ST. ANDREW'S JUNIOR COLLEGE
JC2 PRELIMINARY EXAMINATIONS
HIGHER 2

CANDIDATE NAME	
CLASS	2 4 S

CHEMISTRY **9729/01**
Paper 1 Multiple Choice **18 September 2025**
Candidate answer on the Optical Answer Sheet. **1 hour**
Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write in soft pencil.

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

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

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

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

Any rough working should be done in this booklet.

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

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

[Turn Over

Answer

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

[Turn Over

BP~449

BP~450

1 Which statement is correct?

A One mole of a compound is the amount that contains the same number of atoms as there are in 12.0 g of carbon-12.

B The relative isotopic mass of beryllium-9 is given by the following expression.

$$\frac{\text{average mass of all isotopes of beryllium}}{\frac{1}{12}\text{ the mass of one atom of }^{12}C}$$

C The relative atomic mass of nitrogen is given by the following expression.

$$\frac{\text{average mass of one atom of nitrogen}}{\frac{1}{12}\text{ the mass of one atom of }^{12}C}$$

D The relative molecular mass of Q is given by the following expression.

$$\frac{\text{average mass of one atom of Q}}{\frac{1}{12}\text{ the mass of one atom of }^{12}C}$$

Ans: C

A: Incorrect. The number of moles of a compound is not the same as the number of moles of atoms in a compound.

B: Incorrect. It should be "*the mass of the isotope of Be*"

C: Correct as defined.

D: Incorrect. It should be "*average mass of one molecule of the substance*"

2 10 cm^3 of a gaseous hydrocarbon, C_xH_y, was exploded with an excess of oxygen. There was a contraction of 40 cm^3. When the products were treated with aqueous sodium hydroxide, there was a further contraction of 50 cm^3. All gas volumes were measured at room temperature and pressure.

What is the molecular formula of the hydrocarbon?

A C_4H_8

B C_4H_{10}

C C_5H_{10}

D C_5H_{12}

Ans: D

Volume of CO_2 = 50 cm^3

Let the volume of reacted O_2 be V cm^3

10 + V = 40 + 50

Volume of reacted O_2 =80 cm^3

$C_xH_y(g) + (x + \frac{y}{4})\ O_2(g) \rightarrow x\ CO_2(g) + \frac{y}{2}H_2O(l)$

10	80	50
1	8	5

x = 5

5 + y/4 = 8

y = 12

Molecular formula of the hydrocarbon is **C_5H_{12}**.

3 In which row are X and Y atoms or ions of different isotopes of the same element?

	X			Y		
	Number of electrons	Charge	Nucleon number	Number of electrons	Charge	Nucleon number
A	3	+3	12	9	−3	12
B	8	0	16	11	−1	19
C	10	+1	23	10	+1	24
D	18	−3	31	12	+3	31

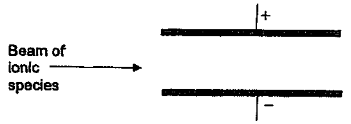
Commented [SKF(1]: Need table outline

Ans: C

Isotopes are elements with the same number of protons but different number of neutrons.

	X		Y		Conclusion
	protons	neutrons	protons	neutrons	
A	6	6	6	6	Same element and isotope
B	8	8	10	9	Different element
C	11	12	11	13	Same element, different isotope
D	15	16	15	16	Same element and isotope

4 Which particle will deflect the most when moving with the same speed through an electric field?



A $^{7}Li^{+}$ **B** $^{11}B^{3+}$ **C** $^{19}F^{-}$ **D** $^{31}P^{3-}$

Ans: B

Angle of deflection is dependent on charge/mass ratio.

The charge/mass of the species are shown below:

A $\frac{+1}{7}$ = +0.14 **B** $\frac{+3}{11}$ = +0.28 **C** $\frac{-1}{19}$ = −0.05 **D** $\frac{-3}{31}$ = −0.10

5 Which molecules are **not** polar?

1 H_2S 2 CS_2 3 SO_2 4 SF_6

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

Ans: B

1: Bent/ polar (2 LP, 2 BP)
2: Linear/ non-polar (0 LP, 2 BP)
3: Bent/ polar (1 LP, 2 BP)
4: Octahedral/ non-polar (0 LP, 6 BP)

[Turn Over

6 A mixture consisting of gaseous compounds, S, T, U and V is slowly cooled.

Gaseous Compound	M_r	Compound
S	72	$CH_3CH_2COCH_3$
T	74	$CH_3CH_2CH(OH)CH_3$
U	72	$(CH_3)_4C$
V	72	$CH_3CH_2CH_2CH_2CH_3$

In which order, from first to last, will the compounds condense to form their liquids?

A T → S → V → U
B U → V → S → T
C S → T → V → U
D V → U → S → T

Ans: A

The stronger the intermolecular forces of attraction, the first the compound will condense, given *Mr* is similar.

Hydrogen bonding> pd-pd> id-id of straight-chained molecule> id-id of branched

Gaseous Compound	M_r	Compound	Intermolecular forces of attraction
S	72	$CH_3CH_2COCH_3$	Pd-pd
T	74	$CH_3CH_2CH(OH)CH_3$	Hydrogen Bonding
U	72	$(CH_3)_4C$	Id-id (weaker)
V	72	$CH_3CH_2CH_2CH_2CH_3$	Id-id (stronger)

7 Which equation corresponds to the enthalpy change stated?

A $S_8(s) + 12O_2(g) \rightarrow 8SO_3(l)$ $\Delta H^{\ominus}_{formation}(SO_3(l))$
B $CaCl_2(s) + aq \rightarrow Ca^{2+}(g) + 2Cl^{-}(g)$ $\Delta H^{\ominus}_{solution}(CaCl_2(s))$
C $2Fe^{3+}(g) + 3O^{2-}(g) \rightarrow Fe_2O_3(s)$ $H^{\ominus}_{lattice\ energy}(Fe_2O_3(s))$
D $H_2SO_4(aq) + Ca(OH)_2(aq) \rightarrow CaSO_4(aq) + 2H_2O(l)$ $\Delta H^{\ominus}_{neutralisation}$

Ans: C

A: 8 X $\Delta H^{\ominus}_{formation}(SO_3(l))$
B: $CaCl_2(s) + aq \rightarrow Ca^{2+}(aq) + 2Cl^{-}(aq)$
C: 1 X $H^{\ominus}_{lattice\ energy}(Fe_2O_3(s))$
D: 2 X $\Delta H^{\ominus}_{neutralisation}$

[Turn Over

BP-451

BP~452

8 *Use of the Data Booklet is relevant to this question.*

A student mixes 20.0 cm^3 of 5.00 mol dm^{-3} sulfuric acid with an equal volume of 6.00 mol dm^{-3} sodium hydroxide. The initial temperature of both solutions is 25.0 °C. The maximum temperature reached after the reaction is 55.0 °C. Assume the density of both solutions is 1 g cm^{-3}.

What is the value of the enthalpy change of neutralisation, in kJ mol^{-1}, calculated using these values?

A −41.8

B −50.2

C −83.6

D −100.3

Ans: A

$Q = mc\Delta T = (40)(4.18)(30) = 5016$ J

No. of moles of H_2SO_4 = 20/1000 x 5 = 0.1 mol

No of moles of H^+ = 0.2 mol

No. of moles of NaOH = 20/1000 x 6 = 0.12 mol

The limiting agent is NaOH.

No. of moles of H_2O = 0.12 mol

$\Delta H = -(5016) / 0.12 = -41800$ J mol^{-1} = −41.8 kJ mol^{-1}

9 The half-life of the first-order gaseous reaction in which M_2 molecules become converted into M atoms is 40 minutes. 1 mol of M_2 is put into a sealed vessel at pressure *p*.

What will be true when 87.5% of M_2 has been converted into M atoms?

1 80 minutes have elapsed.

2 1.5 mol of M have been formed.

3 The total pressure is $\frac{15}{8}p$ (at constant pressure).

A 1, 2 and 3

B 1 and 2 only

C 2 and 3 only

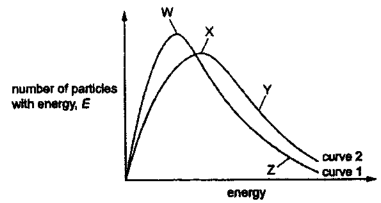
D 3 only

Ans: D

1	120 minutes have elapsed as three half-lives have passed (12.5% of M_2 remains is equivalent to 1/8 = $(1/2)^3$)
2	After the first half-life, 0.5 mol of M_2 will produce 1 mol of M. After the second half-life, 0.25 mol of M_2 will produce 0.5 mol of M. After the third half-life, 0.125 mol of M_2 will produce 0.25 mol of M. Total no. of moles of M = 1 + 0.5 + 0.25 = 1.75 mol
3	True. The initial pressure is *p*, containing only M_2. The change in the *p* is $-0.875p$ for M_2 while $+1.75p$ for M. Hence, The final pressure is $0.125p + 1.75p = 1.875\,p$.

[Turn Over

10 Curves 1 and 2 show the Boltzmann distributions for identical compositions of a reaction mixture which occur at different temperatures.



Which statement is correct?

A Curve 1 applies to the faster reaction and point W indicates particles with lower energy than point Z.

B Curve 1 applies to the faster reaction and point W indicates particles with higher energy than point Z.

C Curve 2 applies to the faster reaction and point X indicates particles with lower energy than point Y.

D Curve 2 applies to the faster reaction and point X indicates particles with higher energy than point Y.

Ans: C

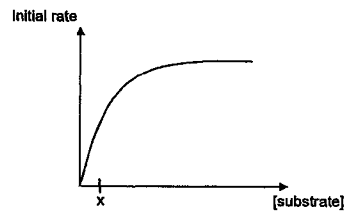
A faster reaction is due to the reaction being conducted at a higher temperature. When temperature of a reaction increases, the molecules would gain kinetic energy and move faster. This would result in its Boltzmann distribution curve to shift to the right with a lower peak.

Hence curve 2 is the one at a higher temperature with a faster rate.

Also, since the x-axis represents energy, point X would thus indicate particles with lower energy when compared with point Y.

[Turn Over

11 The graph shows how the initial rate of reaction varies for an enzyme catalysed reaction as the substrate concentration changes.



Which of the statements correctly describe the situation when [substrate] = x?

1 The initial rate of reaction is affected by increasing [substrate].
2 The order of reaction with respect to [substrate] is 1.
3 There are no more enzyme active sites available.

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

Ans: B

At low [substrate] = x, the active sites are not fully filled, and the rate is directly proportional to [substrate]. The reaction is first–order with respect to [substrate].

12 A sample of 1 mol of XY was placed in an empty 1 dm³ container and allowed to reach equilibrium with a total pressure, *p*, according to the following equation.

$$2XY(g) \rightleftharpoons X_2(g) + Y_2(g)$$

At equilibrium, x mol of XY had dissociated. What is the value of the equilibrium constant, K_p, at the temperature of the experiment?

A $\frac{x^2}{(1-x)^2}$

B $\frac{(1-x)^2}{x^2}$

[Turn Over

C $\frac{4(1-x)^2}{x^2}$

D $\frac{x^2}{4(1-x)^2}$

Ans: D

	2XY (g) ⇌	X_2 (g) +	Y_2 (g)
I	1	0	0
C	–x	$+\frac{1}{2}$x	$+\frac{1}{2}$x
E	1 – x	$\frac{1}{2}$x	$\frac{1}{2}$x

Total number of moles = 1 – x + ½ x + ½ x = 1

Partial pressure of XY = $(\frac{1-x}{1})\,p = (1-x)\,p$

Partial pressure of X_2 and partial pressure of Y_2 = $(\frac{\frac{1}{2}x}{1})\,p = \frac{1}{2}xp$

$$K_p = \frac{(\frac{1}{2}xp)^2}{[(1-x)p]^2} = \frac{(\frac{1}{2}x)^2}{(1-x)^2} = \frac{x^2}{4(1-x)^2}$$

13 Orange dichromate(VI), $Cr_2O_7^{2-}$, and yellow chromate(VI) ions, CrO_4^{2-}, exist in equilibrium in aqueous solution.

$$Cr_2O_7^{2-}(aq) + H_2O(l) \rightleftharpoons 2CrO_4^{2-}(aq) + 2H^+(aq)$$

Which statement about this equilibrium is correct?

A Lowering the pH will increase concentration of CrO_4^{2-} ions.
B Addition of a catalyst will shift the position of equilibrium to the left.
C Addition of water will shift the position of equilibrium to the left.
D In strong alkali, the solution appears yellow.

Ans: D

Lowering the pH increases the concentration of H^+. This will shift the position of equilibrium to the left, resulting in more $Cr_2O_7^{2-}$ ion formed.

The addition of catalyst has no effect on the position of equilibrium.

Adding water will shift the position of equilibrium to the right as there is a greater lowering of concentration of the ions on the right, so the position of equilibrium shifts to replenish the loss of concentration.

Addition of strong alkali neutralises H^+, causing the concentration of H^+ to decrease. This will shift the position of equilibrium to the right, resulting in more yellow CrO_4^{2-} ions formed.

[Turn Over

BP~454

14 The table shows the fifth ionisation energies of four consecutive elements in the Periodic Table.

Element	E	F	G	H
Fifth IE / $kJmol^{-1}$	37832	9445	10989	13327

What is the formula of the chloride of E?

A ECl_2 **B** ECl_3 **C** ECl_4 **D** ECl_5

Ans: C

There is a sharp drop from the fifth IE from E to F, which indicates that F^{4+} is removed from (n+1) quantum shell from E^{4+}. This means that the valence electronic configuration for F^{4+} is $(n+1)s^1$ while E^{4+} has ns^2np^6. This implies that the valence electronic configuration of F is $(n+1)s^2p^3$. This means that the valence electronic configuration for E has (n+1) s^2p^2, having 4 valence electrons. Hence, with Cl, the formula should be ECl_4.

15 Which pair contains an Arrhenius acid and Arrhenius base?

	Acid	Base
A	KCl	NaOH
B	HCl	KOH
C	CH_3COOH	NH_3
D	H_2SO_4	NH_3

Ans: B

Arrhenius acid is a substance that produces H^+ while a Arrhenius base is a substance that produces OH^-. NH_3 is not an Arrhenius base and KCl is salt and not acid.

16 An excess of silver bromide is added to water and the mixture is shaken until equilibrium is reached.

How is the solubility of silver bromide, in this equilibrium mixture, affected by the addition of either

- aqueous ammonia or
- aqueous potassium bromide?

	addition of aqueous ammonia	addition of aqueous potassium bromide
A	decreases	decreases
B	decreases	increases
C	increases	increases
D	increases	decreases

[Turn Over

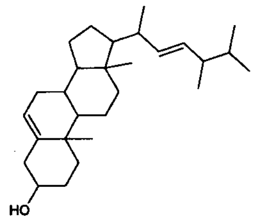
Ans: D

$AgBr(s) \rightleftharpoons Ag^+(aq) + Br^-(aq)$

Addition of aqueous NH_3 will result in formation of complex, $[Ag(NH_3)_2]^+$ which decreases the $[Ag^+]$. Hence POE shift right, increasing the solubility of AgBr

Addition of aqueous KBr increase $[Br^-]$. Hence POE shift left, decreasing the solubility of AgBr.

17 **Brassicasterol is a plant sterol found in sources like rapeseed oil and marine algae.**



brassicasterol

How many stereoisomers does brassicasterol have?

A 2^9

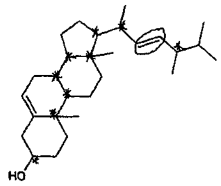
B 2^{10}

C 2^{11}

D 2^{12}

Ans: B

[Turn Over

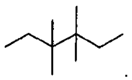


18 In the free radical substitution of 2-methylbutane with chlorine, a mixture of mono-chlorinated compounds was obtained.

Assuming the rate of reaction at all the carbon atoms are the same, which statements are correct?

1 The ratio for the two compounds with the highest yields is 2:1.

2 Homolytic fission only occurs in the initiation step.

3 One of the products formed in this reaction is  .

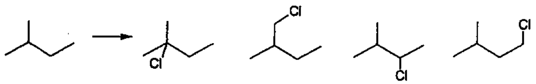
A 1 and 2 only

B 1 and 3 only

C 2 and 3 only

D 1 only

Ans: B



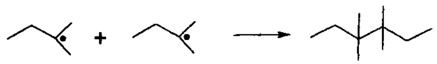
Ratio is 1:6:2:3 (thus ratio of highest yield is 6:3 = 2:1)

Option 1 is correct.

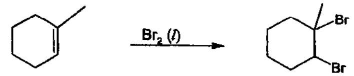
Option 2 is incorrect as homolytic fission occurs in both the initiation and propagation steps.

The product in option 3 (i.e. side product) is formed in the termination step.

[Turn Over



19 Which statement about this reaction is correct?



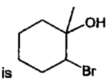
A The product as shown above is the major product when Br_2 (aq) is used instead.

B Electrons in the carbon-carbon σ bond are donated to an electrophile.

C The carbocation has the same hybridisation state as the C in the C=C.

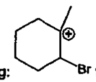
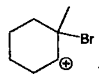
D A primary carbocation is formed in this reaction.

Ans: C

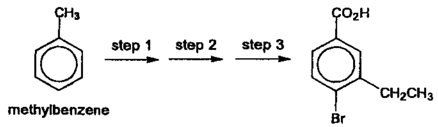
Option A is wrong because the major product is 

Option B is wrong because electrons in C-C π bond is donated to an electrophile and not electrons from the σ bond.

Option C is correct. Both are sp^2.

Option D is wrong:  formed is a tertiary carbocation with 3 R groups and  formed is a secondary carbocation with 2 R groups.

20 Compound P can be synthesised from methylbenzene as shown below.



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BP-455

Which of the following could be a possible sequence for converting methylbenzene to compound P?

	Step 1	Step 2	Step 3
A	CH_3CH_2Cl, $AlCl_3$	Br_2, $AlBr_3$, dark	Hot acidified $KMnO_4$
B	Br_2, $AlBr_3$, dark	Hot acidified $KMnO_4$	CH_3CH_2Cl, $AlCl_3$, heat
C	Br_2, $AlBr_3$, dark	CH_3CH_2Cl, $AlCl_3$	Hot acidified $KMnO_4$
D	Hot acidified $KMnO_4$	CH_3CH_2Cl, $AlCl_3$, heat	Br_2, $AlBr_3$, dark

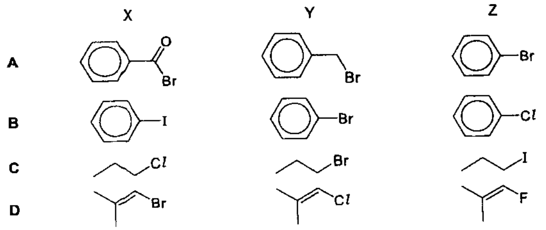
Ans: B

The methylbenzene first undergoes bromination to form 4-bromomethylbenzene. Then undergo oxidation to form benzoic acid. Benzoic acid is deactivating and 3–directing and Br is 2,4-directing hence Friedel–Crafts alkyation takes place in 2 position w.r.t bromine and 3 position w.r.t benzoic acid.

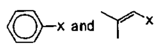
21 Equal amounts of compounds X, Y and Z were heated with ethanolic silver nitrate in three separate test-tubes. After some time, the precipitate formed in each test-tube, if any, was filtered, dried and weighed.

Compound X produced the largest mass of precipitate in the shortest time, while compound Z did not produce any precipitate.

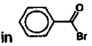
Which of the following could be the identities of X, Y and Z?



Ans: A

 are resistant to nucleophilic substitution as the lone pair of electrons on X is delocalised into the benzene ring and C=C respectively, imparting partial double bond in the C–X bond, making cleavage difficult.

Among the X, the C–I bond being the weakest means that I react the fastest.

As the acyl carbon in  is attached to highly electronegative O besides Br, it is the most electron-deficient, and hence react the fastest, giving the most ppt.

22 Compound W has the empirical formula CH_2O and has the following properties.

- It gives a yellow precipitate when warmed with alkaline aqueous iodine.
- White fumes are produced when it is heated with PCl_3.

What could W be?

A CH_3CO_2H

B $CH_3CH(OH)CO_2H$

C $CH_3COCH_2CH_2CO_2H$

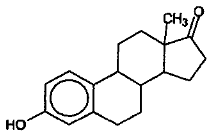
D $HO_2CCH_2CH(OH)CH_2OH$

Ans: B

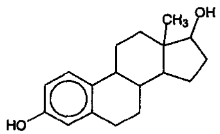
(C has the wrong empirical formula)

		M.F.	E.F.	Alkaline aqueous iodine	white fumes with PCl_3
A	CH_3CO_2H	$C_2H_4O_2$	CH_2O	×	✓
B	$CH_3CH(OH)CO_2H$	$C_3H_6O_3$	CH_2O	✓	✓
C	$CH_3COCH_2CH_2CO_2H$	$C_6H_8O_3$	$C_6H_8O_3$	✓	✓
D	$CH_3COOCH(OH)CH_2OH$	$C_4H_8O_4$	CH_2O	×	✓

23 Two female sex hormones are oestrone and oestradiol.



oestrone



oestradiol

Which of the following reagents could be used to distinguish between the two hormones?

1 Acidified aqueous $K_2Cr_2O_7$
2 Acidified aqueous $KMnO_4$
3 Aqueous alkaline iodine

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

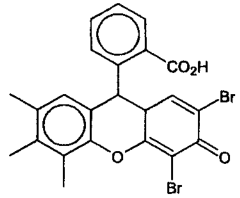
Ans: D

Option 1: PCl_5 will react with oestradiol to produce white fumes of HCl but not with oestrone.

Option 2: Side chain oxidation will take place for both compounds with $KMnO_4/H^+$

Option 3: $LiAlH_4$ in dry ether can reduce ketone in oestradiol but there is no observable change

24 The classic red colour from many lipsticks are obtained from pigments and dyes, such as the compound, eosin. Eosin reacts with proteins of the skin to produce a deep red colour.



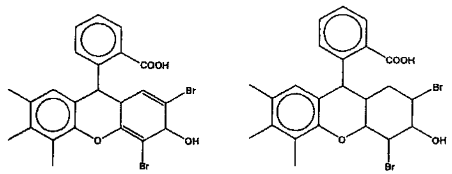
Eosin

Eosin was reduced separately by $NaBH_4$ and by H_2 with Pt.
What is the number of hydrogen atoms added to each molecule of eosin?

	$NaBH_4$	H_2 with Pt
A	2	4
B	2	6
C	4	4
D	4	6

Ans: B

$NaBH_4$ can reduce carbonyl compounds only whereas by H_2 with Pt will reduce the alkenes and carbonyl group in the compound. The product formed are shown below:



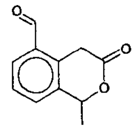
BP-457

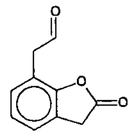
BP ~ 458

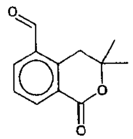
25 Compound X reacts with $[Ag(NH_3)_2]^+$, but not with alkaline Cu^{2+}.

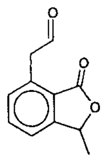
Upon warming X with alkaline aqueous iodine, a yellow precipitate is observed.

What could X be?

A


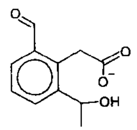
B


C


D


Ans: A

- $[Ag(NH_3)_2]^+$ is Tollens' reagent. It will react with both aromatic and aliphatic aldehydes.
- Alkaline Cu^{2+} is Fehling's solution and it will react with only aliphatic aldehydes.
- Thus A and C are possible answers given the presence of an aromatic aldehyde.
- When undergone alkaline hydrolysis, A has $-CH_3CH(OH)$ structure (as shown in diagram) unlike C. As such, A can form yellow ppt with alkaline aqueous iodine.



26 The ester 2,2-dimethylpropyl ethanoate is found in rare flowers and has a very strong scent.

How may this ester be made in the laboratory?

[Turn Over

1 $(CH_3)_3CCH_2OH + CH_3CO_2H \xrightarrow[\text{heat}]{\text{conc. } H_2SO_4} \text{ester} + H_2O$

2 $(CH_3)_3COH + CH_3CO_2H \xrightarrow[\text{heat}]{\text{conc. } H_2SO_4} \text{ester} + H_2O$

3 $(CH_3)_3CCH_2OH + CH_3COCl \longrightarrow \text{ester} + HCl$

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

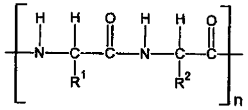
Ans: B

The ester has the structure, $(CH_3)_3CCH_2OCOCH_3$.

Hence the alcohol used must be $(CH_3)_3CCH_2OH$, which will react with the acid chloride, CH_3COCl, or carboxylic acid, CH_3CO_2H, to form 2,2-dimethylpropyl ethanoate.

[Turn Over

27 The diagram below shows the general structure of a protein.



Chymotrypsin is an enzyme that hydrolyses protein into smaller peptides and amino acids. It specifically hydrolyses the peptide bond on the carboxylic end of phenylalanine (Phe).

The structure of hexapeptide Y and the M_r of selected amino acids are given below.

Hexapeptide Y: Val–Ala–Lys–Phe–Ser–Arg

Amino acid	M_r
Valine (Val)	117
Alanine (Ala)	89
Lysine (Lys)	146
Phenylalanine (Phe)	165
Ser (Serine)	105
Arginine (Arg)	174

What are the M_r of the two fragments obtained when hexapeptide Y is hydrolysed by chymotrypsin?

	M_r of fragment 1	M_r of fragment 2
A	517	279
B	463	261
C	316	408
D	352	444

[Turn Over

Ans: B

Val–Ala–Lys–Phe–Ser–Arg will be hydrolysed into 2 peptides:
Val–Ala–Lys–Phe and Ser–Arg

When the peptide bond is formed, -OH from the carboxylic acid end of one amino acid and the -H from the amino end of the neighboring amino acid will be removed as water.

M_r of Val–Ala–Lys–Phe = 117 + 89 + 146 + 165 – (18 x 3) = 463

M_r of Ser–Arg = 105 + 174 – 18 = 261

28 Which factors determine the number of atoms of nickel deposited on the cathode of an electrolytic cell?

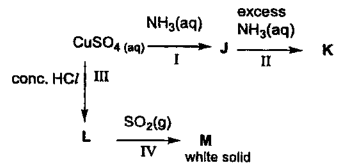
	[Ni^{2+}(aq)]	current	time
A	✓	✓	✓
B	✓	✓	x
C	x	✓	x
D	x	✓	✓

Ans: D

The number of atoms of Ni deposited is dependent on the charge supplied.

Q = I x *t*, which is affected by current and time.

29 Copper(II) sulfate solution reacted as shown in the scheme below.



Which of the following statements is correct?

A NH_3 functions as a ligand in reaction I.

B The coordination number of complex L is 6.

C The oxidation number of Cu in L and **M** is the same.

D Ligand exchange has taken place in reaction II.

[Turn Over

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Ans: D

Option A is incorrect as NH_3 acts as a base.

Option B is incorrect. L is $[CuCl_4]^{2-}$,coordination number 4.

Option C is incorrect.

$2[CuCl_4]^{2-} + SO_2 + H_2O \rightarrow CuCl(s) + 6Cl^- + SO_4^{2-} + 4H^+$

White solid is CuCl. Cu in $[CuCl_4]^{2-}$ is reduced from +2 to +1 in CuCl.

Option D is correct.

When excess aqueous NH_3 is added, ligand exchange occurs to form a deep blue solution.

$[Cu(H_2O)_6]^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+} + 4H_2O$

30 Which of the following statements about manganese are correct?

1 Manganese have a greater number of oxidation states than titanium.

2 Aqueous solution of Mn^{3+} is acidic.

3 Mn^{3+} can catalyse the reaction between $S_2O_8^{2-}(aq)$ and $I^-(aq)$.

A 1, 2 and 3

B 1 and 2

C 2 and 3

D 1 only

Ans: A

Option 1: Correct. Number of oxidation states for the element increases from Sc to Mn.

O.S of Ti : +2, +3, +4

O.S of Mn: +1, +2, +3, +4, +5, +6, +7

Option 2: Correct. To catalyse the reaction, $E^{\ominus}$ of the catalyst must be between + 0.54 and +2.01.

$Mn^{3+}(aq) + e^- \rightleftharpoons Mn^{2+}(aq)$ $E^{\ominus}$=+1.54V

$S_2O_8^{2-}(aq) + 2e^- \rightleftharpoons 2SO_4^{2-}(aq)$ $E^{\ominus}$= +2.01 V

$I_2(aq) + 2e^- \rightleftharpoons 2I^-(aq)$ $E^{\ominus}$=+0.54 V

Option 3: Correct. Mn^{3+} is very polarising due to its high charge density, hence it can be hydrolysed to give H^+.

Commented [NH...]

END OF PAPER

ST. ANDREW'S JUNIOR COLLEGE

JC2 PRELIMINARY EXAMINATIONS

HIGHER 2

CANDIDATE NAME

CLASS

2	4	S		

CHEMISTRY 9729/02

Paper 2 Structured Questions **2 September 2025**

Candidates answer on the Question Paper. **2 hours**

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

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

Write in dark blue or black pen.

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

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

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

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

A Data Booklet is provided.

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

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

For Examiner's Use		
Q1		21
Q2		7
Q3		16
Q4		12
Q5		19
Total		75

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

1 (a) Titanium dioxide, TiO_2, is a white solid, which is an amphoteric oxide. In the structure of titanium dioxide, the titanium ion is bonded to six oxide anions.

(i) Complete the electronic configuration of a titanium atom.

$1s^2$ .... [1]

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^2\ 4s^2$

(ii) Suggest the shape around the titanium ion in titanium dioxide. [1]

Octahedral

(b) (i) Aluminium oxide is another example of an amphoteric oxide.

Write two equations to illustrate the reaction of Al_2O_3 with an acid and a base of your choice respectively. [2]

$Al_2O_3 + 6HCl \rightarrow 2AlCl_3 + 3H_2O$

$Al_2O_3 + 2NaOH + 3H_2O \rightarrow 2Na[Al(OH)_4]$

(ii) The ionic radius of Al^{3+} is 0.050 nm and Ti^{2+} is 0.086 nm.

Explain the difference in ionic radii between Al^{3+} and Ti^{2+}. [2]

Ti^{2+} has a higher nuclear charge than Al^{3+}. Ti^{2+} also has more filled inner shells / electron shells / (principal) quantum shells and the valence electrons are further away from the nucleus and shielding effect increases. The valence electrons are less strongly attracted to the nucleus. Ti^{2+} has a larger ionic size than Al^{3+}.

(c) Titanium(II) chloride is prepared by the thermal decomposition of $TiCl_3$ at 500°C. The reaction is driven by the loss of volatile $TiCl_4$.

$$2TiCl_3\ (s) \rightarrow TiCl_2\ (s) + TiCl_4\ (g)$$

(i) State and explain the sign for ΔS°. [1]

ΔS° is positive or >0 as there is an increase in disorderliness / decrease in orderliness / more ways of arranging when gaseous $TiCl_4$ / more gaseous molecule is formed.

[TURN OVER

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BP-462

(ii) Deduce the sign of the enthalpy change, ΔH, of the thermal decomposition of $TiCl_3$, given that the decomposition is spontaneous only at high temperature. Explain your answer. [1]

$\Delta G = \Delta H - T\Delta S$

The reaction is spontaneous only at high temperature, hence ΔG is negative at high temperature. Since ΔS is positive, ΔH must be positive.

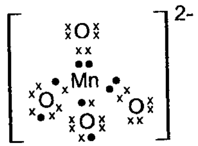
(iii) Explain why $TiCl_3$ forms a violet solution, but $TiCl_4$ forms a colourless solution. [2]

$TiCl_4$ does not have any 3d electrons, hence no d-d transition can occur.

However, $TiCl_3$ has partially filled 3d subshells / orbitals which split into 2 energy levels in the presence of ligands. When an electron from the lower energy d orbital is promoted to a higher energy d orbital, visible light is absorbed. The complementary colour observed is reflected / colour observed is the complementary of light absorbed.

(d) Another transition element that is bonded to oxygen atoms is manganese.
Two examples are manganate(VI) ion, MnO_4^{2-}, and manganate(VII) ion, MnO_4^-.

(i) Given that the structure of MnO_4^{2-} is similar to that of SO_4^{2-}, draw the 'dot–and–cross' diagram of MnO_4^{2-} and state its bond angle. [2]



109.5°

(ii) Acidified potassium manganate(VII), $KMnO_4$, and acidified potassium dichromate, $K_2Cr_2O_7$, can be used as oxidising agents in organic reactions. [2]

[TURN OVER

With reference to relevant E° values, suggest why $KMnO_4$ is a stronger oxidising agent than $K_2Cr_2O_7$.

$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$ $E^\circ = +1.52$ V

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O$ $E^\circ = +1.33$ V

$E^\circ(MnO_4^-/Mn^{2+})$ is more positive as compared to $E^\circ(Cr_2O_7^{2-}/Cr^{3+})$. Hence MnO_4^- is easier to be reduced and is a stronger oxidising agent.

(e) **A**, **B** and **C** are isomers with the molecular formula, $C_5H_{10}O$, that contains one or two of the following functional groups.

- Alkene
- Alcohol
- Carbonyl

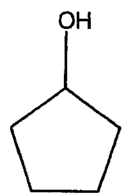
Reactions are carried out on **A**, **B** and **C** and the observations are shown in Table 1.1.

Table 1.1

	with acidified $K_2Cr_2O_7$ (aq)	with acidified $KMnO_4$ (aq)	with 2,4–DNPH	with Br_2 (aq)
A	orange to green	purple to colourless	no reaction	no reaction
B	no reaction	no reaction	orange precipitate	no reaction
C	no reaction	purple to colourless	no reaction	orange to colourless

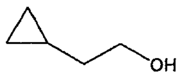
[TURN OVER

(i) **A** is a cyclic compound and does not rotate plane of polarised light. Draw the structure of **A**. [1]

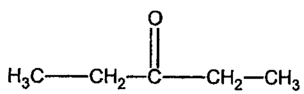


A

Or



(ii) **B** is a symmetrical molecule. Draw the structure of **B**. [1]



B

(iii) Write the equation for the reaction which occurs when **A** reacts completely with an excess of acidified potassium dichromate(VI). Use [O] to represent the oxidising agent in the reaction. [1]

[TURN OVER

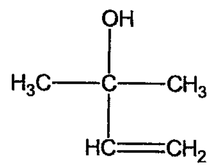
Examiner's Comment:

- Common mistakes include:
  - Writing the molecular formula instead of giving the structural formula of A and the product.
  - Not balancing the equation with H_2O or [O]

(iv) State all possible functional groups in **C**. [1]

Alkene and **tertiary** alcohol

(v) **C** is unable to exhibit stereoisomerism. Draw the structure of **C**. [1]



C

(f) Ketones can undergo oxidation forming esters through the Baeyer–Villiger oxidation reaction by using peroxycarboxylic acids as shown in the equation below. [2]

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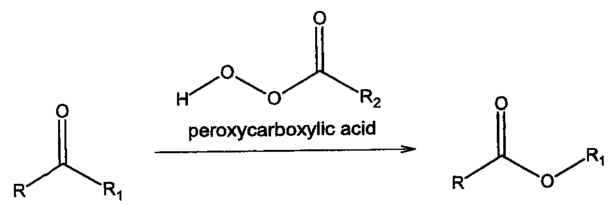
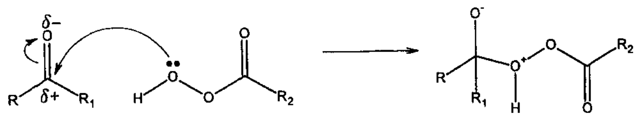


The first step of the mechanism of the Baeyer–Villiger oxidation reaction involves the nucleophilic attack of the lone pair of electrons on the oxygen atom bonded to the hydrogen atom in the peroxycarboxylic acid to the carbonyl carbon in the ketone.

Draw the first step of the mechanism of the Baeyer–Villiger oxidation reaction. Show all relevant dipoles, curly arrows and the structure of the intermediate.



[Total: 21]

2 Ozone, O_3, plays a crucial role in the Earth's atmosphere by absorbing harmful ultraviolet radiation. It is also widely used for its oxidising and disinfecting properties. For example, ozone can be dissolved in ground water or drinking water for disinfection and water quality enhancement.

Fig. 2.1 shows one possible structure of O_3(g).

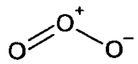


Fig. 2.1

(a) The overall reaction for the decomposition of ozone can be represented as follows.

$$2O_3 \rightarrow 3O_2$$

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The rate of decomposition of ozone in ground water, at pH 8, was investigated and the following results were obtained. The reaction is first order with respect to ozone.

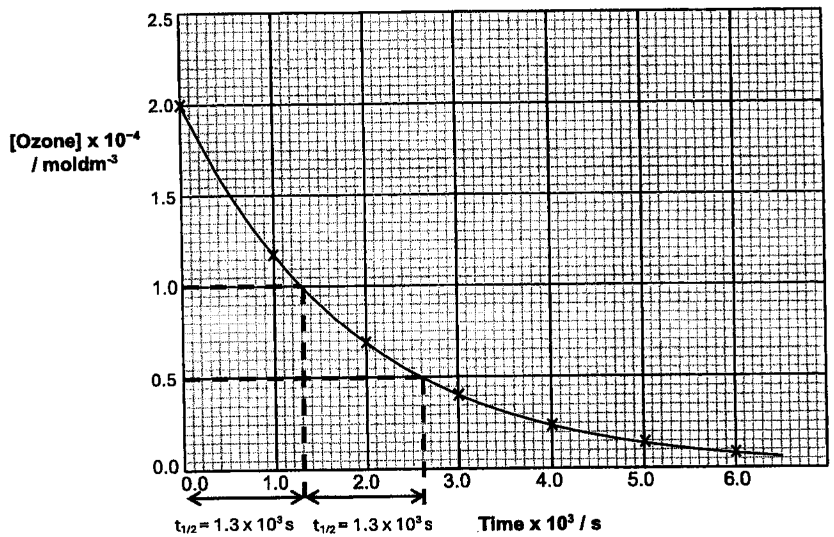

Fig. 2.2

(i) Define the term *order of reaction*. **[1]**

It is the <u>power to which the concentration of the reactant is raised in the experimentally determined rate equation</u>.

(ii) Use the graph in Fig. 2.2 to show that the overall order of reaction is first order. **[1]**

Since the <u>half-life of the reaction</u> for decomposition of ozone is <u>constant</u> at <u>1.3×10^3 s</u>, the order of the reaction is first order with respect to [ozone].

for correct half-life with working on the graph that shows 2 half-lives

[TURN OVER

(iii) Hence, calculate the value of the rate constant, *k*. Include its units. **[1]**

$t_{½} = \frac{\ln 2}{k}$

Using $t_{½} = 1.3 \times 10^3$ s, $k = \frac{\ln 2}{t_{1/2}} = \frac{\ln 2}{1.3 \times 10^3} = 5.33 \times 10^{-4}\ s^{-1}$ [with units]

(iv) The presence of OH^- was found to initiate the decomposition of ozone and the following reaction mechanism was suggested.

Step 1: $O_3 + OH^- \rightarrow HO_2^- + O_2$

Step 2: $HO_2^- + O_3 \rightarrow 2O_2 + OH^-$

State the role of OH^- in this mechanism and explain how the presence of OH^- would affect the rate of the reaction. **[1]**

OH^- is acting as a catalyst as it provides an alternative pathway to lower the activation energy and increases the rate of reaction.

(b) Ozone is a strong oxidising agent, useful for oxidative cleavage of alkenes to form carbonyl compounds.

The reaction of ozone with alkenes can be shown in Fig. 2.3.

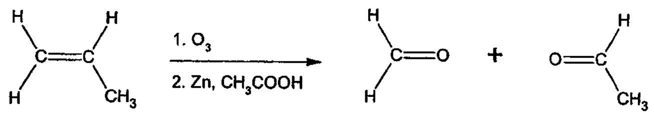

Fig. 2.3

The first step in the mechanism is the initial electrophilic attack by ozone to the carbon-carbon double bond, which then forms the molozonide intermediate. In the second step, the unstable molozonide intermediate undergoes further reaction and breaks apart to form a carbonyl oxide and a carbonyl compound.

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The first and second step of the mechanism is shown in Fig. 2.4.

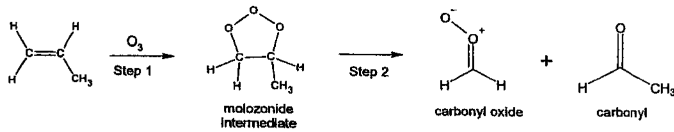


Fig. 2.4

The carbonyl oxide and carbonyl then further react to form the respective carbonyl compounds.

(i) 2-methylbut-2-ene reacts with ozone in a similar reaction to that in Fig. 2.3.

On Fig. 2.5, draw the structure of the molozonide intermediate and suggest the mechanism for the reaction of 2-methylbut-2-ene with ozone in step 1 to form the molozonide intermediate. Include all relevant lone pairs and three curly arrows. **[2]**

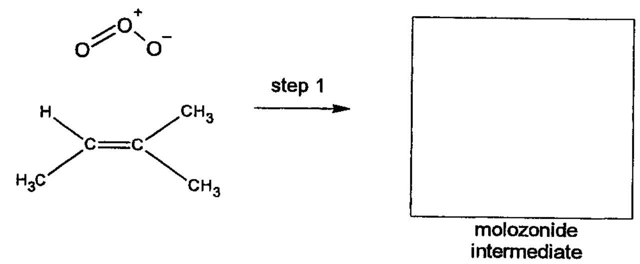
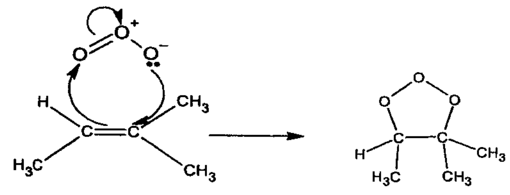


Fig. 2.5



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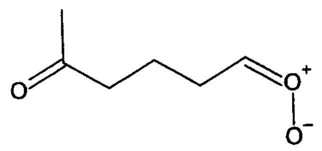
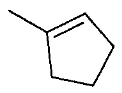
(ii) Compound **F** was formed in step 2 of the mechanism in Fig 2.4 when ozone reacts with another alkene, **G**. Suggest the identity of **G**.



Compound **F**

[1]



[Total: 7]

3 Heavy metal contamination in water poses significant risks to environmental and human well-being. Common heavy metals found in water include cadmium (Cd), lead (Pb) and mercury (Hg).

(a) The standard electrode potential of the Cd^{2+}(aq)/Cd(s) electrode is –0.403V.

(i) Define the term *standard electrode potential, E°*. [1]

The standard electrode potential is the potential difference between standard hydrogen electrode and a half-cell / half-cells of a cell, measured at 298 K, in which the concentration of any reacting species is 1 mol dm^{-3} and any gaseous species is at 1 bar.

(ii) Draw a fully labelled diagram of the experimental set-up used to measure the standard electrode potential, E°, of the Cd^{2+}(aq)/Cd(s) half-cell. [2]

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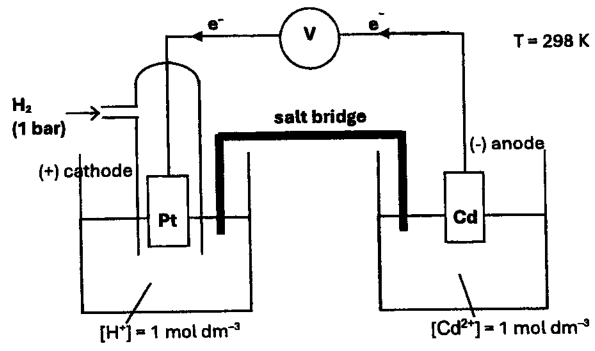

(iii) Predict how the electrode potential, E°, of Cd^{2+}(aq)/Cd(s) will be affected when aqueous sodium hydroxide is added to the Cd^{2+}(aq)/Cd(s) half-cell. Explain your answer. [2]

When OH^- (aq) ions were added to the half cell, $Cd(OH)_2$ will be formed and concentration of Cd^{2+} will decrease.

$$Cd^{2+}(aq) + 2e \rightleftharpoons Cd(s)$$

The equilibrium position shifts left to increase [Cd^{2+}]. Hence, E_{anode} becomes more negative.

(b) A water source was found to be contaminated by heavy metal contaminant, Pb^{2+}.

To determine whether the water is safe to drink, complexometric back titration was employed to determine the concentration of Pb^{2+} in a water sample.

The water sample containing Pb^{2+} will be reacted with an excess amount of $EDTA^{4-}$, where a lead-EDTA complex will be formed in the process.

The general reaction of metal ion, M^{2+} and $EDTA^{4-}$ is as shown:

$$M^{2+} + EDTA^{4-} \rightleftharpoons [M(EDTA)]^{2-}$$

[TURN OVER

The remaining amount of $EDTA^{4-}$ is then determined by titrating with zinc sulfate, with Eriochrome Black T as an indicator.

(i) 10.0 cm^3 of 5.0×10^{-7} mol dm^{-3} of $EDTA^{4-}$ was added to 10.0 cm^3 of water sample containing Pb^{2+}. The resulting solution was found to require 10.0 cm^3 of 2.0×10^{-7} mol dm^{-3} of zinc sulfate solution for complete reaction.

Calculate the amount, in moles, of Pb^{2+} present in 10.0 cm^3 of the water sample. [1]

No of moles of Zn^{2+} = No. of remaining $EDTA^{4-}$ = 2.00×10^{-9} mol

No of moles of Pb^{2+} reacted
= Initial amount of $EDTA^{4-}$ – amount of remaining $EDTA^{4-}$
= $5.00 \times 10^{-9} - 2.00 \times 10^{-9} = 3.00 \times 10^{-9}$ mol

(ii) Calculate the mass of Pb^{2+}, in mg, present in 1 dm^3 of water sample.

Given that the safe limit of maximum mass of Pb^{2+} is 0.0100 mg dm^{-3}, comment on whether the water is safe to drink. [2]

Mass of Pb^{2+} in 10.0 cm^3 of water sample
= $3.00 \times 10^{-9} \times 207.2 = 6.216 \times 10^{-7}$ g

Mass of Pb^{2+} in 1 dm^3 of water sample
= $6.216 \times 10^{-7} \times \frac{1000}{10} = 6.216 \times 10^{-5}$ g = 0.0622 mg

The concentration of Pb^{2+} has exceeded the safe limits, the water is not safe for drinking.

(iii) Hydrogen sulfide, H_2S, is added to another 1 dm^3 of water sample containing 1.0×10^{-9} mol dm^{-3} of Hg^{2+} and Pb^{2+}each.

Table 3.1 shows the K_{sp} values for the corresponding metal sulfides.

Table 3.1

Metal Sulfide	K_{sp} / mol^2dm^{-6}
PbS	9×10^{-29}
HgS	2×10^{-53}

Calculate the minimum concentration of hydrogen sulfide added to remove the maximum concentration of Hg^{2+} without precipitating Pb^{2+}. Hence, determine the maximum mass of HgS precipitated in 1 dm^3. [2]

Ionic Product = K_{sp} of PbS
$(1 \times 10^{-9})[S^{2-}(aq)] = 9 \times 10^{-29}$
$[S^{2-}(aq)] = (9 \times 10^{-29}) / (1 \times 10^{-9}) = 9.0 \times 10^{-20}$ mol dm^{-3}

Ionic Product = K_{sp} of HgS
$[Hg^{2+}(aq)](9.0 \times 10^{-20}) = 2 \times 10^{-53}$
$[Hg^{2+}(aq)] = 2.22 \times 10^{-34}$ mol dm^{-3}

$[Hg^{2+}]$ is almost precipitated since $[Hg^{2+}]$ in solution << initial $[Hg^{2+}]$
Mass of HgS
= $1 \times 10^{-9} \times (200.6 + 32.1) = 2.33 \times 10^{-7}$ g
OR
Mass of HgS
= $(1 \times 10^{-9} - 2.22 \times 10^{-34}) \times (200.6 + 32.1) = 2.33 \times 10^{-7}$ g

(c) DDT is a common ingredient in insecticides and it can enter groundwater as an organic pollutant through processes like runoff and leaching.

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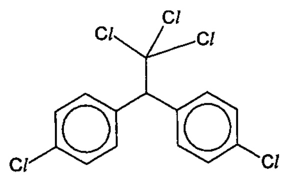
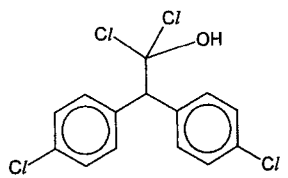


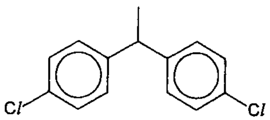
DDT

(i) A student proposed that compound **J** will be formed when DDT is reacted with hot aqueous sodium hydroxide, assuming that the rate of reaction is independent of the concentration of NaOH.



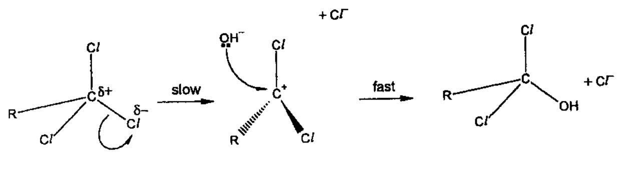
Compound J

Name and describe the mechanism for the reaction between DDT and hot aqueous sodium hydroxide to form compound **J**. Include all relevant lone pairs, dipoles, curly arrows and charges. Include the structure of the organic intermediate.

You may represent  as R.

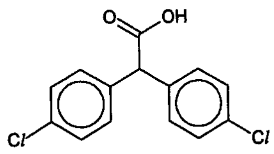
[2]

Nucleophilic Substitution, S_N1

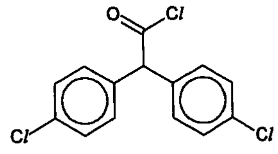


[TURN OVER

(ii) It was found that compound **K** is formed when DDT reacts with hot aqueous sodium hydroxide. **K** then reacts with phosphorus pentachloride to form compound **L**.



compound **K**



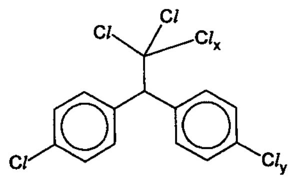
compound **L**

When the same amount of compounds **K** and **L** (not necessarily in that order) are added to separate and equal volumes of water, solutions are formed with pH values of 0.5 and 3.0.
Suggest which pH value is associated with compounds **K** and **L**. Explain your answer.

[2]

pH 0.5 - Compound L　　pH 3.0 - Compound K
L is hydrolysed by water to form carboxylic acid and HC*l*. The strong acid HC*l*, or fully dissociates, accounts for the low pH.

(iii) Explain the difference in reactivity of the two chlorine atoms labelled Cl_x and Cl_y in DDT towards hot aqueous sodium hydroxide.



DDT

[2]

C-Cl_y in DDT does not undergo nucleophilic substitution as the lone pair of electrons of C*l* delocalises into benzene ring, resulting in partial double bond character in the C-C*l* bond, hence the bond is not broken easily.

[Total: 16]

[TURN OVER

4 Haemoglobin is a critical protein found in red blood cells that carries oxygen from the lungs to the rest of the body.

Deoxyhaemoglobin and oxyhaemoglobin both contain iron in the +2 oxidation state. Each Fe^{2+} is coordinated to five nitrogen-containing ligands and one oxygen-containing ligand, forming an octahedral arrangement.

In an octahedral complex such as haemoglobin, the 3d subshell of Fe^{2+} is split into two energy levels.

(a) Using the axes in Fig. 4.1, draw **fully-labelled** diagrams of the following.

- One of the d orbitals at the lower energy level in an octahedral complex.
- One of the d orbitals at the higher energy level in an octahedral complex.

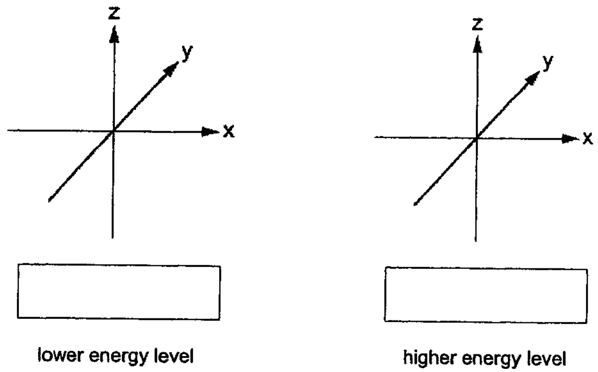
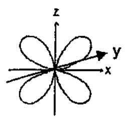


Fig. 4.1 **[2]**

Lower energy level (in between axes)

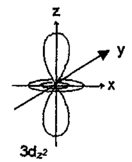


$3d_{xz}$

Comment: aligning with the axis provided, $3d_{xz}$ is the easiest to draw.

Higher energy level (on the axes)

[TURN OVER



$3d_{z^2}$

Comment: aligning with the axis provided, $3d_{z^2}$ is the easiest to draw.

(b) Haemoglobin can react with oxygen and carbon monoxide respectively as shown in the following two equilibria.

equilibrium 1 $Hb(aq) + 4O_2(aq) \rightleftharpoons Hb(O_2)_4(aq)$ $K_{c1} = 3 \times 10^{20}\ mol^{-4}dm^{12}$

equilibrium 2 $Hb(aq) + 4CO(aq) \rightleftharpoons Hb(CO)_4(aq)$ $K_{c2} = 6 \times 10^{22}\ mol^{-4}dm^{12}$

(i) Explain why carbon monoxide is toxic. **[1]**

Carbon monoxide bonds more strongly via a dative covalent bond, to the iron in haemoglobin. CO is a stronger ligand than O_2 and its presence destroys the O_2 carrying capacity of haemoglobin. Thus, CO is toxic.

Carbon monoxide bonds strongly via a dative covalent bond due to higher K_c, destroys the O_2 carrying capacity of haemoglobin.

(ii) Carbon monoxide binds to haemoglobin, Hb, to form carboxyhaemoglobin, $Hb(CO)_4$.

If the percentage of haemoglobin bound to carbon monoxide reaches 45%, the result is fatal to humans.

Use the value of K_{c2} to calculate the concentration of carbon monoxide necessary for 45% of the Hb to be converted to $Hb(CO)_4$. **[2]**

Let x mol dm^{-3} be the initial concentration of Hb(aq)

	Hb(aq)	+ 4CO(aq)	⇌ $Hb(CO)_4(aq)$
Initial conc/ mol dm^{-3}	x		0
Equilibrium conc mol dm^{-3}	0.55 x	?	0.45 x

[TURN OVER

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$K_c = 6 \times 10^{22}$

$[CO]^4 = \dfrac{0.45x}{(0.55x)(6 \times 10^{22})}$

$[CO] = 1.92 \times 10^{-6}$ mol dm^{-3}

(iii) Equilibrium 1 and 2 can be expressed as a single equilibrium 3.

equilibrium 3 $Hb(CO)_4(aq) + 4O_2(aq) \rightleftharpoons Hb(O_2)_4(aq) + 4CO(aq)$

Using K_{c1} and K_{c2}, calculate the value of K_c for equilibrium 3. **[1]**

$K_c = \dfrac{[Hb(O_2)_4][CO]^4}{[Hb(CO)_4][O_2]^4} = \dfrac{[Hb(O_2)_4]}{[O_2]^4} \times \dfrac{[CO]^4}{[Hb(CO)_4]}$

$= K_{c1}[Hb] / K_{c2}[Hb] = K_{c1}/K_{c2} = 1/200 = 5 \times 10^{-3}$

(iv) Use the K_c value calculated in **b(iii)** to suggest the position of equilibrium and the sign for ΔG for equilibrium 3. **[1]**

Position of equilibrium lies to the left and the sign of ΔG is positive

(v) A patient suffering from carbon monoxide poisoning can be treated by giving pure oxygen to breathe. Suggest a reason why this treatment is effective. **[2]**

$Hb(CO)_4 + 4O_2 \rightleftharpoons Hb(O_2)_4 + 4CO$

Or with reference to equilibrium 3

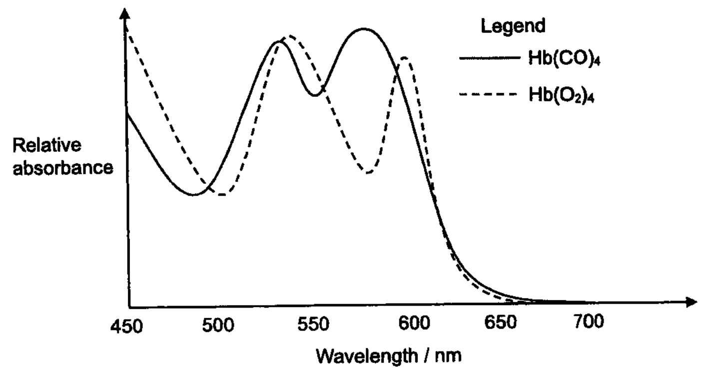
By using pure O_2, the equilibrium position is shifted right due to the very high concentration of O_2

Or

Mass action effect due to high concentration of O_2

The formation of $Hb(O_2)_4$ means that haemoglobin resumes its role as a transporter of oxygen and hence the patient can be revived.

(c) Carboxyhaemoglobin, $Hb(CO)_4$, and oxyhaemoglobin, $Hb(O_2)_4$, were analysed and the absorption spectrum was observed.



Species	Colour Observed
$Hb(CO)_4$	Cherry-red
$Hb(O_2)_4$	Orange-red

Colour	Wavelength (nm)	Colour	Wavelength (nm)
Violet	380 – 400	Yellow	560 – 580
Blue	400 – 490	Orange	580 – 620
Green	490 – 560	Red	620 – 800

(i) With reference to the absorption spectrum, explain why both $Hb(CO)_4$ and $Hb(O_2)_4$ are generally red in colour. **[1]**

The 650 – 800 nm region is not absorbed, thus red colour is reflected.

OR

Both forms of Hb absorb in the 450 – 620 nm region / green absorbed, hence the complementary colour, red, is reflected.

(ii) Suggest why $Hb(CO)_4$ and $Hb(O_2)_4$ have different shades of red. **[2]**

For $Hb(CO)_4$ and $Hb(O_2)_4$, there is a difference in the type of ligand present (O_2 vs CO). This difference resulted in a difference of the extent of the splitting of the d orbitals / in a different energy gap.

[Total: 12]

5 Cycling is a demanding endurance sport that pushes athletes to optimise every aspect of their performance. Chemists play a critical role in this field by enhancing bicycle materials, improving energy metabolism in cyclists and in ensuring safety.

(a) Cyclists often look for ways to reduce the weight of their bicycles, which typically weigh around 7.4 kg. One proposed idea is to inflate bicycle tyres with helium instead of air to reduce weight.

(i) State two basic assumptions of kinetic theory as applied to an ideal gas. **[2]**

There are negligible forces of attraction between the gas particles.

The gas particles occupy a negligible volume compared to the total volume it occupies/volume of the container.

(ii) Using the data in Table 5.1, calculate the respective mass of helium and mass of air required under the same given conditions.

Suggest, with a reason, whether the use of helium provides a significant advantage in terms of mass.

Table 5.1

	Value
Molar mass of helium (He)	4.0 g mol^{-1}
Molar mass of air (approximate)	29.0 g mol^{-1}
Volume of gas in a standard bicycle tyre	2.0 dm^3
Pressure in tyre	8 bar
Temperature	298 K

[3]

n = PV / RT = (8.0 x 100000 x 2.0 x 10^{-3}) / (8.31 x 298) = 0.646 mol

m = 0.646 × 4.00 = 2.58 g

m = 0.646 × 29.0 = 18.73 g

Mass saving = 18.73 – 2.58 = 16.15 g if He is used instead of air. Compared to the mass of the bike, this is only 0.218 %, hence it is not significant.

(iii) Rubber tyres are made of vulcanised rubber, a cross-linked polymer. Although they appear solid, they contain tiny free volumes between polymer chains at the nanometer scale, typically around 0.3 – 0.5 nm.

With reference to the *Data Booklet*, suggest why helium should not be used to inflate the tyres. **[1]**

Atomic size of He = 0.140 nm

The atomic size of He is smaller than the gaps/holes in the rubber structure of the tyre (0.3 – 0.5 nm). The He can escape easily through the gaps/ resulting in fast leakage.

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(b) A bicycle frame must balance tensile strength, weight, durability and cost. Choosing the right material is key to optimising cycling performance.

Tensile strength is the maximum stress that a material can withstand before it shows significant deformation of its body shape.

Table 5.2

Material	Density (g/cm^3)	Tensile Strength (MPa)	Relative Cost	Corrosion Resistance
Aluminium	2.70	310	Moderate	Moderate
Titanium	4.50	900	High	High
Steel	7.85	500	Low	Low
Graphite Fibre	1.60	600	Very High	High

(i) Explain, in terms of structure and bonding, why graphite fibre has relatively high tensile strength. **[1]**

Giant covalent structure with extensive /strong covalent bonds between the carbon atoms.

(ii) Considering the data provided in Table 5.2, recommend the most suitable material for a high-performance racing bicycle frame. Justify your choice in terms of the factors in Table 5.2. **[2]**

Rank each material in terms of each factor

Material	Density rank	Tensile Strength rank	Relative cost rank	Corrosion Resistance rank	Total (the lower the better)
Aluminium	2	4	2	2	10
Titanium	3	1	3	1	8
Steel	4	3	1	3	11
Graphite Fibre	1	2	4	1	8

[TURN OVER

Although titanium and graphite fibre are ranked equally, graphite fibre still wins as it offers much better performance in terms of the density, where the mass of the bicycle is very important, especially when going uphill.

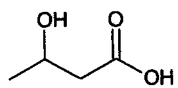
Note: a cheap graphite fibre bike from Decathlon already costs $990! The most expensive graphite fibre bikes, used by top cyclists, cost more than $20,000.

(c) Endurance athletes, such as cyclists, are constantly seeking ways to boost stamina and fight fatigue. One option is to consume BHB energy supplement.

Beta-hydroxybutyrate (BHB), is a lab-made compound that serves as an efficient fuel source for both the brain and body when glucose levels are low.

In cells, BHB enters the mitochondria to produce ATP, which is the body's main source of energy.

Compared to glucose, it generates less waste, helps conserve NAD^+ (a molecule essential for energy metabolism) and avoids blood sugar spikes. However, BHB is also expensive, has a bitter taste, may cause nausea and is absorbed more slowly than glucose. This makes it less ideal for short, intense bursts of energy.



beta-hydroxybutyrate (BHB)

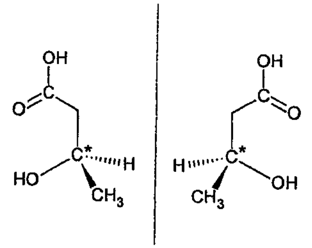
(i) State the systematic name for BHB. **[1]**

3-hydroxybutanoic acid

(ii) BHB has stereoisomers. State the type of stereoisomerism present in BHB and draw the stereoisomers. **[2]**

[TURN OVER

Type of stereoisomerism: Enantiomerism / optical isomerism



(iii) Use the data in Table 5.3, calculate the energy released in kJ g^{-1} for both BHB and glucose when they undergo combustion.

Table 5.3

	Molar mass / g mol^{-1}	Standard enthalpy change of combustion / kJ mol^{-1}
BHB	118.13	−2430
Glucose	180.16	−2805

[1]

Energy per gram for BHB = 2430/118.13 = 20.57 kJ g^{-1}
Energy per gram for glucose = 2805/180.16 = 15.57 kJ g^{-1}

(iv) Based on your calculations in **(c)(iii)**, suggest whether using BHB as an energy supplement would benefit endurance cyclists. Give a reason for your answer. [1]

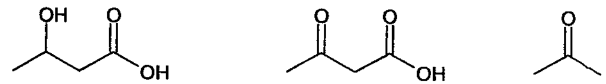
BHB provides more energy per gram (20.57 > 15.57)

Potential advantages: faster energy release, sustained energy in endurance, produces more ATP, higher energy efficiency, alternative when glucose levels fall as it does not spike blood sugar levels for steady performance.

[TURN OVER

(v) Suggest a disadvantage of using BHB as an energy supplement. [1]
It is expensive/ taste issues/ bitter taste / causes nausea/ slower digestion / absorbed more slowly than glucose.

(d) BHB, acetoacetate (AcAc) and acetone are fat-derived compounds made mainly in the liver. They form about 80% of the ketones in the blood and provide energy especially to the brain during fasting, intense exercise or low-carbohydrate diets.



beta-hydroxybutyrate (BHB) acetoacetate (AcAc) acetone

Describe a simple chemical test, with appropriate observations, that can be carried out to distinguish between each of the following pairs of compounds.

- AcAc and acetone
- AcAc and BHB

[4]

- Acetone and AcAc

Add Na_2CO_3 **(aq)** to both compounds in separate test tubes
Acetone: No effervescence observed.
AcAc: Effervescence is observed in 1 test tube. Gas evolved forms white ppt in $Ca(OH)_2$(aq).

- AcAc and BHB

Add 2,4-DNPH to both compounds in separate test tubes
AcAc: Orange ppt formed.
BHB: No orange ppt formed.
OR
Add $KMnO_4$(aq), H_2SO_4 (aq), heat to both compounds in separate test tubes.
AcAc: Purple solution remained.
BHB: Purple solution decolourised.
OR
Add $K_2Cr_2O_7$(aq), H_2SO_4 (aq), heat to both compounds in separate test tubes.

[TURN OVER

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AcAc: Orange solution remained.

BHB: Orange solution turned green.

[Total: 19]

END OF PAPER

ST. ANDREW'S JUNIOR COLLEGE

JC2 PRELIMINARY EXAMINATIONS

HIGHER 2

CANDIDATE NAME

CLASS | 2 | 4 | S | | |

CHEMISTRY — **9729/03**

Paper 3 Free Response — **15 September 2025**

Candidates answer on the Question Paper. — **2 hours**

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work that you hand in.
Write in dark blue or black pen.
You may use a HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the **spaces provided** on the Question Paper.
The use of an approved scientific calculator is expected, where appropriate.
If additional space is required, you should use the pages at the end of this booklet.
The question number must be clearly shown.

Section A
Answer **all** questions.
Section B
Answer **one** question.

For Examiner's Use		
Q1		22
Q2		18
Q3		20
Q4 / Q5		20
Total		80

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

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

Section A

Answer **all** the questions in this section.

1 (a) Calcium carbide, CaC_2, is an ionic compound primarily used in industry to generate acetylene gas, C_2H_2, which has numerous applications in welding, cutting and chemical synthesis.

reaction 1 $CaC_2(s) + 2H_2O(l) \rightarrow Ca(OH)_2(s) + C_2H_2(g)$

(i) The carbon atoms in CaC_2 and C_2H_2 have sp hybridisation and hence they have similar bonding between the two carbon atoms.

Explain what is meant by sp hybridisation with reference to the carbon atoms in C_2H_2. [2]

The mixing/combining of one (2)s and one (2)p orbital of C to form (two) sp hybrid orbitals, which are arranged in a linear manner.

(ii) Suggest how the electrons are arranged in the second shell of sp carbon atom so that the bonding in the two carbon atoms in C_2H_2 can occur. [2]

| 1 | 1 | — *sp orbitals* | 1 | 1 | | — *p orbital*

There are two sp hybrid orbitals and two p orbitals with 1 electron each. C-C σ bond is formed from (head on) sp-sp overlap, when the sp hybrid orbital overlaps head-on with the sp hybrid orbital of C that also contains 1 electron. There is (unhybridised) p orbital with 1 electron. C-C π bond is formed when the p orbital of C overlaps side-on with the p orbtial of C that also contains 1 electron.

(iii) Explain, in terms of structure and bonding, why CaC_2 is a solid at room temperature and pressure while C_2H_2 is a gas. [2]

CaC_2 has a giant ionic lattice structure with strong electrostatic attractions/ionic bond between oppositely charged ions.
C_2H_2 has a simple molecular structure with weak intermolecular instantaneous dipole - induced dipole attractions are easily broken.
More energy required to break the stronger ionic bonds, hence CaC_2 has higher melting point than C_2H_2 and is a solid.

BP-475

(b) Calcium carbide reacts vigorously and explosively with water.
Using the data in Table 1.1, calculate the standard enthalpy change of reaction for reaction 1.

Table 1.1

compound	$\Delta H_f^{\ominus}$ / kJ mol^{-1}
$CaC_2(s)$	– 59.0
$H_2O(l)$	–285.8
$Ca(OH)_2(s)$	– 985.2
$C_2H_2(g)$	+226.6

[2]

$CaC_2(s) + 2H_2O(l) \rightarrow Ca(OH)_2(s) + C_2H_2(g)$

$\Delta H_r^{\ominus}$ = $\Sigma\Delta H_f^{\ominus}$ (products) – $\Sigma\Delta H_f^{\ominus}$ (reactants)
= +226.6 – 985.2 – [–59.0 – (2 × 285.8)]
= <u>–128 kJ mol^{-1}</u>

(c) Caution is required when handling calcium carbide to minimise its exposure to water. Flammable C_2H_2 gas is produced upon reaction of calcium carbide with water and poses explosion risks.

(i) Define the term *standard enthalpy change of combustion, $\Delta H_c^{\ominus}$, of C_2H_2.* **[1]**

The standard enthalpy change of combustion, $\Delta H_c^{\ominus}$, is the <u>enthalpy change/energy change/released</u> when <u>one mole of</u> gaseous <u>C_2H_2 is completely burnt in excess oxygen</u> at standard conditions of <u>298 K and 1 bar.</u>

(ii) Use bond energy values from the *Data Booklet* to calculate the standard enthalpy change of combustion of C_2H_2. **[2]**

H–C≡C–H (g) + $\frac{5}{2}$ O=O (g) → 2 O=C=O (g) + H–O–H (l)

Bonds broken	**Bonds formed**
2 BE(C–H)	4 BE(C=O)
BE (C≡C)	2 BE(O–H)
$\frac{5}{2}$ BE(O=O)	

$\Delta H_c^{\ominus}$ = [2 BE(C–H) + BE (C≡C) + $\frac{5}{2}$ BE(O=O)] – [4 BE(C=O) + 2 BE(O–H)]

[TURN OVER

$\Delta H_c^{\ominus}$ = [2 × (410) + (840) + $\frac{5}{2}$ × (496)] – [4 × (805) + 2 × (460)]
= –1240 kJ mol^{-1}

(iii) The actual standard enthalpy change of combustion of C_2H_2 is –1300 kJ mol^{-1}.

Other than the use of average bond energies, suggest **one other reason** for the difference between the actual value and the value calculated in **(c)(ii)**. **[1]**

Bond energy values are for <u>gaseous compounds, whereas water is a liquid</u>, hence the difference between the standard enthalpy changes of combustion.
OR
The value calculated in (c)(ii) did not take into account the standard <u>enthalpy change of vapourisation/condensation</u> of water.

(iv) Suggest an appropriate storage method for calcium carbide to minimise explosion risks. **[1]**

*Condition must be dry, no water, no flame, no oxidiser
Use airtight, waterproof containers or
(Prevents contact with atmospheric humidity or accidental water exposure)
Store in a cool, dry, well-ventilated area away from water sources (e.g., sprinklers, pipes) or
No open flames/ignition sources in storage areas (acetylene is highly explosive) or
Store away from oxidisers (nitrates, chlorates, peroxides etc) and water or
For bulk storage, use nitrogen (N_2) or argon purging to displace oxygen and prevent acetylene accumulation / store in inert gas
Or
Store in anhydrous condition

(d) C_2H_2 is a weak Brønsted-Lowry acid and reacts with sodium amide, $NaNH_2$, to form an equilibrium mixture containing two acid-base pairs.

equilibrium 2 $C_2H_2 + NaNH_2 \rightleftharpoons Na(C_2H) + NH_3$ $K_c = 1 \times 10^{13}$

(i) With reference to equilibrium 2, explain the terms ***Brønsted-Lowry acid*** and ***conjugate acid-base pair.*** **[2]**

<u>C_2H_2</u> is a Brønsted-Lowry acid as it <u>donates proton</u> to NH_2^-.

[TURN OVER

In the acid-base reaction, a H^+ is transferred from C_2H_2 to a NH_2^-.
C_2H_2 and C_2H^- is a conjugate acid-base pair, which differs by one H^+.
Or
NH_2^- and NH_3

(ii) Identify another acid in the mixture in equilibrium 2 and suggest whether the acid is a stronger or weaker acid than C_2H_2. Explain your answer. **[2]**

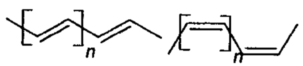
NH_3
It is a weaker acid that C_2H_2 as the large K (>1) value implies that the position of equilibrium lies more on the right, favouring the donation of H^+ from C_2H_2.

(e) C_2H_2 can undergo polymerisation in the presence of suitable catalysts to form polyacetylene, an organic polymer with alternating single and double bonds. It is used in organic semiconductors and its reaction with iodine produces highly electrical conducting material.

$$n\ HC{\equiv}CH \rightarrow -[CH{=}CH]_n-$$

$-[CH{=}CH]_n-$ is known as a repeating unit in polyacetylene.

(i) Two isomers can be obtained when C_2H_2 undergoes polymerisation.
Draw the structures of the two isomers, showing at least **two** repeating units, and state their isomeric relationship. **[2]**



trans cis

Cis-trans isomerism

Polyacetylene ($-[CH{=}CH]_n-$) becomes highly conductive when doped with iodine. The reaction removes an electron from a double bond, creating a radical cation called polaron.

$$-[CH{=}CH]_n- \quad + \quad \tfrac{3}{2}I_2 \rightarrow -[CH{=}CH]_n^{\bullet+} \quad + \quad I_3^-$$

polaron

(ii) State the role of iodine in the reaction. Explain your answer. **[2]**

I_2 serves as the oxidising agent as it gains electron from polyacetylene. Or the oxidation number of iodine changes from 0 to -1 or -1/3, implying it is reduced.

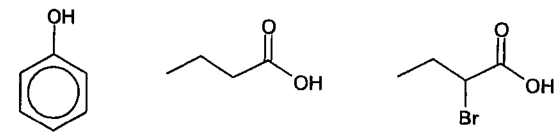
(iii) Suggest why the doping process increases the electrical conductivity of polyacetylene. **[1]**

Polarons formed can act as mobile **charge carriers.**
Detailed reasons (not required)

- I_2 oxidises polyacetylene, removing π-electrons to form I_3^- and leaving radical cations (polarons).
- Polarons delocalise over 4–6 CH units, creating mobile holes.
- These holes move under an electric field, enabling current flow.
- High doping fills the polymer with charge carriers, reducing resistance.

[Total: 22]

2 (a) Deduce the order of increasing acid strength of the following compounds. Explain your answer. **[3]**



phenol butanoic acid 2-bromobutanoic acid

Acidity : phenol < butanoic acid < 2-bromobutanoic acid

$C_6H_5OH \rightleftharpoons H^+ + C_6H_5O^-$
$RCO_2H \rightleftharpoons H^+ + RCO_2^-$

In the phenoxide ion of phenol, $C_6H_5O^-$, the negative charge / lone pair of electrons on O delocalises into the benzene ring. This extent of charge dispersal / stabilisation is less that in the $CH_3CH_2CH_2COO^-$ ion in which the negative charge / lone pair of electrons is delocalised over the O-C-O bond / delocalised over the C=O bond / delocalised over the two O atoms, hence less H^+ donated.

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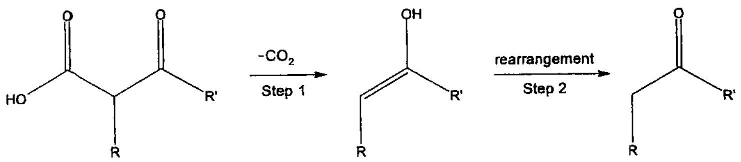
2-bromobutanoic acid is the strongest acid. Bromine is electron withdrawing / electronegative and would disperse the negative charge on O to greater extent. Hence, its anion/conjugate base is most stable and donates H⁺ most readily than butanoic acid.

(b) Decarboxylation is the loss of carbon dioxide from a carboxylic acid group. It plays an important role in organic synthesis and occurs under specific thermal or catalytic conditions.

Two examples of decarboxylation are shown in Fig. 2.1.

Example 1:



Example 2:

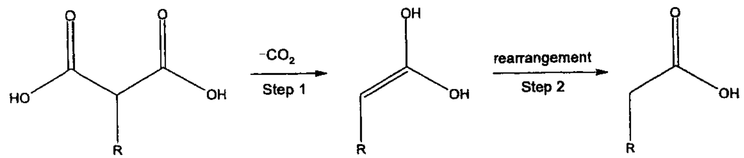
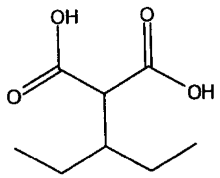


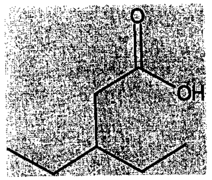
Fig. 2.1

(i) Draw the structure of the organic product formed when compound **K** undergoes decarboxylation.

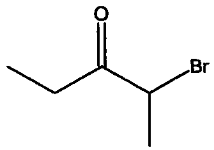


K

[1]



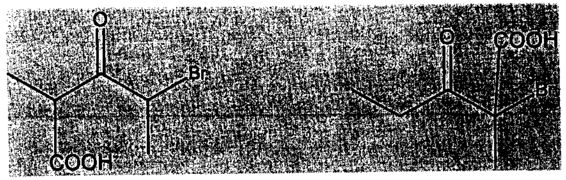
(ii) Two different acids, **M** and **N**, each can undergo decarboxylation to give **L**.



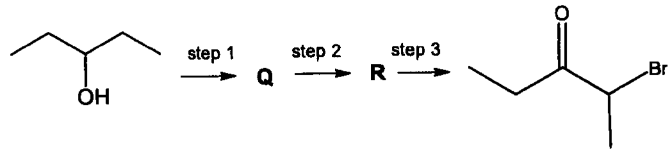
L

[2]

Suggest possible structures of **M** and **N**.



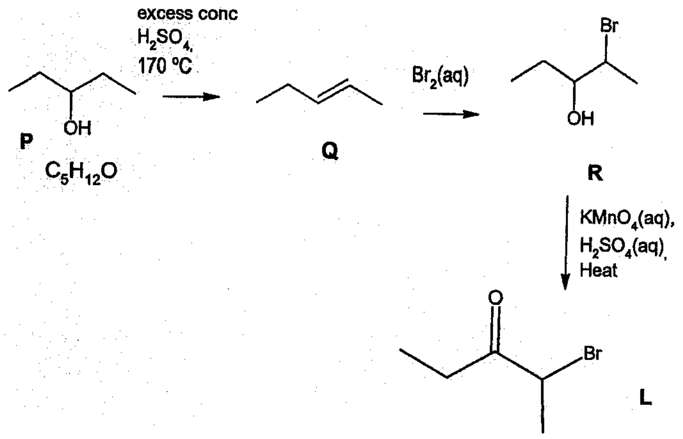
(iii) Compound **L** can also be synthesised from pentan-3-ol by the three-step route shown in Fig. 2.2
State the reagents and conditions required for each step and suggest structures for the organic compounds **Q** and **R**.



L

Fig. 2.2

[5]



(c) The Kolbe electrolysis reaction involves the decarboxylative dimerisation of carboxylate ions to form alkanes at the anode by the following reaction.

$$2R\text{–}CO_2^- \rightarrow R\text{–}R + 2CO_2 + 2e^-$$

R = –CH_3, –CH_2CH_3, etc.

For example, the electrolysis of sodium ethanoate solution produces ethane at the anode.

(i) Suggest the products of the reaction at the cathode and construct an equation for the electrolysis of sodium ethanoate. **[2]**

Products at the cathode: NaOH(aq) and H_2(g)

Anode: $2CH_3CO_2^- \rightarrow CH_3CH_3 + 2CO_2 + 2e^-$

Cathode: $2H_2O + 2e^- \rightarrow 2OH^- + H_2$

Overall: $2CH_3CO_2^- + 2H_2O \rightarrow CH_3CH_3 + 2CO_2 + 2OH^- + H_2$

(ii) Calculate the mass of ethane, C_2H_6, produced when a current of 2.0 A is passed through a solution of sodium ethanoate for 55 minutes. **[2]**

Q = I x t = (2.0)(55 x 60) = 6600 C

$2CH_3CO_2^- \rightarrow CH_3CH_3 + 2CO_2 + 2e^-$

$Q = n_eF$

Amt of e^- = 6600/96500 = 0.06839 mol

Amt of ethane = 0.5 x 0.06839 = 0.03420 mol

Mass of ethane = 0.03420 x 30.0 = 1.03 g

[TURN OVER

(d) Group 2 ethanoates decompose when heated to form carbonates and propanone.

(i) Write an equation for the thermal decomposition of $Ba(CH_3COO)_2$. **[1]**

$Ba(CH_3COO)_2 \rightarrow BaCO_3 + (CH_3)_2CO$

(ii) The trend in the thermal stability of Group 2 ethanoates is similar to that of Group 2 carbonates.

Describe and explain the trend in the thermal stability of Group 2 ethanoates. **[2]**

Down the group, the ionic radius of M^{2+} increases, the <u>charge density decreases</u>, <u>the polarising power of M^{2+} decreases</u> OR <u>the extent of the polarisation of the electron cloud of the anion, $CH_3CO_2^-$ decreases,</u> hence, the <u>C-O bond in the anion is weakened to a lesser extent</u>. <u>More energy</u> is required to decompose MO_2. Hence, the <u>thermal stability of Group 2 ethanoates increases</u> down the group.

[Total: 18]

3 (a) Describe and explain the trend in the thermal stability of the hydrogen halides HC*l*, HBr and HI. Include an equation for the thermal decomposition reaction in your answer. **[3]**

<u>$2HX \rightleftharpoons X_2 + H_2$</u>

<u>Thermal stability decreases</u> from HC*l* to HBr and to HI.

<u>Atomic radius / size of halogen atom increases</u> from C*l* to Br and to I. Hence, the <u>extent of effective orbital overlap between</u> valence orbital of <u>the halogen and</u> 1s of <u>H becomes poorer</u> down the group.

The <u>strength of H-X decreases</u> from HC*l* to HBr and to HI.

OR

<u>Thermal stability decreases</u> from HCl to HBr and to HI.

<u>Electronegativity decreases</u> from Cl to Br and to I.

The <u>smaller the electronegativity difference</u> between the H and X, the <u>less polar</u> the bond, the <u>weaker</u> the bond down the group.

(b) To form concentrated solutions of hydroiodic acid, hydrogen iodide gas is first formed by reaction of hydrogen and iodine gas before being bubbled into water.

$$H_2(g) + I_2(g) \rightleftharpoons 2HI\ (g)$$

[TURN OVER

(i) State the conditions necessary for a gas to approach ideal behaviour. [1]

High temperature, low pressure

(ii) The graphs of pV/RT against p for HI gas and gas J are shown in Fig. 3.1.

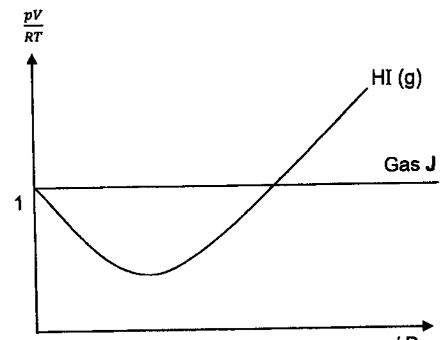


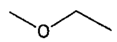
Fig. 3.1

Explain the shape of the graph for HI gas and gas **J**. Your answer should include references to intermolecular forces. [2]

pV/RT is constant for gas J as pressure increases. This is because gas J is an ideal gas with negligible intermolecular forces of attraction.

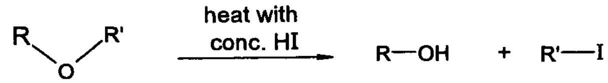
HI gas is a non-ideal gas/real gas with significant intermolecular forces of attraction / permanent dipole-permanent dipole interactions. As the pressure increase, the gas molecules are packed more closely together and intermolecular forces between gas molecules become significant. Hence, HI gas deviates from ideality.

I Ethers have the general structure of R_1–O–R_2, where R_1 and R_2 are alkyl or aryl groups, for example, like methoxyethane.



methoxyethane

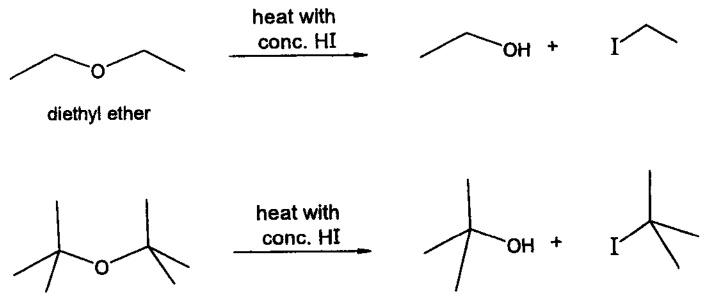
When reacted with hot concentrated solutions of hydroiodic acid, HI, ether can form an alkyl halide and an alcohol as shown in Fig. 3.2.



where R and R' are different alkyl groups

Fig. 3.2

Two examples are shown below.



(i) It was found that primary or secondary ethers, like diethyl ether, reacts via S_N2 mechanism while tertiary ethers, like di-tert-butyl ether, reacts via S_N1 mechanism.

Explain why this reaction proceeds mainly via:

1. S_N2 mechanism for primary or secondary ethers
2. S_N1 mechanism for tertiary ethers

[2]

In primary/secondary ethers, the reactive C does not have many bulky groups around it / experiences least steric hindrance. Hence, I^- can attack the carbon from the back of the C-O bond easily through S_N2. This was not possible for tertiary ethers as it has 3 bulky groups ($-CH_3$) attached to that carbon atom.

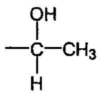
For tertiary ethers, a tertiary carbocation is formed when it undergoes S_N1. The electron donating alkyl groups ($-CH_3$) disperse the positive charge and increase the stability of the tertiary carbocation. This was not possible for primary or secondary ethers as the primary/secondary carbocation formed is not as stable.

(ii) Compound **A**, $C_7H_{16}O$, is an ether, and it reacts with hot concentrated solution of hydroiodic acid, HI, to form compound **B**, $C_6H_{14}O$, and compound **C**.

B is found to rotate plane-polarised light. **B** forms a yellow precipitate with alkaline aqueous iodine. When **B** reacts with hot concentrated H_2SO_4, only compound **D**, C_6H_{12}, is formed.

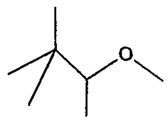
C reacts with hot ethanolic $AgNO_3$ to form yellow precipitate.

With reference to Fig. 3.2, deduce a possible structure for **A**. Hence, suggest the structures for **B**, **C** and **D**. For each reaction, state the type of reaction described and explain what the information tells you about the functional groups present in each compound. [8]

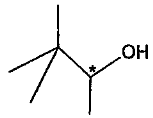
Observations	***Deductions***
Compounds **A**, $C_7H_{16}O$, reacts with hot concentrated solution of hydroiodic acid to form compound **B**, $C_6H_{14}O$ and compound **C**.	Given the molecular formula and the reaction of ether with HI, Compound **B** is an **alcohol / ROH / -OH**. Hence, Compound **C** is an **alkyl halide / RX**
B is found to rotate plane-polarised light.	B contains a **chiral C** that is attached to 4 different groups.
B forms a yellow precipitate with alkaline aqueous iodine.	**B** undergoes **oxidation** with alkaline aqueous iodine  **B** contains a ______ .

When **B** reacts with hot concentrated H_2SO_4, only compound **D**, C_6H_{12}, is formed.	**B** undergoes **elimination** to form **D only.** **D** is an **alkene / C=C** This implies that there is only 1 way of eliminating -H and -OH from **B** OR There are no H attached to adjacent C.
C reacts with hot ethanolic $AgNO_3$ to form yellow precipitate.	**C** undergoes **nucleophilic substitution** to form yellow precipitate, **AgI** . **C** is confirmed an **alkyl iodide /iodoalkane/alkyl halide/halogenoalkane**

A:

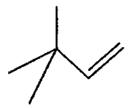


B:



C: CH_3I

D:



(d) Crown ethers are a class of cyclic ethers that have garnered significant attention due to their unique ability to form complexes with cations.

An example of a crown ether is 12-Crown-4 in Fig. 3.3.

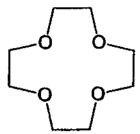


Fig. 3.3

12-Crown-4 forms complexes with various cations such as lithium ion, Li^+, in Fig. 3.4.

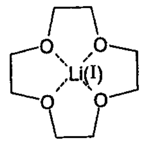


Fig. 3.4

(i) Suggest why 12-Crown-4 was found to be more selective in complexing with lithium ion, Li^+, than potassium ion, K^+. [1]

Li^+ is smaller than K^+ and can fit the size of the cavity/hole in 12-Crown-4 better.

(ii) Suggest the type of interactions between 12-Crown-4 and Li^+. [1]

Ion-dipole interaction OR dative bond

(iii) Crown ethers can be used to selectively remove caesium, a common component in nuclear waste, by complexing with caesium ions.

The radioactive decay of caesium-134 isotope is a first-order reaction with a half life of 2 years.

Use the following equations to calculate the percentage decrease of $^{134}Cs^+$ in a radioactive waste sample six months after it had been collected.

$$k = \frac{0.693}{t_{1/2}}$$

$$\frac{(^{134}Cs^+)_t}{(^{134}Cs^+)_o} = 10^{-\frac{kt}{2.3}}$$

where k is the rate constant,
$(^{134}Cs^+)_t$ is the amount of $^{134}Cs^+$ collected in the sample at time = t,
$(^{134}Cs^+)_0$ is the amount of $^{134}Cs^+$ collected in the sample at time = 0,
t is the time elapsed after the sample was collected.

[2]

$$\frac{(^{134}Cs^+)_t}{(^{134}Cs^+)_0} = 10^{-\frac{kt}{2.3}} = 10^{-\frac{\frac{0.693}{2}\times 0.5}{2.3}} = 0.8408$$

Time can be in years or months

[TURN OVER

Percentage decrease

$= \left(1 - \frac{(^{134}Cs^+)_t}{(^{134}Cs^+)_0}\right) \times 100\%$

= 15.9%

[Total: 20]

Section B

Answer **one** question from this section.

4 (a) Manganese forms stable coloured ions in various oxidation states in aqueous solutions. Some of these manganese ions and their corresponding colours are shown in Table 4.1.

Table 4.1

formula of manganese ion	MnO_4^-	MnO_4^{2-}	Mn^{3+}	Mn^{2+}
colour of aqueous solution	purple	green	violet	pale pink

(i) Explain why manganese can form ions of variable oxidation states. **[1]**

Due to the close similarity in energies of the 3d and 4s subshells/orbitals, both 3d and 4s electrons can be removed from manganese or shared to form stable ions of different oxidation states

(ii) Table 4.2 gives data about some physical properties of the elements, calcium, cobalt and manganese.

Table 4.2

	Calcium	Cobalt	Manganese
relative atomic mass	40.1	58.9	54.9
atomic radius (metallic) /nm	0.197	0.125	0.132
density / g cm^{-3}	1.53	8.83	*x*

Using the data provided in Table 4.2, suggest a value for *x*, the density of manganese. Explain your answer. (No calculations are required.) **[2]**

Density = mass/volume (not marking point)

Accept density values above 1.53 but less than 8.83

Manganese has a larger relative atomic mass than calcium but smaller relative atomic mass than cobalt.

Manganese has a smaller atomic radius than calcium but bigger atomic radius than cobalt.

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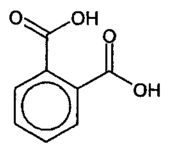
This results in a more closely packed metallic lattice / closer packing in manganese compared to calcium.

OR

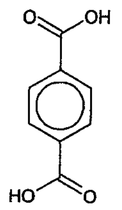
This results in a less closely packed metallic lattice / poorer packing in manganese compared to cobalt.

(b) 2-(hydroxymethyl)benzoic acid acts as a bidentate ligand and forms complexes with transition metal ions such as Fe^{3+}.

(i) 2-(hydroxymethyl)benzoic acid can be formed from phthalic acid. Explain the difference in boiling point between phthalic acid and its isomer, terephthalic acid.



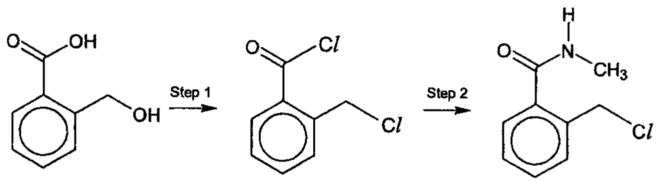
phthalic acid



terephthalic acid [2]

Phthalic acid and terephthalic acid are both polar simple covalent molecules with hydrogen bonding. However, phthalic acid can form intra-molecular hydrogen bond, resulting in less extensive / weaker intermolecular hydrogen bonding. Lesser energy is required to overcome the hydrogen bond OR Phthalic acid has a lower boiling point.

Compound **Y** can be made from 2-(hydroxymethyl)benzoic acid in the following two steps.



2-(hydroxymethyl)benzoic acid **X** **Y**

(ii) Explain the different reactivities of the two chlorine atoms in compound **X**. [2]

The C atom of C=O is more electron deficient or more δ+ as it is connected to two / more electronegative atoms, C*l* and O. Hence, the electron deficient C is more readily attacked by nucleophiles.

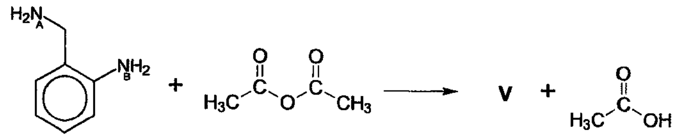
For the other Cl atom, the carbon is only bonded to one / less electronegative C*l* atom and is less electron deficient or less δ+, so it is less readily attacked by nucleophiles.

(iii) Suggest reagents and conditions for step 1 and step 2. [2]

Step 1: $SOCl_2$ or PCl_5 or PCl_3, heat

Step 2: CH_3NH_2

(c) Ethanoic anhydride, $(CH_3CO)_2O$, reacts in a similar way with amines as acyl chlorides. The following reaction is a nucleophilic acyl substitution between $(CH_3CO)_2O$ and compound **U**.



U ethanoic anhydride 1 mole

Fig. 4.1

(i) Explain the relative basicity of N_A and N_B atom in compound **U**. [2]

The phenylamine, N_B has the lone pair of electrons on N delocalises into the benzene ring and decreases its availability for donation to H^+, making phenylamine less basic.

The aliphatic amine, N_A has the electron donating group that increases the availability of lone pair of electrons on N for donation to H^+, making the aliphatic amine more basic.

(ii) In nucleophilic substitution reactions, stronger bases tend to be stronger nucleophiles.

Suggest the structure of compound **V**, $C_9H_{12}N_2O$. [1]

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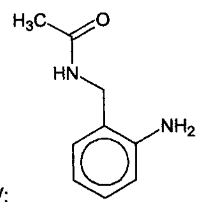


Compound V:

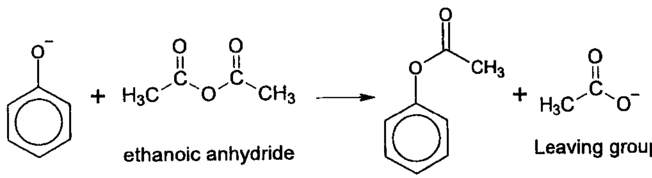
Note: Aliphatic amine is stronger nucleophile than phenylamines. The lone pair of electrons on N of phenylamine is delocalised into the benzene ring, hence it is less available to act as a nucleophile.

(iii) One of the factors that affects the rate of nucleophilic acyl substitution is the nature of the leaving group on the acid anhydride or acyl chloride.

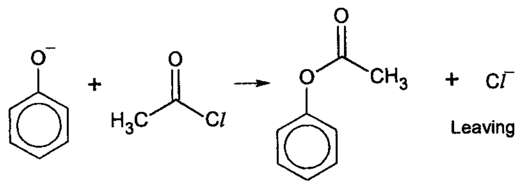
Leaving groups (e.g. Cl^-, CH_3COO^-) that give rise to more stable anions are more readily substituted, therefore increasing the rate of the reaction.

A student proposed two reactions to synthesise phenyl ethanoate using phenoxide ions.

Reaction **1**



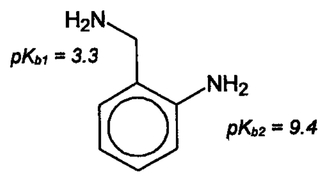
Reaction **2**



Explain why reaction **1** is a better method to synthesise phenyl ethanoate than reaction **2**. **[1]**

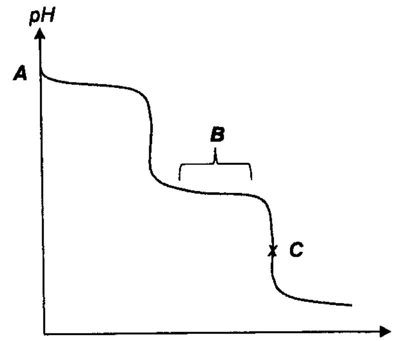
The lone pair of electrons / negative charge on the leaving group, $CH_3CO_2^-$ is delocalised over two highly electronegative oxygen atoms / delocalised over O-C-O. Hence, $CH_3CO_2^-$ is more stable, making it a better leaving group.

(d) The two pK_b values for each amine groups in **U** is shown below.

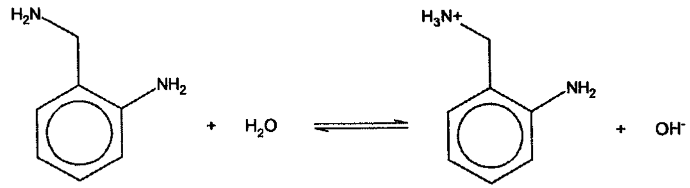


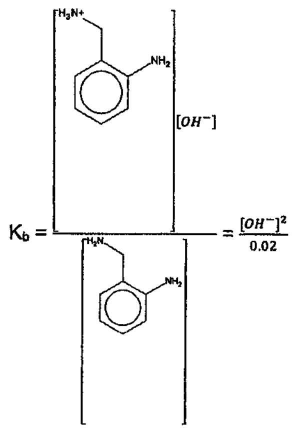
U

The pH curve below shows the addition of 0.010 mol dm^{-3} HC*l* to 10.0 cm^3 of 0.020 mol dm^{-3} compound **U**.



(i) Calculate the pH at point **A**. **[2]**





(formula not required)

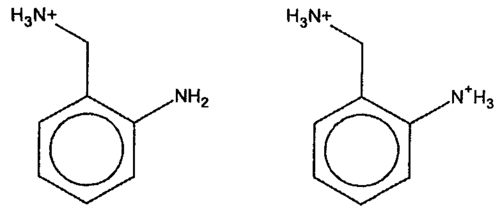
$10^{-3.3} = \frac{[OH^-]^2}{0.02}$

$[OH^-] = 3.166 \times 10^{-3}$ mol dm^{-3}

pOH = – lg 3.166×10^{-3} = 2.50

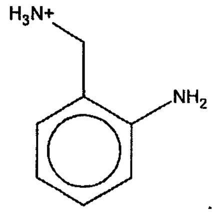
pH = 14 – 2.50 = 11.5

(ii) Draw the two organic structures at region **B** and explain how these species help to maintain the pH of the solution when a small amount of H^+ or OH^- is added. **[3]**



Base | Conjugate acid

Small amount of <u>H^+ ions</u> are removed by the <u>large amount of</u>



Small amount of <u>OH^- ions</u> are removed by the <u>large amount of</u>.

(iii) Calculate the concentration of the salt at point **C**. **[2]**

No of moles of the salt formed = $\frac{10}{1000} \times 0.02 = 2 \times 10^{-4}$ mol

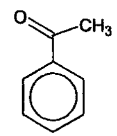
Volume of HC*l* at second equivalence point

$= \frac{\frac{10}{1000} \times 0.02}{0.01} \times 1000 \times 2 = 40$ cm^3

Concentration of the salt = $\frac{2 \times 10^{-4}}{\frac{10+40}{1000}} = 4 \times 10^{-3}$ mol dm^{-3}

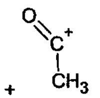
[Total: 20]

5 **(a)** Aluminium is a lightweight, strong and corrosion-resistant metal, widely used in aerospace, construction, packaging and electrical transmission. Its compounds are important in manufacturing, water treatment and pharmaceuticals. One such compound is anhydrous aluminium chloride which catalyses the synthesis of acetophenone from benzene, which is similar to Friedel-Crafts alkylation.



Acetophenone

(i) Write an equation to show how aluminium chloride functions as a Lewis acid catalyst in the synthesis of acetophenone by using a suitable acyl chloride. **[1]**

$AlCl_3 + CH_3COCl \rightarrow AlCl_4^- +$ 

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(ii) Explain, with the aid of an equation, why aluminium chloride must be anhydrous in order for it to function as a Lewis acid catalyst during the synthesis of acetophenone from benzene. **[2]**

$AlCl_3 + 6H_2O \rightarrow [Al(H_2O)_6]^{3+} + 3Cl^-$

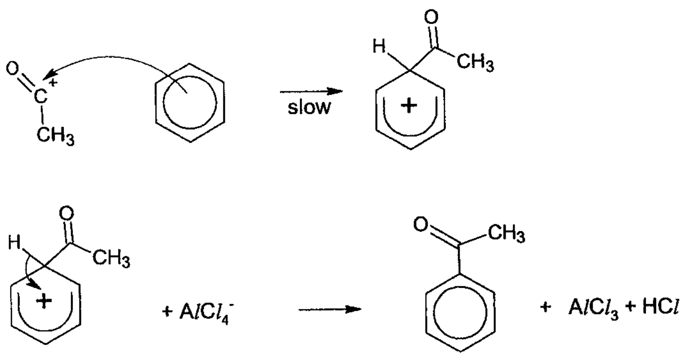
OR

$[Al(H_2O)_6]^{3+}(aq) + H_2O(l) \rightleftharpoons [Al(OH)(H_2O)_5]^{2+}(aq) + H_3O^+(aq)$

In the presence of water, Al^{3+} no longer has empty orbitals as $AlCl_3$ forms the octahedral complex, $[Al(H_2O)_6]^{3+}$.

(iii) Describe the mechanism for the synthesis of acetophenone from benzene, showing curly arrows, charges and any relevant lone pairs. **[2]**

Electrophilic Substitution



- Name of mechaniam
- 1st curly arrow in first step
- Slow
- Structure of intermediate
- 2nd curly arrow in second step
- Regeneration of catalyst and side pdt

(iv) Suggest a simple chemical test to confirm the presence of acetophenone. **[2]**

Reagents and Conditions: I_2 (aq), NaOH (aq), warm

Observations: Yellow ppt formed indicates the presence of acetophenone.

OR

Reagents and Conditions: 2,4-DNPH

Observations: Orange ppt formed indicates the presence of acetophenone.

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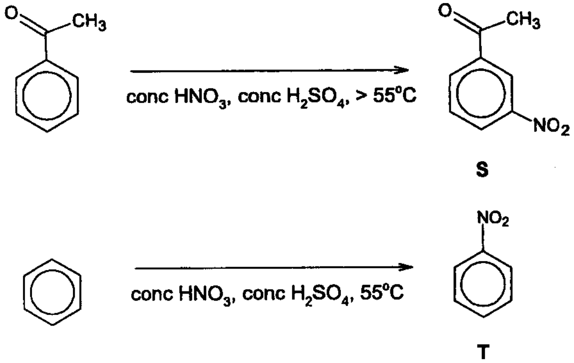
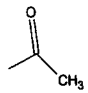
(b) (i) Both acetophenone and benzene react with nitric acid, but under different conditions to form compounds **S** and **T** respectively.



Explain why different conditions are needed for these two reactions. **[2]**

 is a deactivating / electron withdrawing group, reducing the electron density in the benzene ring / less susceptible / less reactive to electrophilic attack. Hence, a harsher condition of a higher temperature is needed.

(ii) The solubility of **S** and **T** in water are shown in Table 5.1.

Table 5.1

Compound	Solubility in water / mg dm^{-3}
S	108
T	80

Explain, in terms of structure and bonding, the difference in solubility between **S** and **T**. **[2]**

Both S and T are polar simple covalent molecules with permanent dipole – permanent dipole (pd – pd) between molecules.

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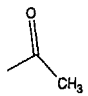
S is more soluble because the extra  results in a more extensive / stronger hydrogen bonding√ formed with water molecules which releases more energy to overcome the pd-pd between molecules of S/T and hydrogen bonding between water.

(c) **E**, **F** and **G** are three elements in Period 3 of the Periodic Table. The pH of the solutions of their oxides and chlorides are as shown in Table 5.2.

Table 5.2

	E	F	G
pH of oxides	9	7	2
pH of chlorides	6	3	2

(i) Identify the elements **E**, **F** and **G**. **[1]**

E is Mg

F is A*l*

G is P or S

(ii) Explain your choice of the elements in **(c)(i)** **[3]**

E is Mg. From the pH of it's oxide, it is a basic oxide. Given that it's chloride is slightly acidic, partial hydrolysis must have occurred due to the more polarising Mg^{2+} as compared to Na^{+}.

F is A*l*. pH of it's oxide is 7 because it is insoluble in water due to its high lattice energy or strong ionic bonds. It's chloride is more acidic because Al^{3+} is more polarising than Mg^{2+}, increasing the extent of hydrolysis.

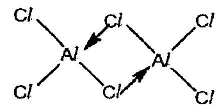
G is P. From the pH of it's oxide, it is an acidic oxide. The low pH of it's chloride suggests that complete hydrolysis have occurred, resulting in the formation of HC*l*, a strong acid.

(d) In the gaseous phase, aluminium chloride dimerises to form Al_2Cl_6, as shown in the equation below.

$$2\,AlCl_3\,(g) \rightarrow Al_2Cl_6\,(g) \qquad \Delta H_{dimerisation} = -158.8\ kJ\ mol^{-1}$$

[TURN OVER

(i) Draw the structure of the dimer, Al_2Cl_6 and state the shapes around A*l* and C*l* atom. **[2]**



Around A*l*: tetrahedral

Around C*l*: bent

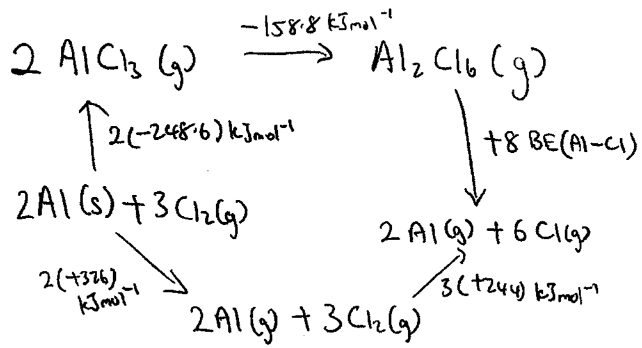
(ii) The average bond energy for the A*l*–C*l* bond in Al_2Cl_6 can be determined using the relevant data in the *Data Booklet* and the following data.

Enthalpy change of dimerisation of Al_2Cl_6 (g) = –158.8 kJ mol^{-1}

Enthalpy change of formation of $AlCl_3$ (g) = – 248.6 kJ mol^{-1}

Enthalpy change of atomisation of A*l* (s) = + 326 kJ mol^{-1}

Construct an energy cycle to calculate the average bond energy for the A*l*–C*l* bond in Al_2Cl_6. **[3]**



2(–248.6) + (–158.8) + 8 BE(A*l* – C*l*) = 2(+326) + 3(+244)

BE(A*l* – C*l*) = + 255 kJ mol^{-1}

[Total: 20]

END OF PAPER

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