the full credit if their explanation is detailed enough: specifying the carbon involved, explaining why the carbonyl carbon is electron deficient and thus subject to attack by the nucleophile CN^- .
- Some candidates explained that C=C is electron-rich and hence repels the nucleophile. This is incorrect as C=O is also electron-rich. The main reason is due to the lack of an electron-deficient carbon in C=C.

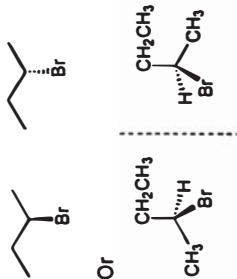
- (iii) Electrophilic Addition



Examiner's Comments

- Candidates should take note that when asked to describe a mechanism, they should name the mechanism involved.
- The start (electron source) and end of curly arrows (electron sink) must be specific.
- Ambiguous drawing resulted in loss of marks.
- Most candidate illustrated understanding of Markovnikov's rule and gave the correct carbocation resulting in formation of the major product.

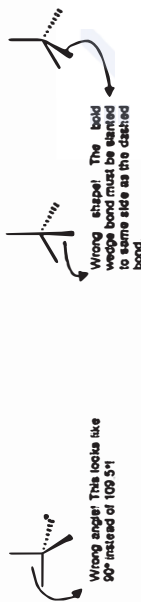
- (iv) The carbocation intermediate is trigonal planar about the sp^2 carbon, subsequent attack of Br^- nucleophile from top and bottom of the plane occurs with equal chance resulting in a racemic mixture.



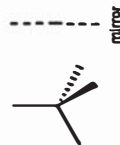
Examiner's Comments

- Some candidates failed to understand the requirements of this question and just conveniently state that a racemic mixture is formed, without explaining why it is formed. Planar shape of the carbocation intermediate must be stated, so as to link to the equal probability of attack by the Br^- from either side of the planar intermediate.
- Candidates were unable to support their answer with correct 3D diagrams. Some candidates are to note the significance of the wedge-dash notation, and hence, angle the four bonds around the chiral carbon in the correct tetrahedral configuration. 3D diagrams which do not make sense were not accepted. It is also good practice to include a mirror plane when drawing the pair of enantiomers, to facilitate a clear presentation of the work done.

Wrong drawings:



Accepted 3D drawings of enantiomers:



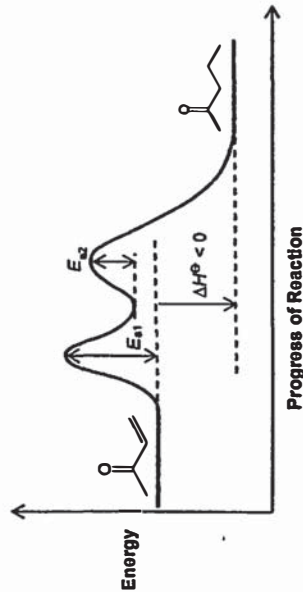
Please adhere to the above convention as stated in the syllabus. Note that the bold wedge (---) is slanted to the same side as the dashed bond (-----). The shape is clearly tetrahedral with 109.5° as bond angles.



Examiner's Comments

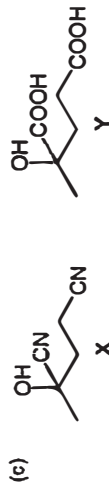
- A fair number of candidates illustrated good understanding of curly arrows and were able to use the information given in the question to construct the correct mechanism, illustrating the correct flow of curly arrows to obtain the required intermediate and product.
- Candidates are reminded that mechanistic arrows depict movement of electrons and wherever necessary, essential lone pair of electrons must be displayed.

(ii)



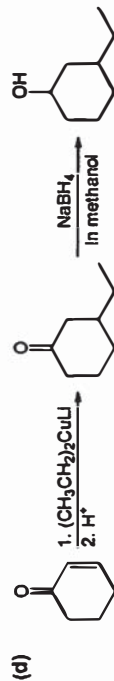
Examiner's Comments

- Some candidates confused energy profile diagram with energy level diagram. A fair number also wrongly labelled the x-axis as 'time'. A small number wrongly illustrated an endothermic reaction (products of higher energy than reactants) instead of the correct exothermic reaction (products of lower energy than reactants).
- A significant number of candidates only included one activation energy in their diagram. This is incorrect since the question stated that this mechanism contains two steps. Since it is given in the question that Step 1 is the slow step, candidates are to show an obvious difference between the two activation energies with $E_{a1} > E_{a2}$. Sketches of activation energies which are too similar with each other are penalised.
- Candidates are reminded that for all energy profile diagrams, it is expected to label the reactants and products on their diagram. Candidates who failed to do so were penalised.



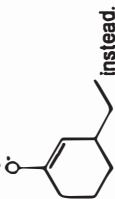
Examiner's Comments

- Some candidates failed to apply the information given on page 12 that C4 is the carbon which is electron-deficient and gave the incorrect structure for X, where CN is added on C3.
- Most candidates understood the acidic hydrolysis of nitriles and gave the corresponding structure Y where -CN groups are hydrolysed to -COOH.



Examiner's Comments

- In this synthesis question, the sequence of the steps is important. In order to introduce the ethyl group on the ring, Gilman reagent has to be the first step followed by the reduction of ketone. No credit was awarded for using a wrong sequence.
- The *reacton* intermediate of step 1 refers to the resultant product after using Gilman reagent followed by H^+ . Some candidates gave the *reactive* intermediate



2017 H2 Chemistry Preliminary Practical Examination – Answers

General Notes:

- All final answers must be rounded off to 3 significant figures, except for:
- 1(b)(ii) mean volume of FA 2 used (to 2 d.p.); 1(c)(iv) value of x (whole number)
- All units must be present in working and final answers.
- All appropriate presentation (e.g. table of results for recording data), working and statements.

1(b)(i) Results

Mass of FA 1 used = 3.074 g (TARE)

- The mass reading must be within the correct range: 3.050 – 3.140 g.
- Record mass readings to 3 decimal places.
- Indicate "TARE" if tare function was used.

Titration number	1	2
Final burette reading / cm ³	24.20	24.20
Initial burette reading / cm ³	0.00	0.00
Volume of FA 2 used / cm ³	24.20	24.20
Values used	✓	✓

- Tables must be constructed with proper headers and units.
- Burette readings must be recorded to 2 decimal places.

1(b)(ii)

$$\text{Mean volume of FA 2 used} = \frac{24.20 + 24.20}{2} = \underline{24.20 \text{ cm}^3}$$

- Mean titre volume should be recorded to 2 decimal places.

1(c)(i)

$$\text{Amount of thiosulfate ions} = 0.05 \times \frac{24.20}{1000} = \underline{1.21 \times 10^{-3} \text{ mol}}$$

1(c)(ii)

$$\text{Amount of Cu}^{2+} \text{ in } 25.0 \text{ cm}^3 \text{ of FA 4} = \text{amount of S}_2\text{O}_3^{2-} = \underline{1.21 \times 10^{-3} \text{ mol}}$$

1(c)(iii)

$$\text{Conc. of Cu}^{2+} \text{ in FA 4} = \frac{1.21 \times 10^{-3}}{25.0 \times 10^{-3}} = \underline{0.0484 \text{ mol dm}^{-3}}$$

1(c)(iv)

$$\text{Amount of CuSO}_4 \cdot x\text{H}_2\text{O weighed out} = \text{amount of Cu}^{2+} \text{ in } 250 \text{ cm}^3 = 0.0484 \times 250 \times 10^{-3} = 0.0121 \text{ mol}$$

$$M_r \text{ of CuSO}_4 \cdot x\text{H}_2\text{O} = \frac{3.074}{0.0121} = \underline{254}$$

$$63.5 + 32.1 + 4 \times 16.0 + 18.0x = 254$$

$$\therefore x = 5.24 \approx \underline{5}$$

1(d)

The initial burette reading has an error of +0.05 cm³ and the final burette reading has an error of -0.05 cm³.

1(e)(i)



1(e)(ii)

- Using an analytical/weighting balance, weigh and record the mass of a clean, empty and dry crucible.
- Weigh out accurately about 5.00 g of solid Cu(OH)₂·nCuCO₃ into the crucible. Record the total mass of the crucible and the solid Cu(OH)₂·nCuCO₃.
- Place the crucible on a pipe-clay triangle. Using a Bunsen burner, heat the crucible and its contents gently at first, and then heat strongly for 10 minutes.
- Cool and weigh the crucible and its contents.
- Repeat the heating-cooling-weighting process until consistent results are obtained. (i.e. when two consecutive mass readings have a difference less than 0.01 g).

An appropriate mass should be used for heating, i.e. at least half of the 5 g sample given.

1(e)(iii)

Mass of empty crucible / g	A
Mass of crucible and Cu(OH) ₂ ·nCuCO ₃ / g	B
Mass of crucible and its contents after first heating / g	C
Mass of crucible and its contents after second heating / g	D
Mass of crucible and its contents after third heating / g	D

- Tables must be constructed with proper headers and units.
- 2 consistent mass readings of the crucible and its contents after heating must be shown.

1(e)(iv)

$$\text{Amount of CuO obtained} = \frac{D-A}{63.5+16.0} = \frac{D-A}{79.5} \text{ mol}$$

Amount of Cu in Cu(OH)₂·nCuCO₃ = amount of CuO obtained

$$\% \text{ by mass of Cu} = \frac{63.5 \times (D-A)}{79.5 \times (B-A)} \times 100\%$$

2(b)(i) & (v)

[I ₂] / mol dm ⁻³	Time / s	[S ₂ O ₈ ²⁻] / mol dm ⁻³
0.001	13	0.009
0.002	25	0.008
0.004	53	0.006
0.006	92	0.004
0.008	154	0.002

- Tables must be constructed with proper headers and units.
- All times must be recorded to the nearest second, as required in the question.

2(b)(ii)

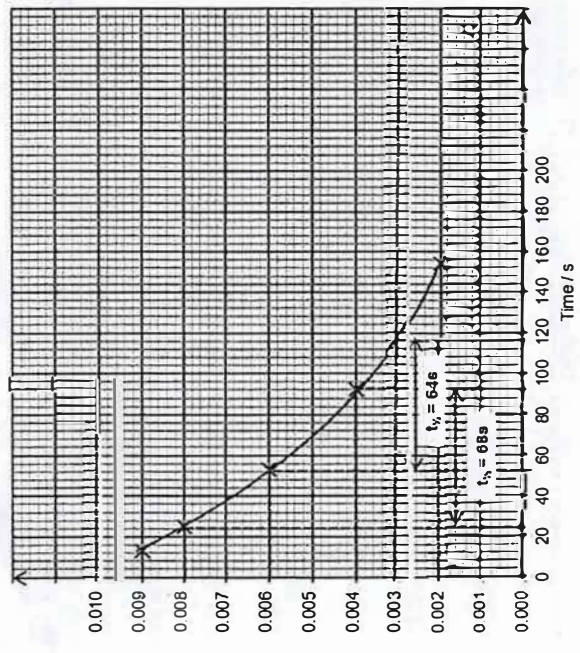
This ensures that the iodide concentration is effectively constant, so the effect of [S₂O₈²⁻] on the rate of reaction can be studied.

2(b)(iii)

$$[\text{S}_2\text{O}_8^{2-}] = \frac{20}{1000} \times 0.020 = \underline{0.0100 \text{ mol dm}^{-3}}$$

2(b)(iv) When $[I_2]_{\text{produced}} = 0.001 \text{ mol dm}^{-3}$, $[S_2O_8^{2-}]_{\text{reacted}} = 0.001 \text{ mol dm}^{-3}$
 $[S_2O_8^{2-}]_{\text{remaining}} = 0.010 - 0.001 = \underline{9.00 \times 10^{-3} \text{ mol dm}^{-3}}$

2(c) $[K_2S_2O_8] / \text{mol dm}^{-3}$



- The x-axis and y-axis should be correctly labelled and with the correct units.
- Appropriate scales must be used and interval markings clearly shown.
- Data points should be plotted correctly.
- The line of best fit must be drawn. The data points should fit into a curve.
- Anomalous points, if any, should be circled.

2(d) Time taken for $[S_2O_8^{2-}]$ to decrease from $0.008 \text{ mol dm}^{-3}$ to $0.004 \text{ mol dm}^{-3}$
 $= 92 - 24 = 68 \text{ s}$

Time taken for $[S_2O_8^{2-}]$ to decrease from $0.008 \text{ mol dm}^{-3}$ to $0.004 \text{ mol dm}^{-3}$
 $= 116 - 52 = 64 \text{ s}$

Since half-life is approximately constant, order of reaction w.r.t. $K_2S_2O_8 = 1$

Construction lines to find half-life values should be clearly drawn on the graph.

2(e)(i) When $[KI] \times 2$, initial rate $\times \frac{0.00363}{0.000910} = 4 = 2^2$
 Order of reaction with respect to KI = 2

2(e)(ii) Rate = $k[KI]^2[K_2S_2O_8]$

2(f) maximum total percentage error = $\pm \frac{0.5 + 0.5}{20 + 20} \times 100 = \pm 2.5\%$

2(g) The concentrations of the iodine solutions prepared will be lower than actual, hence the time taken to reach each concentration will be lower than actual.

3(a)	Test	Observations	Remarks
(i)	To 1 cm depth of FA 7 in a test-tube, add an equal depth of aqueous sodium carbonate.	Reddish-brown ppt formed Effervescence of CO ₂ gas which gave a white ppt in aqueous Ca(OH) ₂ (aq).	FA7 is Fe ₂ (SO ₄) ₃ Ppt is Fe(OH) ₃ (s), not Fe ₂ (CO ₃) ₃
(ii)	To 1 cm depth of FA 7 in a test-tube, add 1 cm depth of dilute hydrochloric acid, then add 1 cm depth of aqueous barium chloride.	Brown/orange solution turns yellow No gas evolved White ppt formed.	Ppt is BaSO ₄ (s)
(iii)	To 2 cm depth of dilute sulfuric acid in a boiling tube, add 1 spatula of FA 8. Warm the mixture cautiously for at least one minute. Leave the mixture to cool and decant the solution into another test tube. To 1 cm depth of the resulting solution, add dilute aqueous ammonia.	Effervescence of H ₂ gas which extinguished a lighted splint with a pop sound. White ppt formed, soluble in excess aqueous ammonia to give a colourless solution.	2H ⁺ (aq) + Zn(s) (FA8) → Zn ²⁺ (aq) + H ₂ (g) Decanted solution contains Zn ²⁺ (aq) from the reaction between H ⁺ (aq) and Zn(s) (FA8). White ppt is Zn(OH) ₂ (s) Colourless solution contains [Zn(NH ₃) ₂] ²⁺ (aq).

3(a)	Test	Observations	Remarks
(iv)	To 3 cm depth of FA 7 in a boiling tube, add 2 spatulas of FA 8. Warm the mixture cautiously for one minute, then leave to cool and filter the mixture. To 1 cm depth of the filtrate, add dilute aqueous sodium hydroxide.	Effervescence of H ₂ gas which extinguished a lighted splint with a 'pop' sound. Residue is grey. Filtrate is colourless (or pale green). Green ppt formed, insoluble in excess sodium hydroxide. White ppt formed, soluble in excess sodium hydroxide to form a colourless solution.	FA7 is Fe ₂ (SO ₄) ₃ & FA8 is Zn Fe ³⁺ (aq) + Zn(s) → Fe ²⁺ (aq) + Zn ²⁺ (aq) Residue contains unreacted Zn(s) Filtrate contains Fe ³⁺ (pale green) and Zn ²⁺ (colourless) from the reaction between FA7 and FA8. Green ppt is Fe(OH) ₃ (s) White ppt is Zn(OH) ₂ (s) Colourless solution contains [Zn(OH) ₄] ²⁻ (aq).

Ions present	Evidence
Fe ³⁺	In test (i), when FA7 was reacted with aq. Na ₂ CO ₃ , a reddish-brown ppt of Fe(OH) ₃ was formed together with effervescence of CO ₂ gas. OR In test (iv), when FA7 was reacted with FA8 (reducing agent), Fe ²⁺ was formed which formed a green ppt of Fe(OH) ₂ with aq. NaOH.
SO ₄ ²⁻	In test (ii), white ppt of BaSO ₄ , which was insoluble in HCl, was formed with aqueous BaCl ₂ .

Identity of FA 8	Evidence
Zn	In test (iii), when aq. NH ₃ was added to the filtrate, a white ppt of Zn(OH) ₂ was formed that was soluble in excess aq. NH ₃ to form a colourless solution containing [Zn(NH ₃) ₄] ²⁺ .

- 3(b)
- Using a dropper, place 1 cm³ of the three unknown organic compounds in separate test-tubes. Then add 1 cm depth of Tollen's reagent and warm the reaction mixture in a hot water bath.

Result: Only propanal would react with Tollens reagent to form a silver mirror and hence can be identified.
 - Using a dropper, place 1 cm³ of the two remaining unknown organic compound in separate test-tubes. Then add a few drops of 2,4-dinitrophenylhydrazine.

Result: Only pentan-3-one would react with 2,4-dinitrophenylhydrazine to form an orange precipitate and hence can be identified.
 - Using a dropper, place 1 cm³ of the remaining unknown organic compound in a boiling tube. Add 3 cm³ of aqueous NaOH and heat.

Result: Ethanamide will undergo hydrolysis to form NH₃(g) which turns damp red litmus paper blue and hence can be identified.

- The appropriate apparatus and quantities must be given for each test.
- The question requires a positive test to be given for each compound.
- The appropriate reagent(s), conditions and observations must be given for each test. Please take note:
 - The use of Tollen's or Fehling's reagent involves heating / warming of the organic compound together with the reagent.
 - Ethanamide should be heated strongly with aq. NaOH to evolve NH₃(g). Warming or gentle heating with aq. NaOH would not cause NH₃ to be evolved.
 - If ethanamide is heated with an acid, such as H₂SO₄(aq), NH₄⁺(aq) is formed instead of NH₃(g) and no alkaline gas will be detected with damp red litmus paper.

