NAME		**Class**	

ST ANDREW'S JUNIOR COLLEGE

JC2 PRELIMINARY EXAMINATION

Chemistry (9729) **17 September 2018**

Paper 1 Multiple Choice **1 hour**

Additional Materials: Multiple Choice Answer Sheet, Data Booklet

READ THESE INSTRUCTIONS:

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 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 **14** printed pages.

1 To identify an oxide of nitrogen, the oxide is mixed with an excess of hydrogen and passed over a catalyst at a suitable temperature.

$$N_xO_y \xrightarrow[\text{catalyst}]{H_2\,(g)} x\,NH_3 + y\,H_2O$$

The water collected weighs 0.133 g. The ammonia produced is neutralised by 18.50 cm^3 of 0.2 mol dm^{-3} HC*l*.

Which of the following could be the oxide?

1 N_2O

2 NO_2

3 NO_3

4 N_2O_4

A 3 only

B 1 and 2 only

C 2 and 3 only

D 2 and 4 only

2 This question is about sparingly soluble salts.

	AgC*l*	**AgI**	**HgI$_2$**
K_{sp}	1.0×10^{-10}	8.3×10^{-16}	1.1×10^{-21}

From the above information, which statements are **not** true?

A For a solution containing 1 mol dm^{-3} of NaC*l* and NaI, the concentration of chloride ions when AgI just starts to precipitate is 1 mol dm^{-3}.

B The solubility of HgI_2 is 6.50×10^{-8} mol dm^{-3}.

C The solubility of HgI_2 is the lowest.

D The units for K_{sp} for HgI_2 is mol^3 dm^{-9}.

3 The following tests were performed on an aqueous solution containing bromide and iodide ions.

Step	**Test**	**Observations**
1	Add excess $AgNO_3$(aq).	A mixture of cream and yellow precipitate were formed.
2	To the mixture from step 1, add concentrated NH_3.	The cream precipitate dissolved to form a colourless solution. The yellow precipitate was insoluble.
3	Filter the mixture from step 2.	Filtrate was a colourless solution. Residue was a yellow solid.
4	Add Cl_2(aq) to filtrate.	Brown solution is formed.

Which of the following statements is correct?

A In step 2, the cream precipitate dissolved because the addition of concentrated NH_3 results in formation of a complex which decreases the K_{sp} of AgBr.

B In step 2, the yellow precipitate was insoluble because the K_{sp} of AgI is higher than the K_{sp} of AgBr.

C In step 2, the yellow precipitate was insoluble because the ionic product of AgI is higher than the K_{sp} of AgI.

D In step 4, a disproportionation reaction has taken place.

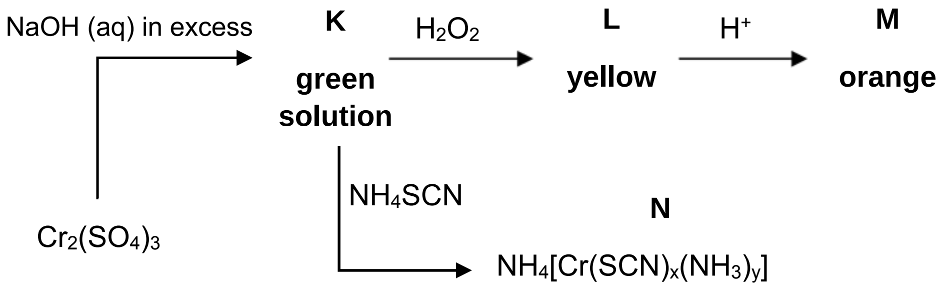
4 A stable ion of **Q** has the following properties:

- has a noble gas configuration
- has more protons than electrons
- was obtained by removing electrons from the same orbital

Which of the following could be **Q**?

A Al **B** Ca **C** Cu **D** S

5 Chromium and its compounds undergo the following reactions.



N has the following composition by mass: Cr, 15.5%; S, 38.1%; N, 29.2%.

Which of the following can be deduced from the above reaction scheme?

A The values of x and y in **N** are 4 and 2 respectively.

B The types of reactions that occur are ligand exchange and redox only.

C The formula of **K** is $Cr(OH)_2(H_2O)_6$.

D H_2O_2 is a reducing agent in the conversion of **K** to **L**.

6 Which one of the following statements about Group 2 elements and their compounds is correct?

A Beryllium chloride has a higher boiling point than magnesium chloride as it has a more exothermic lattice energy than magnesium chloride.

B The reducing power of Group 2 elements increases down the group.

C 1 mole of barium carbonate, on heating over a short period of time, decomposes to give more carbon dioxide gas than 1 mole of magnesium carbonate.

D Barium has a higher melting point than magnesium due to more electrons.

7 Liquefaction can be defined as a process that generates a liquid from a gas and this can be done by altering pressure. In the liquefaction of CH_4 and NH_3, the pressure needed for NH_3 is less than CH_4.

Which of the following reasons best explains this observation?

A NH_3 has stronger intermolecular forces of attraction than CH_4.

B NH_3 has weaker bond energy than CH_4.

C NH_3 molecules are bigger than CH_4 molecules.

D NH_3 molecules possess less kinetic energy than CH_4 molecules.

8 Phosphate buffers are commonly used in biological chemistry research.

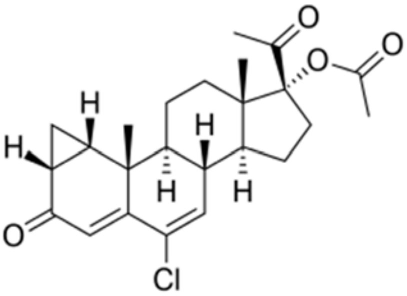
$$H_2PO_4^- \rightleftharpoons HPO_4^{2-} + H^+ \qquad pK_a = 6.7$$

A phosphate buffer with pH 7.4 was prepared using NaH_2PO_4 and Na_2HPO_4 solutions. The total hydrogen phosphates concentration ($[HPO_4^{2-}] + [H_2PO_4^-]$) of the buffer was 0.3 mol dm^{-3}.

What are the concentrations of NaH_2PO_4 and Na_2HPO_4 used to create this buffer?

	$[NaH_2PO_4]$ / mol dm^{-3}	**$[Na_2HPO_4]$ / mol dm^{-3}**
A	0.23	0.07
B	0.07	0.23
C	0.10	0.50
D	0.05	0.25

9 Cyproterone acetate (CPA) is a drug that is used in the treatment of prostate cancer.



CPA

Which of the following statements about CPA are incorrect?

1 One mole of silver is formed when one mole of CPA is warmed with $[Ag(NH_3)_2]^+$.

2 Two moles of yellow precipitate is formed when one mole of CPA is warmed with alkaline iodine solution.

3 One mole of silver chloride is formed when one mole of CPA is heated with ethanolic silver nitrate.

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

10 Consider the following equilibrium:

$$2Q_2\,(g) \; + \; R_2\,(g) \rightleftharpoons 2Q_2R(g)$$

When Q_2 is allowed to react with R_2 in a molar ratio of 2:1 at a total initial pressure of 3 atm, 20% of the equilibrium mixture is found to be Q_2R.

What is the equilibrium constant, K_p, of this reaction?

A 0.0174 atm^{-1}

B 0.0781 atm^{-1}

C 0.194 atm^{-1}

D 0.232 atm^{-1}

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

Iodine clock reaction can be used to study how the concentration of iodide ions affect the rate of oxidation of iodide ions with peroxodisulfate ions. Peroxodisulfate ions convert iodide ions into iodine slowly.

$S_2O_8^{2-}(aq) + 2I^-(aq) \rightarrow \; 2SO_4^{2-}(aq) + I_2(aq)$

The rate of the reaction can be increased by the addition of catalysts such as aqueous iron (III) ions.

A possible catalysed reaction pathway involves the following steps:

Step 1: $2Fe^{3+}(aq) + 2I^-(aq) \rightarrow I_2(aq) + 2Fe^{2+}(aq)$

Step 2: $S_2O_8^{2-}(aq) + 2Fe^{2+}(aq) \rightarrow 2SO_4^{2-}(aq) + 2Fe^{3+}(aq)$

Which of the following statements are **correct**?

1 Aqueous cobalt(II) ions can be used as a catalyst in this reaction.

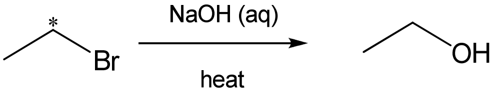
2 $S_2O_8^{2-}$ is a stronger oxidising agent than Fe^{3+}.

3 The $E_{cell}^{\ominus}$ for step 2 is more positive than step 1.

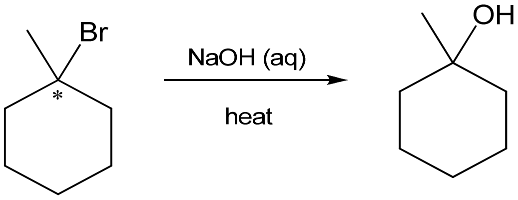
A 2 only **B** 1 and 3 only **C** 2 and 3 only **D** 1, 2 and 3

12 Which of the following reactions has no change in the hybridisation state of the carbon atom indicated with an asterisk (*) from the reactant to the **intermediate** in the mechanism?

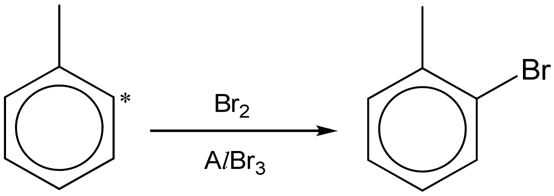
A



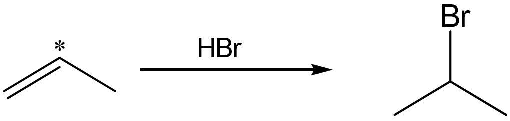
B



C



D



13 What is the volume of vapour formed when 10 cm^3 of liquid ethanol (density: 0.789 g cm^{-3}) is heated to 300 °C at a pressure of 5 bar?

A 85.5 cm^3

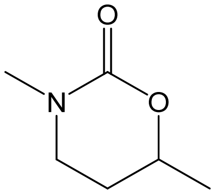
B 855 cm^3

C 163.3 cm^3

D 1633 cm^3

14 Which compounds liberate carbon dioxide gas when heated with acidified potassium manganate(VII)?

1



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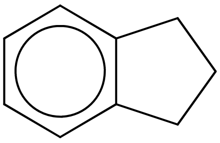

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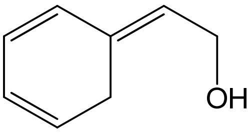


A 1 and 2 only

B 2 and 3 only

C 1, 2 and 3

D None of the above

15 Trifluorooxonium has the formula $OF_3{}^{n+}$ and its shape is trigonal pyramidal.

What is the value of *n* in trifluorooxonium?

A 1 **B** 2 **C** 3 **D** 4

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

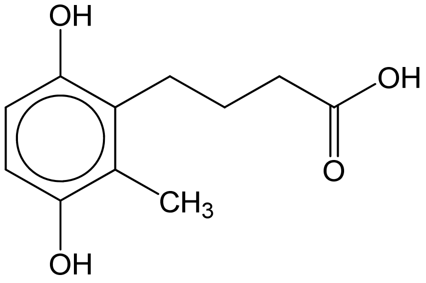
Which set of reagents, when added in the order shown below, would convert $Fe^{3+}(aq)$ to $[Fe(CN)_6]^{3-}(aq)$?

$$Fe^{3+}(aq) \xrightarrow{\text{step 1}} Fe^{2+}(aq) \xrightarrow{\text{step 2}} \mathbf{X} \xrightarrow{\text{step 3}} [Fe(CN)_6]^{3-}(aq)$$

	step 1	step 2	step 3
A	$Zn(s)$	$CN^-(aq)$	$SO_2(g)$
B	$I^-(aq)$	$CN^-(aq)$	$Cl_2(g)$
C	$H_2O_2(aq)$	$I^-(aq)$	$CN^-(aq)$
D	$Ag(s)$	$I^-(aq)$	$CN^-(aq)$

17 Compound **X** is dissolved in heavy water, D_2O. It contains a number of hydrogen atoms which can be easily be replaced by deuterium, D.

[D, deuterium = ^2H]



Compound **X**

What is the maximum number of hydrogen atoms which could be replaced by deuterium atoms in each molecule of **X**?

A 1 **B** 2 **C** 3 **D** 4

18 Which of the following, when mixed together at 298K and 1 bar, represent the standard enthalpy change of neutralisation?

1 500 cm^3 of 1 mol dm^{-3} HNO_3 and 500 cm^3 of 1 mol dm^{-3} KOH

2 500 cm^3 of 1 mol dm^{-3} H_2SO_4 and 500 cm^3 of 1 mol dm^{-3} $Ca(OH)_2$

3 1 dm^3 of 1 mol dm^{-3} HNO_3 and 500 cm^3 of 1 mol dm^{-3} $Ca(OH)_2$

4 1 dm^3 of 1 mol dm^{-3} H_2SO_4 and 1 dm^3 of 1 mol dm^{-3} KOH

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

19 Which of the following cannot act as a ligand?

A AlH_4^-

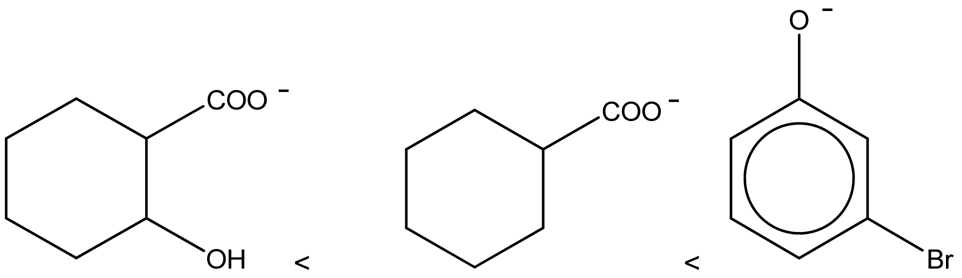
B N_2H_4

C CH_3OH

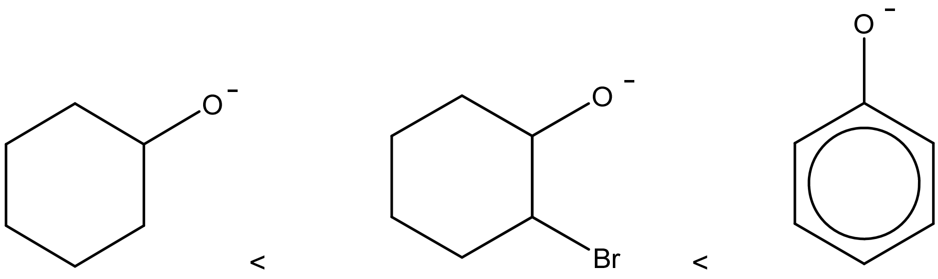
D CO

20 Which of the following shows an increasing trend in K_b ?

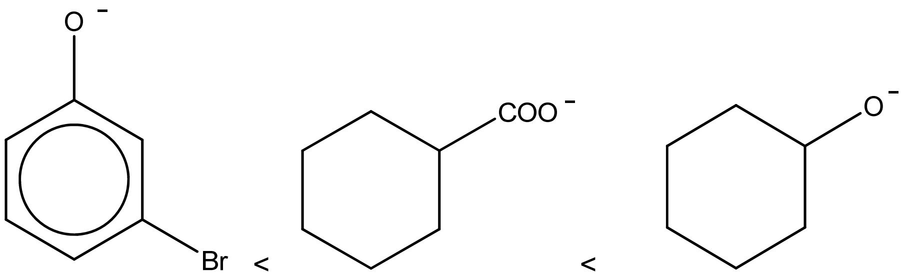
A



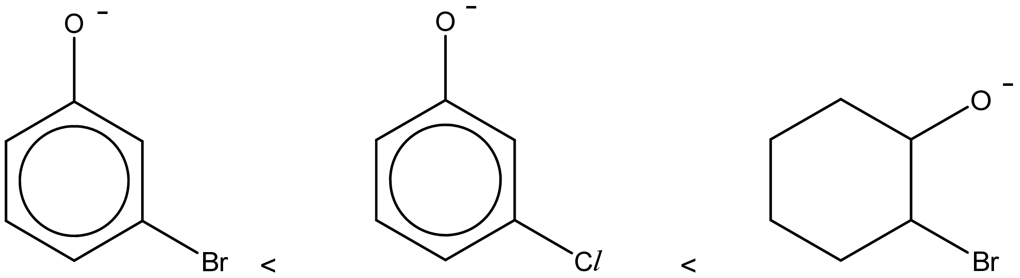
B



C



D



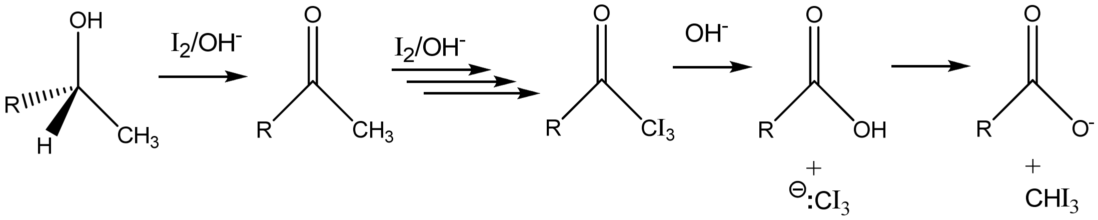
21 Which quantity would best indicate the strength of intermolecular hydrogen bonds in HF?

- **A** enthalpy change of vapourisation
- **B** enthalpy change of formation
- **C** enthalpy change of atomisation
- **D** bond dissociation energy

22 The following data refer to cobalt as a typical transition element and calcium as an s-block element. Which of the following properties shows the correct data for both elements?

	Property	**Cobalt**	**Calcium**
A	Metallic radius / nm	0.150	0.117
B	Electrical conductivity / relative units	10.2	50
C	Melting point / °C	1495	1965
D	Density / g cm^{-3}	8.9	1.54

23 The reaction of methyl alcohols with alkaline aqueous iodine can be described by the simplified scheme as shown below:



Which of the following reactions have taken place?

1 Oxidation

2 Acid-base reaction

3 Nucleophilic addition

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

24 Nitrogen, ^{14}N, is the final product formed by the radioactive decay of ^{14}C, which is a first-order reaction with a half-life of 5.73 x 10^3 years.

What would be the age of a substance, originally nitrogen free, in which the molar proportion of ^{14}C : ^{14}N is 2 : 5?

A 0.29 x 10^4 years

B 1.04 x 10^4 years

C 1.58 x 10^4 years

D 1.95 x 10^4 years

25 The properties of the oxides of four Period 3 elements **W, X, Y** and **Z** are given below.

- The oxide of **W** is insoluble in water and in dilute acid but soluble in concentrated sodium hydroxide.
- The oxide of **X** is amphoteric.
- The oxide of **Y** reacts with dilute potassium hydroxide at room temperature.
- The oxide of **Z** dissolves in water to form a solution of pH = 13.

Which of the following is correct in order of increasing atomic number?

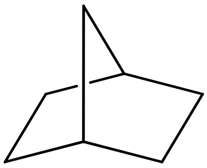
A **Z, X, W, Y**

B **W, X, Y, Z**

C **Z, W, X, Y**

D **Z, Y, W, X**

26 Norcarane undergoes free radical substitution with limited bromine in the presence of ultraviolet light to form mono-brominated compound **Y**.



Norcarane

How many isomers of **Y** (including stereoisomers) will be formed at the end of the reaction?

A 3 **B** 4 **C** 6 **D** 8

27 The following are information for a reaction involving **X** and **Y**:

- it is first order with respect to [**X**] and zero order with respect to [**Y**].
- its rate constant doubles for each 10 °C rise in temperature

Which of the following statements are true about this reaction?

1 The half-life of the reaction remains the same when [**X**] doubles.

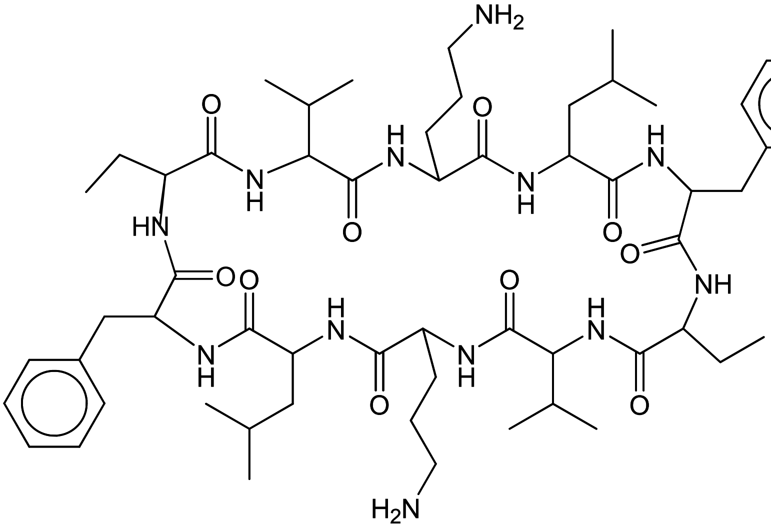
2 The half-life of the reaction doubles when [**Y**] is halved.

3 When the temperature of the reaction increases from 298K to 318K, the rate of the reaction will be quadrupled.

4 The rate of the reaction will change when [**X**] is halved and temperature increases from 298K to 308K.

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

28 Gramicidin Soviet is an antibiotic that is effective against some fungi. It is made up of several α amino acids.



Gramicidin Soviet

Which statement about Gramicidin Soviet is correct?

A It is made up of 5 different amino acids.

B 1 mole of Gramicidin Soviet consists of 9 amide bonds.

C 1 mole of Gramicidin Soviet reacts with 10 moles of hot dilute H_2SO_4.

D Upon reaction with hot dilute NaOH, the products formed have high melting point as they can form strong intermolecular hydrogen bonding.

29 A humidity meter is made by soaking filter paper in an aqueous solution of cobalt(II) ions in HC*l* (aq). The equation for the equilibrium reaction can be represented as follows:

$$\underset{\text{pink}}{Co^{2+}(aq)} + 4Cl^{-}(aq) \rightleftharpoons \underset{\text{blue}}{CoCl_4^{2-}(aq)} \qquad \Delta H = +ve$$

Which of the following statements are correct?

1 On a very humid day, the filter paper will appear more pink.

2 When the filter paper is diluted with more water, there will be no colour change.

3 On a very hot day, the filter paper will appear more blue.

4 When the filter paper is placed in a sealed container under high pressure, there will be no colour change.

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

30 The position of equilibrium lies to the right in each of these reactions.

Reaction 1: $N_2H_4 + HBr \rightleftharpoons N_2H_5^+ + Br^-$

Reaction 2: $N_2H_5^+ + NH_3 \rightleftharpoons NH_4^+ + N_2H_4$

Based on this information, which statements are correct?

1 Br^- is the conjugate base of HBr.

2 $N_2H_5^+$ is the Bronsted base in **Reaction 2**.

3 The order of acid strength is HBr > $N_2H_5^+$ > NH_4^+.

4 N_2H_4 is the Lewis acid in **Reaction 1**.

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

~ END OF PAPER ~

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[Please Turn Over

Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8	Q9	Q10
D	C	C	B	A	B	A	D	D	C

Q11	Q12	Q13	Q14	Q15	Q16	Q17	Q18	Q19	Q20
D	D	D	C	A	B	C	C	A	A

Q21	Q22	Q23	Q24	Q25	Q26	Q27	Q28	Q29	Q30
A	D	B	B	A	B	B	A	C	A

1 To identify an oxide of nitrogen, the oxide is mixed with an excess of hydrogen and passed over a catalyst at a suitable temperature.

$$N_xO_y \xrightarrow[\text{catalyst}]{H_2\,(g)} x\,NH_3 \;+\; y\,H_2O$$

The water collected weighs 0.133 g. The ammonia produced is neutralised by 18.50 cm^3 of 0.2 mol dm^{-3} HC*l*.

Which of the following could be the oxide?

1 N_2O

2 NO_2

3 NO_3

4 N_2O_4

A 3 only

B 1 and 2 only

C 2 and 3 only

D 2 and 4 only

Answer: D

No. of moles of water = 0.133/18 = 0.00739

No. of moles of NH_3 = 18.50/1000 x 0.2 = 0.0037

Ratio of NH_3 to water is 1: 2

Therefore, x : y (i.e. N to O) of oxide is also 1:2

2 This question is about sparingly soluble salts.

	AgC*l*	**AgI**	**HgI_2**
K_{sp}	1.0×10^{-10}	8.3×10^{-16}	1.1×10^{-21}

From the above information, which statements are **not** true?

A For a solution containing 1 mol dm^{-3} of NaC*l* and NaI, the concentration of chloride ions when AgI just starts to precipitate is 1 mol dm^{-3}.

B The solubility of HgI_2 is 6.50×10^{-8} mol dm^{-3}.

C The solubility of HgI_2 is the lowest.

D The units for K_{sp} for HgI_2 is mol^3 dm^{-9}.

Answer: C

Option A: Since silver chloride and silver iodide has the same number of ions, the solubility is directly proportional to the K_{sp}. Hence silver iodide is precipitated before silver chloride. When silver iodide precipitates, chloride ions are still in solution and have not precipitated yet. Hence, the concentration of chloride ions is still 1 mol dm^{-3}.

Option B: Let solubility of HgI_2 be x, hence $K_{sp} = 4x^3$. $x = 6.50 \times 10^{-8}$ mol dm^{-3}

Option C: The solubility of AgC*l* = 1 x 10^{-5} mol dm^{-3}, AgI = 2.88 x 10^{-8} mol dm^{-3}. AgI is less soluble than HgI.

Option D: For HgI_2 $K_{sp} = [Hg^{2+}][I]^2$, hence units is (mol dm^{-3})^3 = mol^{3}dm^{-9}

3 The following tests were performed on an aqueous solution containing bromide and iodide ions.

Step	Test	Observations
1	Add excess $AgNO_3$(aq).	A mixture of cream and yellow precipitate were formed.
2	To the mixture from step 1, add concentrated NH_3.	The cream precipitate dissolved to form a colourless solution. The yellow precipitate was insoluble.
3	Filter the mixture from step 2.	Filtrate was a colourless solution. Residue was a yellow solid.
4	Add C*l*$_2$(aq) to filtrate.	Brown solution is formed.

Which of the following statements is correct?

A In step 2, the cream precipitate dissolved because the addition of concentrated NH_3 results in formation of a complex which decreases the K_{sp} of AgBr.

B In step 2, the yellow precipitate was insoluble because the K_{sp} of AgI is higher than the K_{sp} of AgBr.

C In step 2, the yellow precipitate was insoluble because the ionic product of AgI is higher than the K_{sp} of AgI.

D In step 4, a disproportionation reaction has taken place.

Answer: C

The yellow precipitate remained in step 2 because IP of AgI > Ksp of AgI.

4 A stable ion of **Q** has the following properties:

- has a noble gas configuration
- has more protons than electrons
- was obtained by removing electrons from the same orbital

Which of the following could be **Q**?

A	A*l*	**B**	Ca	**C**	Cu	**D**	S

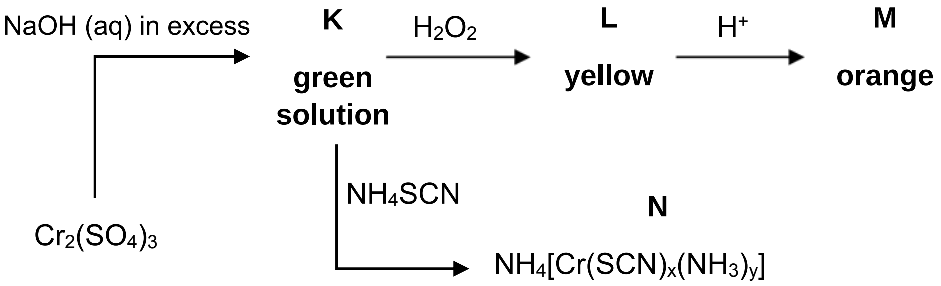
Answer: B

From the first 2 properties, **Q** has to be a main group metal.

Hence, option C and D are incorrect.

Since it was obtained by removing electrons from the same orbital, **Q** has to be either a metal in Group 1 or 2.

5 Chromium and its compounds undergo the following reactions.



N has the following composition by mass: Cr, 15.5%; S, 38.1%; N, 29.2%.

Which of the following can be deduced from the above reaction scheme?

A The values of x and y in **N** are 4 and 2 respectively.

B The types of reactions that occur are ligand exchange and redox only.

C The formula of **K** is $Cr(OH)_2(H_2O)_6$.

D H_2O_2 is a reducing agent in the conversion of **K** to **L**.

Answer: A

Option A: The empirical formula: Cr, 15.5%; S, 38.1%; N, 29.2%

Cr : S : N = 0.298 : 1.19 : 2.09 = 1: 4 : 7

From K to N, there should be no change in oxidation state and merely a ligand exchange. In N, the coordination number is 6 and the oxidation number of Cr = +3. Given that there is one cation NH_4^+, hence the overall charge is -1. Thus, There are $4SCN^-$ ligands to make the overall charge -1.

Option B: The conversion of L to M is also an acid base reaction where L is CrO_4^{2-} and M is $Cr_2O_7^{2-}$.

Option C: K is $Na_3[Cr(OH)_6]$ (aq). K is not a solid unlike the formula given in option C.

Option D: H_2O_2 is an oxidising agent in the conversion of K to L as the oxidation number of Cr increases from +3 to +6.

6 Which one of the following statements about Group 2 elements and their compounds is correct?

A Beryllium chloride has a higher boiling point than magnesium chloride as it has a more exothermic lattice energy than magnesium chloride.

B The reducing power of Group 2 elements increases down the group.

C 1 mole of barium carbonate, on heating over a short period of time, decomposes to give more carbon dioxide gas than 1 mole of magnesium carbonate.

D Barium has a higher melting point than magnesium due to more electrons.

Answer: B

Option A: Beryllium chloride is a simple covalent molecule while magnesium chloride is an ionic compound. Hence beryllium chloride should have a lower boiling point as it has weaker id-id interactions than the strong ionic bonds in magnesium chloride.

Option B: The E^{θ} value for M^{2+} / M is more negative down the group, indicating M is more easily oxidised hence its reducing power increases down the group.

Option C: Ba^{2+} has a smaller charge density than Mg^{2+} and distorts electron cloud of CO_3^{2-} to smaller extent, hence C – O bond is weakened to a smaller extent and more energy is required to decompose $BaCO_3$. Hence, less CO_2 is given off when $BaCO_3$ is decomposed.

Option D: Ba and Mg are both metallic with strong electrostatic forces of attraction between metal cation and sea of delocalised electrons. The number of electrons in the sea of delocalised electrons would be the same as both lose 2 valence electrons per atom. Ba^{2+} has a smaller charge density so the metallic bonds are weaker and less energy required to break them. Barium should have a lower melting point.

7 Liquefaction can be defined as a process that generates a liquid from a gas and this can be done by altering pressure. In the liquefaction of CH_4 and NH_3, the pressure needed for NH_3 is less than CH_4.

Which of the following reasons best explains this observation?

A NH_3 has stronger intermolecular forces of attraction than CH_4.

B NH_3 has weaker bond energy than CH_4.

C NH_3 molecules are bigger than CH_4 molecules.

D NH_3 molecules possess less kinetic energy than CH_4 molecules.

Answer: A

The process of liquefaction is making the molecules of gas come closer together via pressurisation. If the intermolecular forces between the molecules are stronger, the pressure required would be less. Since NH_3 has hydrogen bond and is stronger than instantaneous dipole-induced dipole in CH_4, pressure needed for NH_3 would be less than CH_4.

8 Phosphate buffers are commonly used in biological chemistry research.

$$H_2PO_4^- \rightleftharpoons HPO_4^{2-} + H^+ \qquad pK_a = 6.7$$

A phosphate buffer with pH 7.4 was prepared using NaH_2PO_4 and Na_2HPO_4 solutions. The total hydrogen phosphates concentration ($[HPO_4^{2-}]$ + $[H_2PO_4^-]$) of the buffer was 0.3 mol dm^{-3}.

What are the concentrations of NaH_2PO_4 and Na_2HPO_4 used to create this buffer?

	$[NaH_2PO_4]$ / mol dm^{-3}	**$[Na_2HPO_4]$ / mol dm^{-3}**
A	0.23	0.07
B	0.07	0.23
C	0.10	0.50
D	0.05	0.25

Answer: D

$pH = pK_a + lg\ [Na_2HPO_4]/\ [NaH_2PO_4]$

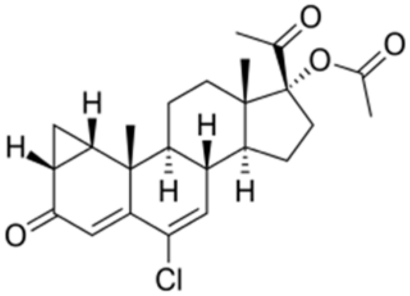
Hence, $7.4 = 6.7 + lg\ [Na_2HPO_4]/\ [NaH_2PO_4]$

$7/10 = lg\ [Na_2HPO_4]/\ [NaH_2PO_4]$

$[Na_2HPO_4]/\ [NaH_2PO_4] = 5$

Hence, the answer can be C or D. However, since the ($[HPO_4^{2-}]$ + $[H_2PO_4^-]$)= 0.30, thus D is the answer.

9 Cyproterone acetate (CPA) is a drug that is used in the treatment of prostate cancer.



CPA

Which of the following statements about CPA are incorrect?

1 One mole of silver is formed when one mole of CPA is warmed with $[Ag(NH_3)_2]^+$.

2 Two moles of yellow precipitate is formed when one mole of CPA is warmed with alkaline iodine solution.

3 One mole of silver chloride is formed when one mole of CPA is heated with ethanolic silver nitrate.

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

Answer: D

Statement 1: False. No aldehyde is present.

Statement 2: False. Only one mole of yellow precipitate is formed when one mole of CPA is subjected to iodoform test.

Statement 3: False. C*l* forms a partial double bond with C=C. Hence it does not undergoes hydrolysis with $AgNO_3$

10 Consider the following equilibrium:

When Q_2 is allowed to react with R_2 in a molar ratio of 2:1 at a total initial pressure of 3 atm, 20% of the equilibrium mixture is found to be Q_2R.

What is the equilibrium constant, K_p, of this reaction?

A 0.0174 atm^{-1}

B 0.0781 atm^{-1}

C 0.194 atm^{-1}

D 0.232 atm^{-1}

Answer: C

Since total pressure is 3 atm and the mole ratio between Q_2 and R_2 is 2:1, their respective partial pressure is 2 atm and 1 atm.

$$2Q_2\,(g) \;+\; R_2\,(g) \rightleftharpoons 2Q_2R(g)$$

	$2Q_2$	R_2	$2Q_2R$
Initial:	2	1	0
change:	-2x	-x	+2x
equilibrium:	2 - 2x	1 – x	2x

Total pressure of gas at equilibrium = (2-2x)+(1-x) +2x = 3-x

According to question,

$2x/(3-x) = 0.20$

$x = 0.273$ atm

Thus,

partial pressure of Q_2 = 2 – 2(0.273) = 1.454 atm

partial pressure of R_2 = 1 - 0.273 = 0.727 atm

partial pressure of Q_2R = 2 x 0.273 = 0.546 atm

$K_p = (0.546)^2 / [(1.454)^2(0.727)] = 0.194\ \text{atm}^{-1}$

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

Iodine clock reaction can be used to study how the concentration of iodide ions affect the rate of oxidation of iodide ions with peroxodisulfate ions. Peroxodisulfate ions convert iodide ions into iodine slowly.

$$S_2O_8^{2-}(aq) + 2I^-(aq) \rightarrow 2SO_4^{2-}(aq) + I_2(aq)$$

The rate of the reaction can be increased by the addition of catalysts such as aqueous iron (III) ions.

A possible catalysed reaction pathway involves the following steps:

Step 1: $2Fe^{3+}(aq) + 2I^-(aq) \rightarrow I_2(aq) + 2Fe^{2+}(aq)$

Step 2: $S_2O_8^{2-}(aq) + 2Fe^{2+}(aq) \rightarrow 2SO_4^{2-}(aq) + 2Fe^{3+}(aq)$

Which of the following statements are **correct**?

1 Aqueous cobalt(II) ions can be used as a catalyst in this reaction.

2 $S_2O_8^{2-}$ is a stronger oxidising agent than Fe^{3+}.

3 The $E_{cell}^{\ominus}$ for step 2 is more positive than step 1.

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

Answer: D

$Co^{3+} + e \rightleftharpoons Co^{2+}$ + 1.89

$Fe^{3+} + e \rightleftharpoons Fe^{2+}$ + 0.77

$S_2O_8^{2-}$ + 2e ⇌ $2SO_4^{2-}$ + 2.01

I_2 + 2e ⇌ $2I^-$ + 0.54

Statement 1:

Step 1: $2Co^{2+}(aq)$ + $S_2O_8^{2-}(aq) \rightarrow 2Co^{3+}(aq) + 2SO_4^{2-}(aq)$

Step 2: $2I^-(aq) + 2Co^{3+}(aq) \rightarrow I_2(aq) + 2Fe^{3+}(aq)$

$E_{cell}^{\ominus}$ for step 1: 2.01 – 1.89 = +0.12 V

$E_{cell}^{\ominus}$ for step 2: 1.89 – 0.54 = +1.35 V

Statement 2:

$S_2O_8^{2-}$ is a stronger oxidising agent than Fe^{3+} as it is more easily reduced due a more positive reduction potential +2.01 vs + 0.77 V.

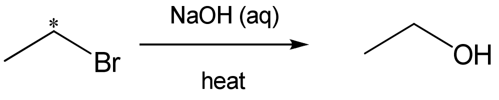
Statement 3:

$E_{cell}^{\ominus}$ for step 1: 0.77 – 0.54 = +0.23 V

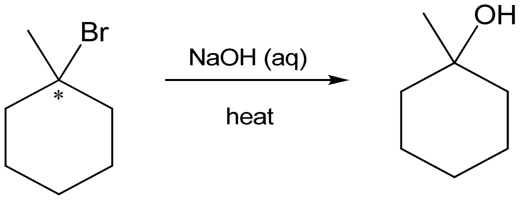
$E_{cell}^{\ominus}$ for step 2: 2.01 – 0.77 = +1.24 V

12 Which of the following reactions has no change in the hybridisation state of the carbon atom indicated with an asterisk (*) from the reactant to the **intermediate** in the mechanism?

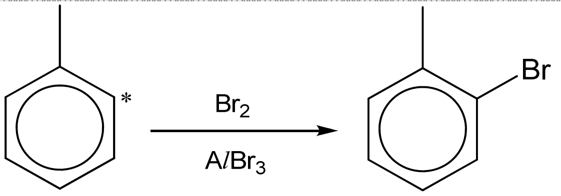
A



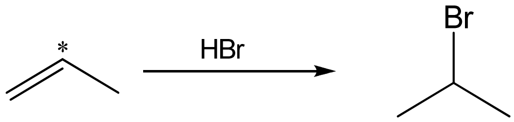
B



C



D

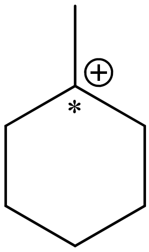


Answer: D

Option A: C atom with * is sp^3 hybridised in the reactant. Nucleophilic substitution (S_N2) mechanism as it is a primary RX. There is no intermediate. The product is formed via a transition state (C atom with * will not be sp^3 hybridised anymore because it is bonded to 5 groups).

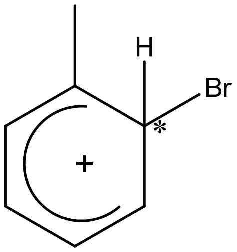
Option B: C atom with * is sp^3 hybridised in the reactant. Nucleophilic substitution (S$_N$1) mechanism as it is a tertiary RX. Intermediate is a carbocation where the C atom with * is sp^2 hybridised.

Intermediate:



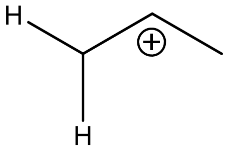
Option C: C atom with * is sp^2 hybridised in the reactant. Electrophilic substitution mechanism. The C atom with * in the intermediate is sp^3 hybridised.

Intermediate:



Option D: C atom with * is sp^2 hybridised in the reactant. Electrophilic addition mechanism. The C atom with * in the intermediate is also sp^2 hybridised.

Intermediate:



13 What is the volume of vapour formed when 10 cm^3 of liquid ethanol (density: 0.789 g cm^{-3}) is heated to 300 °C at a pressure of 5 bar?

A	85.5 cm^3
B	855 cm^3
C	163.3 cm^3
D	1633 cm^3

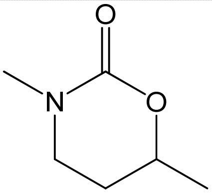
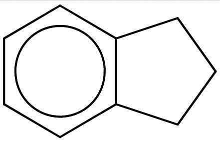
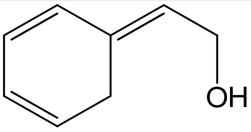
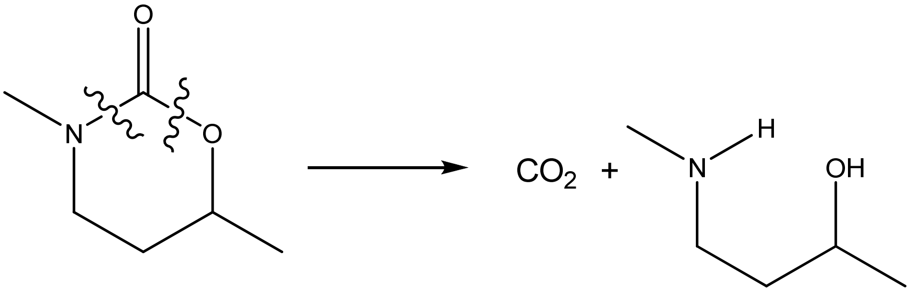
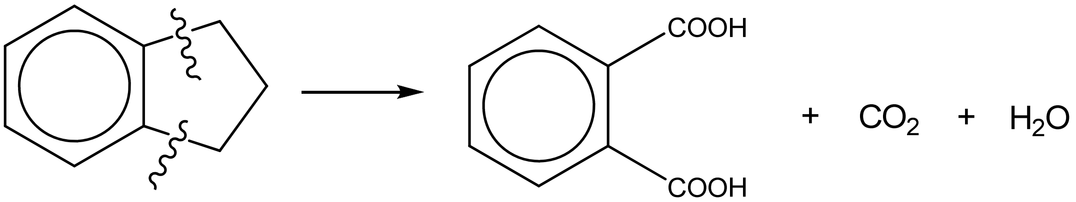
Answer: D

Mass of ethanol = 10 x 0.789 = 7.89

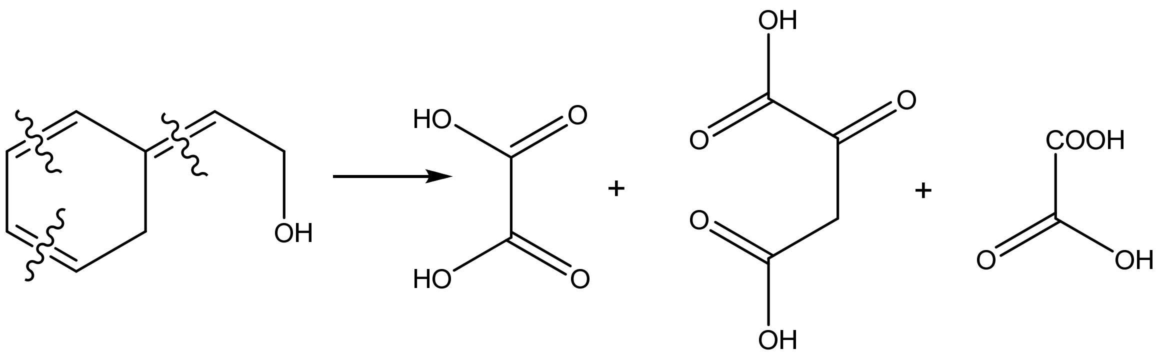
No. of moles of ethanol = 7.89/46 = 0.1715

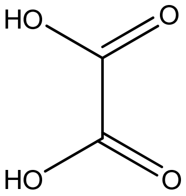
Therefore, using pV = nRT,

V = [0.1715 x 8.31 x (300+273)] / (5 x 10^5) = 0.001633 m^3 = 1633 cm^3

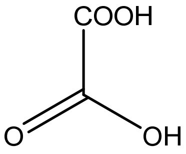
14	Which compounds liberate carbon dioxide gas when heated with acidified potassium manganate(VII)?		
		1	
		2	
		3	
	A	1 and 2 only	
	B	2 and 3 only	
	C	1, 2 and 3	
	D	None of the above	
		Answer: C  1:  2:	

3:





and



are further oxidised to CO_2 and H_2O

15 Trifluorooxonium has the formula OF_3^{n+} and its shape is trigonal pyramidal.

What is the value of n in trifluorooxonium?

A	1	**B**	2	**C**	3	**D**	4

Answer: A

Since its shape is trigonal pyramidal, that must mean that around O there are 3 bp and 1lp. The 3 bp are formed between one electron from F and 1 from O and the lp belongs to O. With only 5 valence electrons around O than the usual 6, the entire ion is short of 1 electron and hence n = 1

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

Which set of reagents, when added in the order shown below, would convert $Fe^{3+}(aq)$ to $[Fe(CN)_6]^{3-}(aq)$?

$$Fe^{3+}(aq) \xrightarrow{\text{step 1}} Fe^{2+}(aq) \xrightarrow{\text{step 2}} \mathbf{X} \xrightarrow{\text{step 3}} [Fe(CN)_6]^{3-}(aq)$$

	step 1	step 2	step 3
A	Zn(s)	$CN^-(aq)$	$SO_2(g)$
B	$I^-(aq)$	$CN^-(aq)$	$Cl_2(g)$
C	$H_2O_2(aq)$	$I^-(aq)$	$CN^-(aq)$
D	Ag(s)	$I^-(aq)$	$CN^-(aq)$

Answer: B

Step 1: redox

$2Fe^{3+} + 2I^{-} \rightarrow 2Fe^{2+} + I_2$ $E^{\ominus}_{cell} = +0.77 - (+0.54) > 0$ V

Step 2: ligand exchange

$Fe(H_2O)_6^{2+} + 6CN^{-} \rightarrow Fe(CN)_6^{4-} + 6H_2O$

Step 3: redox

$Fe(CN)_6^{4-} + \frac{1}{2}Cl_2 \rightarrow Fe(CN)_6^{3-} + Cl^{-}$

$E^{\ominus}_{cell} = +1.36 - (+0.36) > 0$ V

For **A**, step 3 is incorrect as SO_2 cannot be reduced by $Fe(CN)_6^{4-}$.

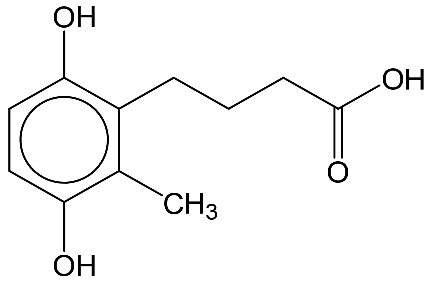
For **C**, step 2 is incorrect as Fe^{2+} is oxidised to Fe^{3+} while I^{-} cannot be reduced.

For **D**, step 1 is incorrect as reaction is not feasible since $E^{\ominus}_{cell} = +0.77 - (+0.80) < 0$ V.

Step 2 is incorrect as Fe^{2+} is oxidised to Fe^{3+} while I^{-} cannot be reduced.

17 Compound **X** is dissolved in heavy water, D_2O. It contains a number of hydrogen atoms which can be easily be replaced by deuterium, D.

[D, deuterium = ^{2}H]



Compound **X**

What is the maximum number of hydrogen atoms which could be replaced by deuterium atoms in each molecule of **X**?

A 1 **B** 2 **C** 3 **D** 4

Answer: C

Phenol and carboxylic acid will dissociate in water to form O^{-} and COO^{-} respectively.

$D_2O \rightleftharpoons D^{+} + OD^{-}$

The D^{+} can bond with the phenoxide ions and carboxylate ion. Since there are 2 phenols and 1 carboyxlic acid in compound **X**, 3 hydrogen atoms could be replaced.

18 Which of the following, when mixed together at 298K and 1 bar, represent the standard enthalpy change of neutralisation?

1	500 cm^3 of 1 mol dm^{-3} HNO_3 and 500 cm^3 of 1 mol dm^{-3} KOH
2	500 cm^3 of 1 mol dm^{-3} H_2SO_4 and 500 cm^3 of 1 mol dm^{-3} $Ca(OH)_2$
3	1 dm^3 of 1 mol dm^{-3} HNO_3 and 500 cm^3 of 1 mol dm^{-3} $Ca(OH)_2$
4	1 dm^3 of 1 mol dm^{-3} H_2SO_4 and 1 dm^3 of 1 mol dm^{-3} KOH

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

Answer: C

Standard enthalpy change of neutralisation is when 1 mole of water is produced.

Option 1 produced 0.5 moles of water while the other options produce 1 mole of water.

19 Which of the following cannot act as a ligand?

A AlH_4^-

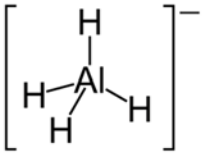
B N_2H_4

C CH_3OH

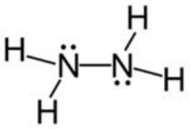
D CO

Answer: A

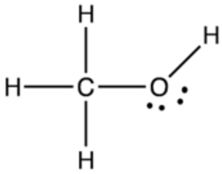
Option A: No available lone pair for dative bonding



Option B:

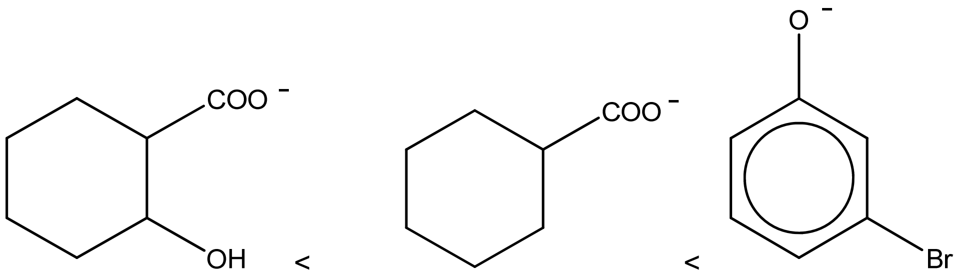
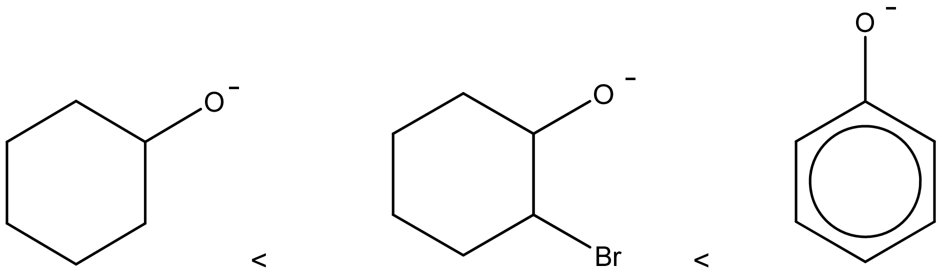
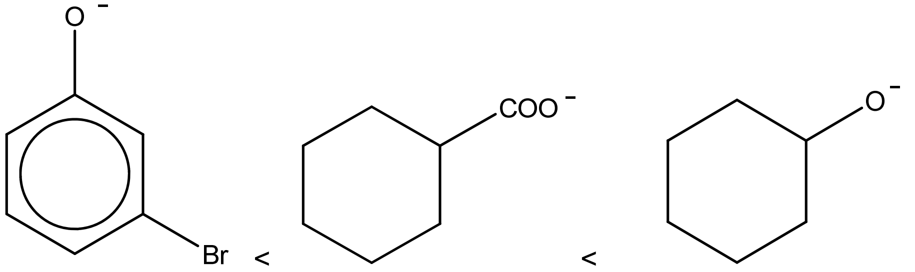
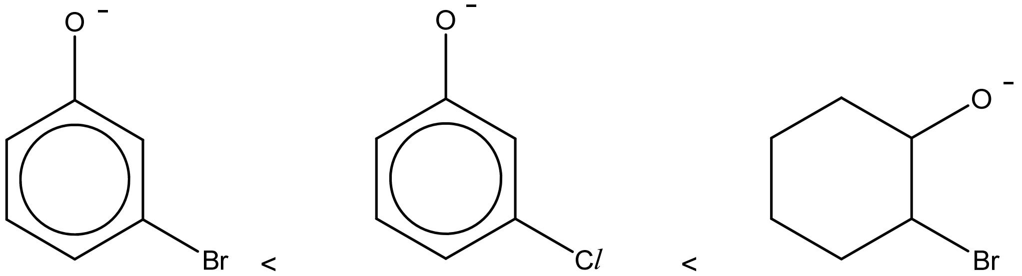


Option C:



Option D: $:C\equiv O:$

20 Which of the following shows an increasing trend in K_b ?

	A	
	B	
	C	
	D	
		Answer: A Increasing trend in K_b = increasing basicity = increasing strength of conjugate base = decreasing acidity of the original acid. Carboxylic acids are stronger acids than phenols which are stronger acids than alcohols. Hence the carboxylate ions are the weakest conjugate bases, followed by phenoxide ions, followed by alkoxide ions which are the strongest conjugate bases. Option A: OH is electron withdrawing group which stabilises the conjugate base further, hence the negative charge does not accept H^+ readily, thus it's the weakest base. Option B: Alkoxide ions are supposed to stronger conjugate bases than phenoxide ions. Option C: Phenoxide ions are supposed to be stronger conjugate bases than carboxylate ions.

Option D: C*l* is more electronegative than Br, hence the negative charge on O is less available to accept H^+ when C*l* is attached to the ring compared to Br.

21 Which quantity would best indicate the strength of intermolecular hydrogen bonds in HF?

A enthalpy change of vapourisation

B enthalpy change of formation

C enthalpy change of atomisation

D bond dissociation energy

Answer: A

Hydrogen bond is only formed between HF and NH_3 when dissolve in water. The other 3 energy change involved breaking and forming of other kinds of bonds (e.g. covalent bond) and not the hydrogen bond.

22 The following data refer to cobalt as a typical transition element and calcium as an s-block element. Which of the following properties shows the correct data for both elements?

	Property	**Cobalt**	**Calcium**
A	Metallic radius / nm	0.150	0.117
B	Electrical conductivity / relative units	10.2	50
C	Melting point / °C	1495	1965
D	Density / g cm^{-3}	8.9	1.54

Answer: D

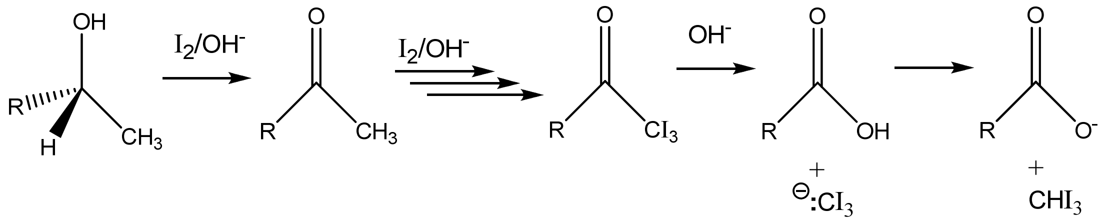
Option A: Co has more protons than Ca, hence the nuclear charge is higher than Ca. Co also has more electrons than Ca but the increase in shielding effect is minimal. Although the additional 2 electrons in Co are added in an inner sub-shell, they still provide a relatively poor shielding for the outermost 4s electrons. Hence, the valence 4s electrons in Co experiences a greater effective nuclear charge and are attracted more strongly to the nucleus than those in Ca, resulting in a smaller radius.

Option B: Cobalt should have higher conductivity than calcium due to more delocalised electrons from 3d and 4s.

Option C: Cobalt should have higher m.p than calcium. For cobalt, both 3d and 4s electrons are delocalised to form a ‘sea’ of electrons for strong metallic bonding. Hence, strong electrostatic forces holding the metallic cations (which has a larger cationic charge and smaller cationic radius) together.

Option D: While the size of the atom, measured by the metallic radius, decreases slightly from scandium to zinc, the relative atomic mass increases considerably. This results in an increase in density from scandium to zinc. The d-block metals are, in general, denser than the s-block metals.

23 The reaction of methyl alcohols with alkaline aqueous iodine can be described by the simplified scheme as shown below:



Which of the following reactions have taken place?

1 Oxidation
2 Acid-base reaction
3 Nucleophilic addition

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

Answer: B

Statement 1: Iodoform test is an oxidation reaction. Alcohol is oxidised to a carboxylic acid (carboxylate).

Statement 2: Acid-base reaction occurs in the last step where CI_3^- acts as base to accept H^+ from OH in RCOOH (which acts as acid).

Statement 3: There is no addition reaction taking place.

24 Nitrogen, ^{14}N, is the final product formed by the radioactive decay of ^{14}C, which is a first-order reaction with a half-life of 5.73 x 10^3 years.

What would be the age of a substance, originally nitrogen free, in which the molar proportion of ^{14}C : ^{14}N is 2 : 5?

A	0.29 x 10^4 years
B	1.04 x 10^4 years
C	1.58 x 10^4 years
D	1.95 x 10^4 years

Answer: B

Original amount of ^{14}C is 7 parts (2+5).

Since radioactive decay of ^{14}C is first order,

$2/7 = (1/2)^n$ where n is the no. of half-life that took place for ^{14}C.

n =1.807

Therefore, age of the substance is $1.807 \times 5.73 \times 10^3 = 1.04 \times 10^4$ years.

25 The properties of the oxides of four Period 3 elements **W, X, Y** and **Z** are given below.

- The oxide of **W** is insoluble in water and in dilute acid but soluble in concentrated sodium hydroxide.
- The oxide of **X** is amphoteric.
- The oxide of **Y** reacts with dilute potassium hydroxide at room temperature.
- The oxide of **Z** dissolves in water to form a solution of pH = 13.

Which of the following is correct in order of increasing atomic number?

A **Z, X, W, Y**

B **W, X, Y, Z**

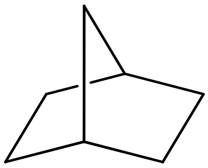
C **Z, W, X, Y**

D **Z, Y, W, X**

Answer: A

W is Silicon. X is Aluminium. Y is either Phosphorus or Sulfur. Z is Sodium.

26 Norcarane undergoes free radical substitution with limited bromine in the presence of ultraviolet light to form mono-brominated compound **Y**.

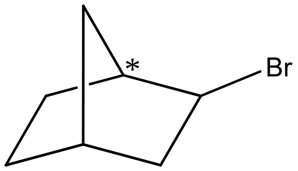


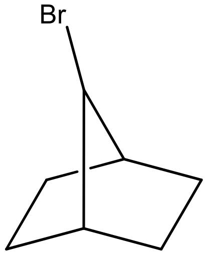
Norcarane

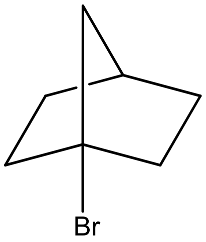
How many isomers of **Y** (including stereoisomers) will be formed at the end of the reaction?

A	3	**B**	4	**C**	6	**D**	8

Answer: B







There are 3 structural isomers. One of them has a chiral carbon (C*) so there are 4 isomers including stereoisomers.

27 The following are information for a reaction involving **X** and **Y**:

- it is first order with respect to [**X**] and zero order with respect to [**Y**].
- its rate constant doubles for each 10 °C rise in temperature

Which of the following statements are true about this reaction?

1 The half-life of the reaction remains the same when [**X**] doubles.

2 The half-life of the reaction doubles when [**Y**] is halved.

3 When the temperature of the reaction increases from 298K to 318K, the rate of the reaction will be quadrupled.

4 The rate of the reaction will change when [**X**] is halved and temperature increases from 298K to 308K.

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

Answer: B

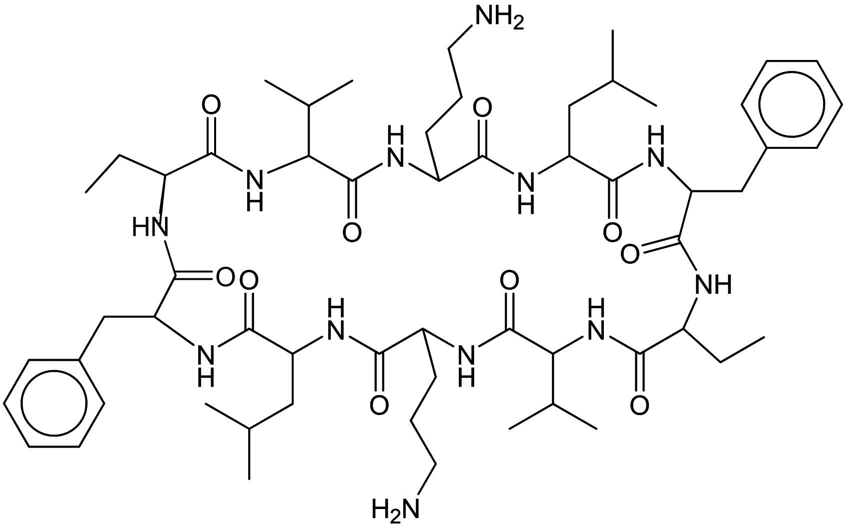
Statement 1 is correct as half-life is not affected by change in [X].

Statement 2 is wrong as [Y] does not affect the rate of reaction at all.

Statement 3 is correct as temperature increased by 20 °C and that would cause rate to increase 4 times.

Statement 4 is wrong as rate will not change due to it decreased 2 times due to [X] is halved but increase 2 times due to temperature increase by 10 °C.

28 Gramicidin Soviet is an antibiotic that is effective against some fungi. It is made up of several α amino acids.



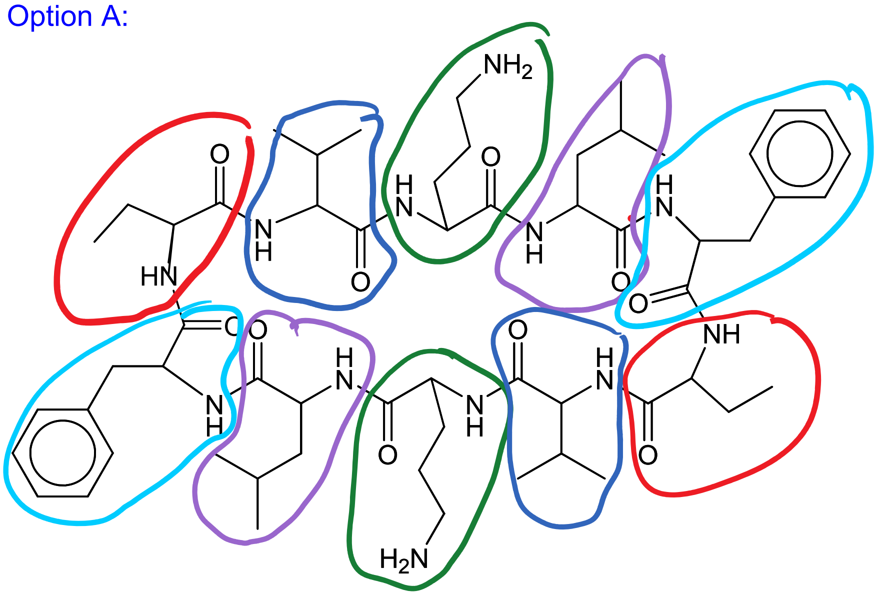
Gramicidin Soviet

Which statement about Gramicidin Soviet is correct?

A	It is made up of 5 different amino acids.
B	1 mole of Gramicidin Soviet consists of 9 amide bonds.
C	1 mole of Gramicidin Soviet reacts with 10 moles of hot dilute H_2SO_4.
D	Upon reaction with hot dilute NaOH, the products formed have high melting point as they can form strong intermolecular hydrogen bonding.

Answer: A

Option A:



Gramicidin Soviet

There are 5 different amino acids (marked by the different colours).

Option B: There are 10 amide bonds.

Option C: 10 moles of amide bonds will be hydrolysed by 10 moles of hot dilute H_2SO_4. However, there are amine groups in the side-chains which would also be neutralised by dilute H_2SO_4. Hence, more than 10 moles of hot dilute H_2SO_4 will react with 1 mole of Gramicidin Soviet.

Option D: Upon reaction with hot dilute NaOH, the products formed are ionic salts (the COOH groups obtained after hydrolysis of amide bonds will be neutralised to form COO^-). These salts have high melting point as they can form strong electrostatic forces of attraction between ions, and NOT form intermolecular hydrogen bonding.

29 A humidity meter is made by soaking filter paper in an aqueous solution of cobalt(II) ions in HC*l* (aq). The equation for the equilibrium reaction can be represented as follows:

$$\underset{\text{pink}}{Co^{2+}(aq)} + 4Cl^-(aq) \rightleftharpoons \underset{\text{blue}}{CoCl_4^{2-}(aq)} \qquad \Delta H = +ve$$

Which of the following statements are correct?

1 On a very humid day, the filter paper will appear more pink.

2 When the filter paper is diluted with more water, there will be no colour change.

3 On a very hot day, the filter paper will appear more blue.

4 When the filter paper is placed in a sealed container under high pressure, there will be no colour change.

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

Answer: C

Statements 1 and 2: When humidity increase and solution is diluted, amount of water increases and all the ions will be diluted. Since reactants have 5 ions and product only has 1 ion, the concentration of reactants will drop more than the products. Hence, by LCP, equilibrium position will shift to the left and the filter paper will appear more pink. Thus statement 1 is correct but not statement 2.

Statement 3: it is correct as on a hot day, temperature increase and by LCP, equilibrium position will shift to the right to favor the endothermic reaction to absorb the excess heat and hence the filter paper will appear more blue.

Statement 4: since pressure only affects gaseous species and there are no gaseous species in this reaction, equilibrium position is not affected and hence there is no colour change.

30 The position of equilibrium lies to the right in each of these reactions.

Reaction 1: $N_2H_4 + HBr \rightleftharpoons N_2H_5^+ + Br^-$

Reaction 2: $N_2H_5^+ + NH_3 \rightleftharpoons NH_4^+ + N_2H_4$

Based on this information, which statements are correct?

1 Br^- is the conjugate base of HBr.
2 $N_2H_5^+$ is the Bronsted base in **Reaction 2**.
3 The order of acid strength is HBr > $N_2H_5^+$ > NH_4^+.
4 N_2H_4 is the Lewis acid in **Reaction 1**.

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

Answer: A

Statement 1: HBr is a bronsted acid as it donates a proton. Hence the **product formed (bromide ion) is a conjugate base.**

Statement 2: $N_2H_5^+$ is the Bronsted acid in **Reaction 2 as it donates a proton**.

Statement 3: Since the POE lies to the right for both reactions, HBr is a stronger acid than $N_2H_5^+$ from Reaction 1 as it prefers to donate a proton. Likewise for Reaction 2 where $N_2H_5^+$ is a stronger acid than NH_4^+.

Statement 4: N_2H_4 is the Lewis base in **Reaction 1** as it donates a lone pair of electrons for dative bonding to a proton from HBr.

~ END OF PAPER ~

Name		**Class**	

ST ANDREW'S JUNIOR COLLEGE

JC2 PRELIMINARY EXAMINATION

Chemistry (9729) **12 September 2018**

Paper 2 Structured Questions **2 hours**

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS:

Write in dark blue or black pen.

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

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

Answer **all** questions 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:

Question	**1**	**2**	**3**	**4**	**5**	**Total**
Marks	19	20	10	7	19	75

This document consists of **20** printed pages (including this page).

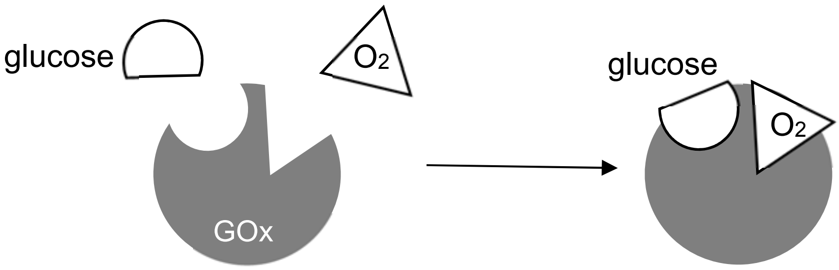
Answer **all** the questions.

1 Glucose oxidase (GOx) is an enzyme found in certain species of insects and fungi that catalyses the oxidation of glucose to gluconic acid.

$$\underset{\text{glucose}}{C_6H_{12}O_6} + O_2 + H_2O \xrightarrow{\text{GOx}} \underset{\text{gluconic acid}}{C_6H_{12}O_7} + H_2O_2$$

(a) Write two half-equations to show that this is a redox reaction. **[2]**

(b) The binding of reactants to GOx can be simplified with a diagram as shown below.



(i) Explain why GOx can be described as a *biological catalyst*. **[2]**

(ii) Based on the diagram above, suggest why the sign of ∆S is negative for the reaction. **[1]**

1 (b) (iii) Sketch a graph showing how the rate of this GOx-catalysed reaction varies with the concentration of glucose.

[1]

(c) The overall equation can be re-expressed to show the change in functional group.

$$\underset{\text{glucose}}{C_5H_{11}O_5CHO} + O_2 + H_2O \longrightarrow \underset{\text{gluconic acid}}{C_5H_{11}O_5COOH} + H_2O_2$$

Calculate the enthalpy change of reaction for the conversion of glucose into gluconic acid. Use relevant data from the *Data Booklet*. **[2]**

1 **(d)** Experiments were done to determine the kinetics of the reaction.

In the first investigation, the following reaction mixture was prepared.

initial [glucose] = 5.00×10^{-3} mol dm^{-3}

initial [GOx] = 1.00×10^{-2} mol dm^{-3}

initial [O_2] = 1.00×10^{-2} mol dm^{-3}

The following results in **Table 1** were obtained.

Table 1

***t*/s**	**[glucose] / mol dm^{-3}**
0	5.00×10^{-3}
10	3.40×10^{-3}
20	2.50×10^{-3}
30	1.80×10^{-3}
60	6.00×10^{-4}

1 **(d)** **(i)** To determine the order of reaction with respect to [glucose], use these data to plot a suitable graph on the grid below.

[2]

(ii) Hence, deduce the order of reaction with respect to [glucose], showing all your working and drawing clearly on your graph. **[2]**

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1 (d) (iii) In the second and third investigations, the concentrations of oxygen and GOx were changed, but the initial [glucose] was kept the same as before. The following results in **Table 2** were obtained.

Table 2

Investigation	**Initial [O_2] (mol dm^{-3})**	**Initial [GOx] (mol dm^{-3})**	**Initial rate (mol dm^{-3} s^{-1})**
1	1.00×10^{-2}	1.00×10^{-2}	**Y**
2	5.00×10^{-3}	1.00×10^{-2}	2.00×10^{-4}
3	5.00×10^{-3}	2.50×10^{-3}	5.00×10^{-5}

Use your graph in **(d)(i)** to determine the initial rate **Y**, showing all your working and drawing clearly on your graph. Hence, use the information in **Table 2** to determine the orders of reaction with respect to [O_2] and [GOx]. Explain your reasoning.

[3]

1 **(e)** GOx can be used in a biosensor to convert glucose present in body fluids into gluconic acid. The amount of hydrogen peroxide produced is then reduced electrochemically to determine the amount of glucose present.

A 0.1 cm^3 of blood sample from a patient was tested to diagnose if he was at risk of diabetes. The diagnosis is based on the concentration of glucose in the blood.

Condition	**[glucose] in blood (x 10^{-3} mol dm^{-3})**
Normal	less than 5.6
Pre-diabetes	5.6 − 6.9
Diabetes	More than 6.9

The biosensor gave a current of 1.01 mA for 1 min. (1000 mA = 1A)

(i) Calculate the number of moles of hydrogen peroxide produced. Hence, diagnose the condition of the patient. **[3]**

(ii) Before the test, the blood sample has to be treated to remove some components present. Suggest why a treated blood sample was necessary for the biosensor to give an accurate reading. **[1]**

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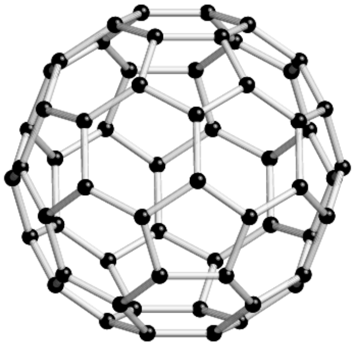
[Total: 19]

[Please Turn Over

2 This question deals with carbon and silicon which are both elements in Group 14.

(a) C_{60} and diamond are allotropes of carbon. C_{60} is a simple covalent molecule while diamond is a giant covalent molecule. State the type of bonding and describe the lattice structure of solid C_{60}.



C_{60}

[2]

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(b) 0.144 g of C_{60} was placed in a 100 cm^3 container of hydrogen gas at 20 °C and 1.00×10^5 Pa.

The reaction occurred as shown in the equation.

$$C_{60}\,(s) + xH_2\,(g) \rightarrow C_{60}H_{2x}\,(s)$$

When all the C_{60} had reacted, the pressure was found to be 2.21×10^4 Pa at the same temperature.

(i) Calculate the amount, in moles, of C_{60} that reacted. **[1]**

2 **(b)** **(ii)** Calculate the amount, in moles, of hydrogen gas that reacted with C_{60}. **[2]**

(iii) Use your answers from **(i)** and **(ii)** to deduce the molecular formula of the hydrocarbon, $C_{60}H_{2x}$. **[2]**

(c) **(i)** Graphite is another allotrope of carbon. State the type of hybridisation and draw the arrangement of the hybrid orbitals about each C atom. **[2]**

(ii) Graphite is a good conductor of electricity. Explain, with reference to orbital overlap, how graphite has a high electrical conductivity. **[2]**

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2 **(c)** **(iii)** The values for the enthalpy change of combustion of graphite and diamond are given in the table below.

Substance	**Enthalpy change of combustion / kJ mol^{-1}**
Graphite	−394
Diamond	−396

The products of the combustion reactions of graphite and diamond are carbon dioxide and water.

Suggest why the enthalpy change of combustion of graphite is less exothermic than that of diamond. **[1]**

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(d) Silicon is another element in Group 14 which shows the same kind of bonding and structure as diamond.

(i) When silicon reacts with magnesium, Mg_2Si forms. Mg_2Si is thought to contain the Si^{4-} ion. Compare and explain the difference between the atomic and anionic radii of silicon. **[2]**

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2 **(d)** **(ii)** Suggest why the second ionisation energy of silicon is lower than that of aluminium. **[2]**

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(iii) Solid Mg_2Si reacts with dilute hydrochloric acid to form gaseous SiH_4 and a solution of magnesium chloride only. Write an equation, including state symbols, to show the reaction of solid Mg_2Si with dilute hydrochloric acid. **[1]**

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(iv) Describe the reaction, if any, of $NaCl$ and $SiCl_4$ with water, relating any differences to their bonding. Give relevant equations for any reactions and suggest the pH values of each resulting solution. **[3]**

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[Total: 20]

3 Hydrocarbons that contain other elements are known as heterocompounds. A special class of heterocompounds are thiols. Thiols are sulfur analogs of alcohols and have the general formula R-SH. Its structure is similar to that of an alcohol, but with sulfur in place of oxygen. One such example is CH_3SH.

(a) State the bond angle about the oxygen atom in CH_3OH and explain if the bond angle is bigger than the bond angle about the sulfur atom in CH_3SH. **[3]**

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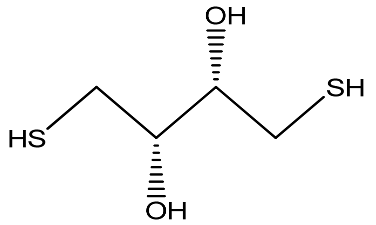
(b) Thiols can be converted to produce compounds called disulfides. This type of reaction is common in protein structures where it forms disulfide linkages (**–S–S–**) between two thiols as shown in the following equation:

$$2\ RS\text{-}H \rightarrow R\text{-}S\text{-}S\text{-}R + H_2$$

Based on the above equation, suggest two disulfide products that could be formed when $HOCH_2CH_2SH$ and $HOCH_2CH(CH_3)SH$ are reacted. **[1]**

(c) Dithiothreitol (**DTT**) is an organic molecule with molecular formula, $C_4S_2O_2H_{10}$. It has both the functional group of an alcohol and a thiol. The structure of **DTT** is given below.



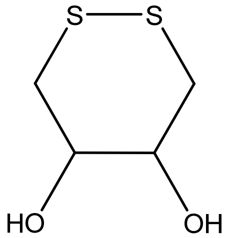
DTT can be oxidised under suitable conditions to form product **X** with molecular formula, $C_4S_2O_2H_8$.

3 **(c)** **(i)** Draw the structural formula of product **X**. **[1]**

(ii) Product **X** can then undergo nucleophilic addition with hydrogen cyanide under suitable conditions.

Suggest the conditions for this reaction to take place and hence, describe the mechanism of the reaction, In your answer you should show all charges and lone pairs and show the movement of electrons by curly arrows. **[3]**

3 **(d)** **DTT** can be oxidised to form a stable six-membered ring with an internal disulfide bond as shown in the following structure.



The oxidised form of **DTT** has a restricted rotation about the C-C bond with the two –OH groups hence enabling it to exhibit cis-trans isomerism.
Draw the cis-trans isomers of the oxidised form of **DTT**. **[2]**

[Total: 10]

4 Iron salts, usually iron(II) sulfate, catalyses the decomposition of aqueous hydrogen peroxide to water and oxygen. The reaction mechanism involves OH and HO_2 free radicals. The reaction mechanism is given below.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO\bullet + OH^-$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HOO\bullet + H^+$$

(a) Define *free radical*. **[1]**

....

....

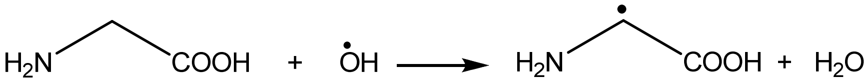
4 **(b)** Draw the dot-and-cross diagram for HO_2 free radical. **[1]**

(c) State the type of catalysis that takes place between iron(II) sulfate and hydrogen peroxide and state the property of iron(II) sulfate that allows it to carry out its function as a catalyst in the above decomposition reaction. **[2]**

Type of catalysis: ……………………..……….

Property: ……………………………………………………………………………………

(d) OH radicals can modify amino acids. They behave similarly to chlorine radicals by abstracting a hydrogen in the propagation step of free radical substitution mechanisms. This is represented using glycine as shown below.



glycine

(i) Suggest why the rate of propagation is slower when glycine exists as an anion. **[1]**

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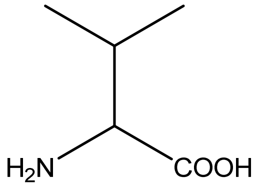
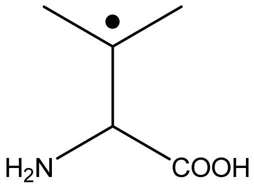
4 (d) (ii) Valine is another amino acid that can react with OH radicals. The structure of valine is as shown below.



Valine

Valine reacts with OH radicals to form three radical products, of which two are shown below.



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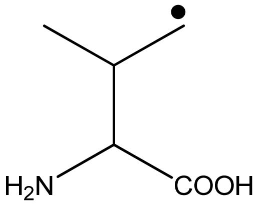

Product A

Product B

Suggest a reason why product **A** is more stable. **[1]**

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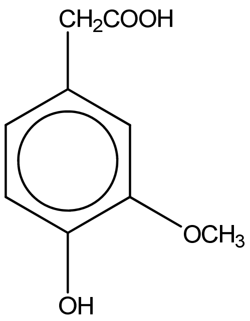
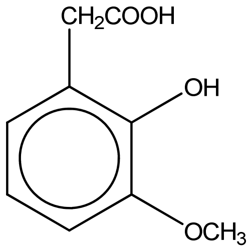
(iii) Draw the structural formula of the third radical product for the above reaction in **(ii)**. **[1]**

[Total: 7]

5 **(a)** The concentration of hydrogen peroxide can be determined by fluorescence reaction between homovanillic acid (HVA) and hydrogen peroxide. HVA can be found in urine and can be found to exist in two constitutional forms as shown below.



HVA - I

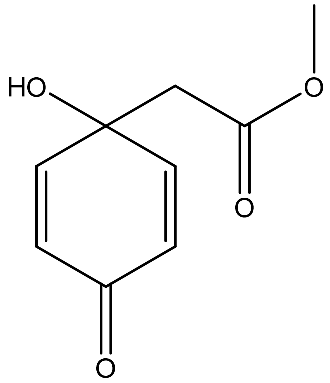


HVA-II

(i) There are two pK_a values associated with **HVA - I**: 3.7 and 5.3. Explain the difference in the pK_a values. **[2]**

(ii) Draw the structural formula of the monoanion produced from the first dissociation of **HVA – II**.
Hence, explain why the first pK_a value of **HVA – II** is much lower than the first pK_a value of **HVA – I.** **[2]**

5 (a) (iii) An isomer of HVA is jacaranone which is used in cancer treatments. Its structure is given below.



jacaranone

Identify the functional groups present in jacaranone. **[2]**

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(iv) Suggest a simple chemical test which could distinguish between **HVA - I** and jacaranone. Write the balanced equation for the positive test. **[3]**

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Balanced equation:

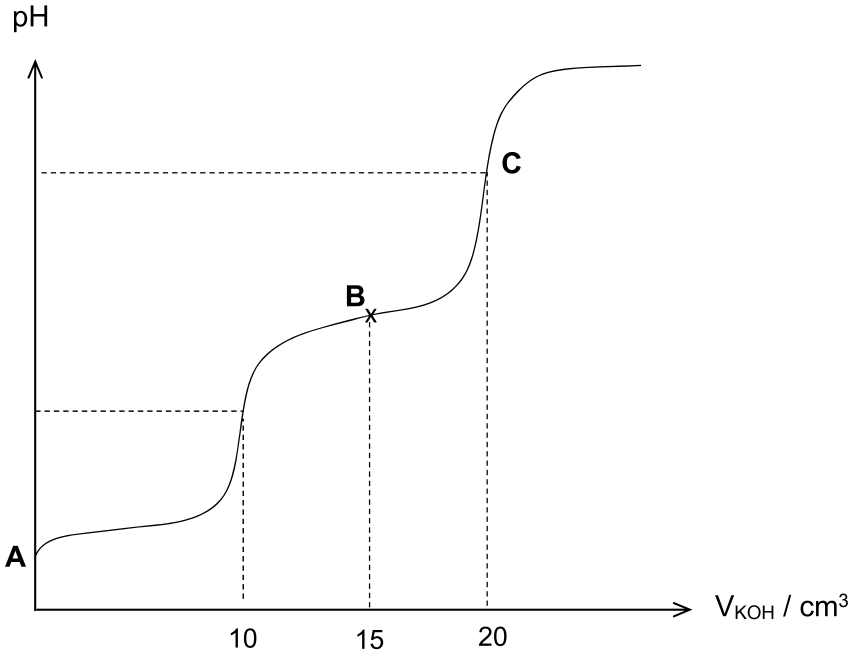
5 **(a)** **(v)** Draw all the carbon-containing products formed when jacaranone is heated with acidified $KMnO_4$. **[3]**

(b) **HVA - I**, $C_9H_{10}O_4$, is a weak dibasic acid which dissociates in water as follows:

$$C_9H_{10}O_4 \rightleftharpoons C_9H_9O_4^- + H^+ \qquad pK_{a1} = 3.7$$

$$C_9H_9O_4^- \rightleftharpoons C_9H_8O_4^{2-} + H^+ \qquad pK_{a2} = 5.3$$

A quantitative analysis was performed on a 25.0 cm^3 sample of **HVA - I**. It was titrated against 0.75 mol dm^{-3} of potassium hydroxide. The resulting pH curve was plotted as shown below.



(i) Calculate the concentration of **HVA - I** present in the sample. **[2]**

5 (b) (ii) Using the first pK_a value, calculate the initial pH at point **A**. **[2]**

(iii) State the pH at point **B** and hence, explain the significance of point **B**. **[2]**

pH: ………………..

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(iv) Write an equation to show that pH at point **C** is more than 7. **[1]**

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[Total: 19]

~ END OF PAPER ~

NAME		Class	

ST ANDREW'S JUNIOR COLLEGE

JC2 PRELIMINARY EXAMINATION

12 September 2018

2 hours

Chemistry (9729)

Paper 2 Structured Questions

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS:

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

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

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

For Examiner's use:

Question	1	2	3	4	5	Total
Marks	/ 19	/ 20	/ 10	/ 7	/ 19	/ 75

This document consists of **20** printed pages (including this page).

Answer **all** the questions.

1 Glucose oxidase (GOx) is an enzyme found in certain species of insects and fungi that catalyses the oxidation of glucose to gluconic acid.

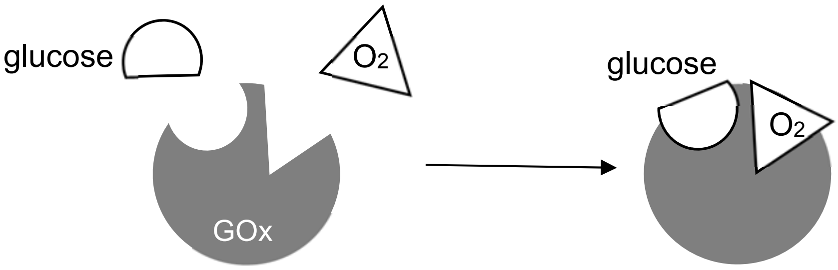
$$\underset{\text{glucose}}{C_6H_{12}O_6} + O_2 + H_2O \xrightarrow{\text{GOx}} \underset{\text{gluconic acid}}{C_6H_{12}O_7} + H_2O_2$$

(a) Write two half-equations to show that this is a redox reaction. **[2]**

$C_6H_{12}O_6 + H_2O \rightarrow C_6H_{12}O_7 + 2H^+ + 2e^-$

$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$

(b) The binding of reactants to GOx can be simplified with a diagram as shown below.



(i) Explain why GOx can be described as a *biological catalyst*. **[2]**

GOx allows certain reactants to bind specifically to it for the conversion into products.

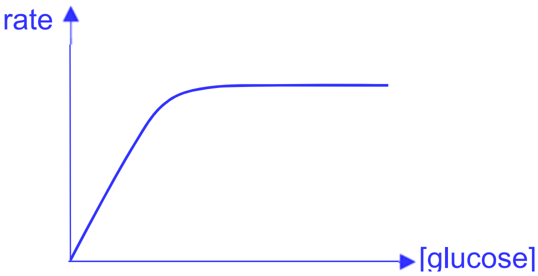
GOx speeds up the rate of reaction by providing an alternative pathway of lower activation energy. OR It is regenerated / remained chemically unchanged at the end of the reaction.

(ii) Based on the diagram above, suggest why the sign of ΔS is negative for the reaction. **[1]**

The 2 reactants and GOx must come together to form one large entity. OR There is a decrease in number of (gaseous) particles.

Hence, the products are less disordered than the reactants.

(iii) Sketch a graph showing how the rate of this GOx-catalysed reaction varies with the concentration of glucose. **[1]**



(c) The overall equation can be re-expressed to show the change in functional group.

$$C_5H_{11}O_5CHO + O_2 + H_2O \longrightarrow C_5H_{11}O_5COOH + H_2O_2$$

glucose gluconic acid

Calculate the enthalpy change of reaction for the conversion of glucose into gluconic acid. Use relevant data from the *Data Booklet*. **[2]**

Bonds broken in reactant: C—H, ~~C=O~~, O=O, ~~2O—H~~

Bonds formed in product: ~~C=O~~, C—O, O—H + ~~2O—H~~ + O—O

$\Delta H = (410 + 496) - (360 + 460 + 150) = -64.0 \text{ kJ mol}^{-1}$

(d) Experiments were done to determine the kinetics of the reaction.

In the first investigation, the following reaction mixture was prepared.

initial [glucose] = 5.00×10^{-3} mol dm^{-3}

initial [GOx] = 1.00×10^{-2} mol dm^{-3}

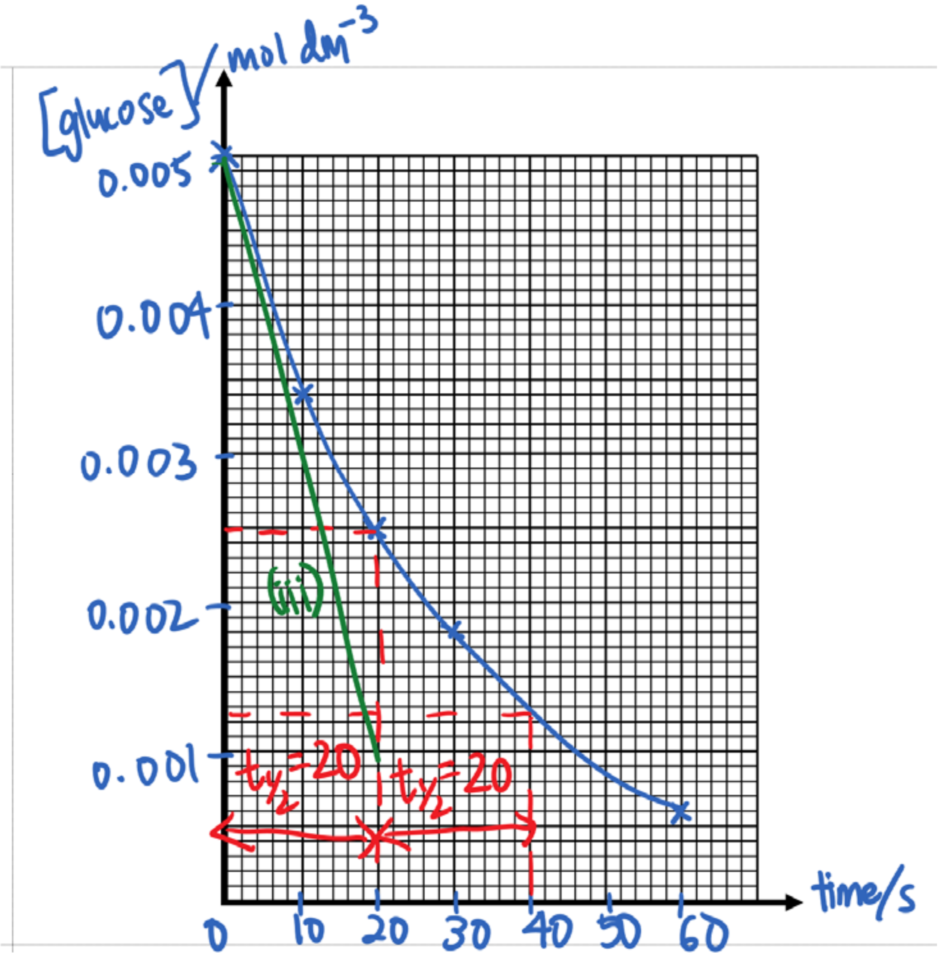
initial [O_2] = 1.00×10^{-2} mol dm^{-3}

The following results in **Table 1** were obtained.

Table 1

t/s	[glucose] / mol dm^{-3}
0	5.00×10^{-3}
10	3.40×10^{-3}
20	2.50×10^{-3}
30	1.80×10^{-3}
60	6.00×10^{-4}

(i) To determine the order of reaction with respect to [glucose], use these data to plot a suitable graph on the grid below.



[2]

Guidelines for scale:

x-axis: *t*/s, 1 big square = 20s

y-axis: [glucose] / mol dm^{-3}, 1 big square = 1.0 X 10^{-3} mol dm^{-3}

(ii) Hence, deduce the order of reaction with respect to [glucose], showing all your working and drawing clearly on your graph. **[2]**

Show two $t_{1/2}$ clearly on the graph.

Since $t_{1/2}$ is (approximately) constant at 20s, the reaction is first order with respect to [glucose].

In the second and third investigations, the concentrations of oxygen and GOx were changed, but the initial [glucose] was kept the same as before. The following results in **Table 2** were obtained.

Table 2

Investigation	Initial [O_2] (mol dm^{-3})	Initial [GOx] (mol dm^{-3})	Initial rate (mol dm^{-3} s^{-1})
1	1.00×10^{-2}	1.00×10^{-2}	**Y**
2	5.00×10^{-3}	1.00×10^{-2}	2.00×10^{-4}
3	5.00×10^{-3}	2.50×10^{-3}	5.00×10^{-5}

(iii) Use your graph in **(d)(i)** to determine the initial rate **Y**, showing all your working and drawing clearly on your graph. Hence, use the information in **Table 2** to determine the orders of reaction with respect to [O_2] and [GOx]. Explain your reasoning. **[3]**

$$\mathbf{Y} = \frac{(5.0 \times 10^{-3} - 1.0 \times 10^{-3})}{20} = 2.00 \times 10^{-4}$$

Using investigation 1 and 2, when [O_2] is halved, the initial rate remains the same. Hence, the reaction is zero order with respect to [O_2].

Using investigation 2 and 3, when [GOx] decreases 4 times, the initial rate decreases 4 times. Hence, the reaction is first order with respect to [GOx].

(e) GOx can be used in a biosensor to convert glucose present in body fluids into gluconic acid. The amount of hydrogen peroxide produced is then reduced electrochemically to determine the amount of glucose present.

A 0.1 cm^3 of blood sample from a patient was tested to diagnose if he was at risk of diabetes. The diagnosis is based on the concentration of glucose in the blood.

Condition	**[glucose] in blood (x 10^{-3} mol dm^{-3})**
Normal	less than 5.6
Pre-diabetes	5.6 − 6.9
Diabetes	More than 6.9

The biosensor gave a current of 1.01 mA for 1 min. (1000 mA = 1A)

(i) Calculate the number of moles of hydrogen peroxide produced. Hence, diagnose the condition of the patient. **[3]**

$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$

Amt of charge = $1.01 \times 10^{-3} \times 60 = 0.0606$ C

Amt of e^- = $0.0606 / 96500 = 6.2798 \times 10^{-7}$ mol

Amt of H_2O_2 = $6.2798 \times 10^{-7} / 2 = 3.14 \times 10^{-7}$ mol (3sf)

Amt of glucose = amt of H_2O_2 = 3.14×10^{-7} mol

[glucose] = $3.14 \times 10^{-7} / (0.1 \times 10^{-3}) = 3.14 \times 10^{-3}$ mol dm^{-3}

The patient is normal.

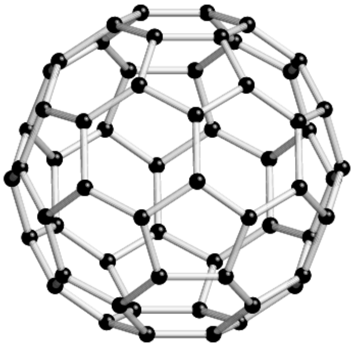
(ii) Before the test, the blood sample has to be treated to remove some components present. Suggest why a treated blood sample was necessary for the biosensor to give an accurate reading. **[1]**

The blood has to be treated to remove some components that can be reduced or oxidised by the biosensor or GOx .

[Total: 19]

2 This question deals with carbon and silicon which are both elements in Group 14.

(a) C_{60} and diamond are allotropes of carbon. C_{60} is a simple covalent molecule while diamond is a giant covalent molecule. State the type of bonding and describe the lattice structure of solid C_{60}.



C_{60}

[2]

Type of bonding: Within each C_{60} molecule, there is strong covalent bonds between carbon atoms.

Describe lattice structure: C_{60} exists as a regular lattice of simple covalent molecules with instantaneous dipole-induced dipole interactions between C_{60} molecules.

(b) 0.144 g of C_{60} was placed in a 100 cm^3 container of hydrogen gas at 20 °C and 1.00×10^5 Pa.

The reaction occurred as shown in the equation.

$$C_{60}\,(s) + xH_2\,(g) \rightarrow C_{60}H_{2x}\,(s)$$

When all the C_{60} had reacted, the pressure was found to be 2.21×10^4 Pa at the same temperature.

(i) Calculate the amount, in moles, of C_{60} that reacted. **[1]**

Amount of C_{60} = $0.144 / 720 = 2 \times 10^{-4}$

(ii) Calculate the amount, in moles, of hydrogen gas that reacted with C_{60}. **[2]**

$pV = nRT$

$\therefore \Delta n = (p1 - p2)V / RT$

$\Delta n = (1.00 \times 10^5 - 2.21 \times 10^4).100 \times 10^{-6} / 8.31 \times 293 = 0.00320$ mol

(iii) Use your answers from **(i)** and **(ii)** to deduce the molecular formula of the hydrocarbon, $C_{60}H_{2x}$. **[2]**

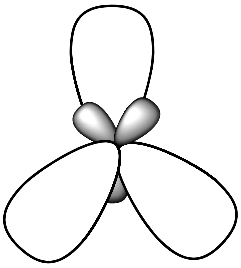
C_{60}:H_2 = 2.00 × 10^{-4} : 0.00320 = 1:16

X = 16

$C_{60}H_{32}$

(c) **(i)** Graphite is another allotrope of carbon. State the type of hybridisation and draw the arrangement of the hybrid orbitals about each C atom. **[2]**

sp^2



(ii) Graphite is a good conductor of electricity. Explain, with reference to orbital overlap, how graphite has a high electrical conductivity. **[2]**

The unhybridised p orbitals on each carbon are overlapping sideways.

This side–on overlap results in the formation of a π-electron cloud.

The π electrons are delocalised and account for the high electrical conductivity of graphite.

(c) **(iii)** The values for the enthalpy change of combustion of graphite and diamond are given in the table below.

Substance	**Enthalpy change of combustion / kJ mol^{-1}**
Graphite	−394
Diamond	−396

The products of the combustion reactions of graphite and diamond are carbon dioxide and water.

Suggest why the enthalpy change of combustion of graphite is less exothermic than that of diamond. **[1]**

The C-C bonds in graphite are stronger than that in diamond. (or words to the effect, e.g. graphite is energetically more stable than diamond / has lower energy content)

(d) Silicon is another element in Group 14 which shows the same kind of bonding and structure as diamond.

(i) When silicon reacts with magnesium, Mg_2Si forms. Mg_2Si is thought to contain the Si^{4-} ion. Compare and explain the difference between the atomic and anionic radii of silicon. **[2]**

The number of protons in both the atom and its anion is the same, hence **nuclear charge remains constant**. The anion has **more electrons** and hence **valence electrons are less strongly attracted to the nucleus**, resulting in **larger anionic radius in** Si^{4-} when compared to Si.

(ii) Suggest why the second ionisation energy of silicon is lower than that of aluminium. **[2]**

Al^+ : $[Ne]3s^2$

Si^+ : $[Ne]3s^23p^1$

The second electron to be removed from Si is in the p orbital which is further away from the nucleus than the s orbital and it faces additional shielding effect from the 3s electrons. Less energy required to remove it.

(iii) Solid Mg_2Si reacts with dilute hydrochloric acid to form gaseous SiH_4 and a solution of magnesium chloride only. Write an equation, including state symbols, to show the reaction of solid Mg_2Si with dilute hydrochloric acid. **[1]**

$Mg_2Si(s) + 4HCl\,(aq) \rightarrow SiH_4(g) + 2MgCl_2(aq)$

(iv) Describe the reaction, if any, of NaC*l* and SiC*l*₄ with water, relating any differences to their bonding. Give relevant equations for any reactions and suggest the pH values of each resulting solution. **[3]**

As covalent character of chlorides increases, the more complete the hydrolysis / the more acidic the solution is.

NaC*l* **dissolves** in water to form a neutral solution of **pH 7**. $SiCl_4$ undergoes complete hydrolysis to form an acidic solution of **pH 2**.

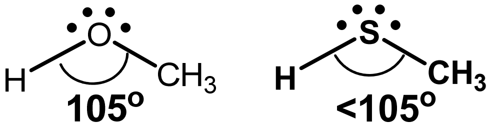
$SiCl_4(l) + 2H_2O(l) \rightarrow SiO_2\,(s) + 4HCl(aq)$

[Total: 20]

[Please Turn Over

3 Hydrocarbons that contain other elements are known as heterocompounds. A special class of heterocompounds are thiols. Thiols are sulfur analogs of alcohols and have the general formula R-SH. Its structure is similar to that of an alcohol, but with sulfur in place of oxygen. One such example is CH_3SH.

(a) State the bond angle about the oxygen atom in CH_3OH and explain if the bond angle is bigger than the bond angle about the sulfur atom in CH_3SH. **[3]**



Both CH_3OH and CH_3SH have 2 bond pairs of electrons and 2 lone pairs of electrons around O and S stoms respectively. In CH_3OH, **oxygen has a greater electronegativity than sulfur** in CH_3SH.

The **bond pair of electrons are more strongly attracted to oxygen**, resulting in **greater repulsion between the bond pairs** in CH_3OH.

Hence, the **H-S-C bond angle in CH_3SH is less than 105°**

(b) Thiols can be converted to produce compounds called disulfides. This type of reaction is common in protein structures where it forms disulfide linkages (**–S–S–**) between two thiols as shown in the following equation:

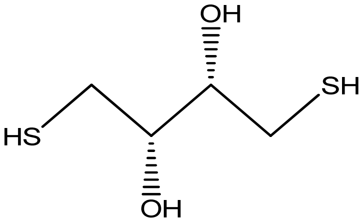
$$2\ RS\text{-}H \rightarrow R\text{-}S\text{-}S\text{-}R + H_2$$

Based on the above equation, suggest two disulfide products that could be formed when $HOCH_2CH_2SH$ and $HOCH_2CH(CH_3)SH$ are reacted.

[1]

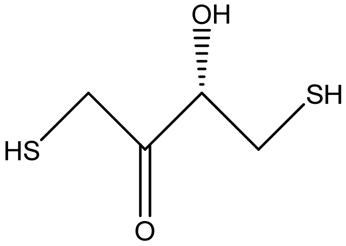
Any two of the three below:
$HOCH_2CH_2S\text{-}SCH_2CH_2OH$,
$HOCH_2CH_2S\text{-}SCH(CH_3)CH_2OH$,
$HOCH_2CH(CH_3)S\text{-}SCH(CH_3)CH_2OH$

(c) Dithiothreitol (**DTT**) is an organic molecule with molecular formula, $C_4S_2O_2H_{10}$. It has both the functional group of an alcohol and a thiol. The structure of **DTT** is given below.



DTT can be oxidised under suitable conditions to form product **X** with molecular formula, $C_4S_2O_2H_8$.

(i) Draw the structural formula of product **X**. **[1]**



(ii) Product **X** can then undergo nucleophilic addition with hydrogen cyanide under suitable conditions.

Suggest the conditions for this reaction to take place and hence, describe the mechanism of the reaction, In your answer you should show all charges and lone pairs and show the movement of electrons by curly arrows. **[3]**

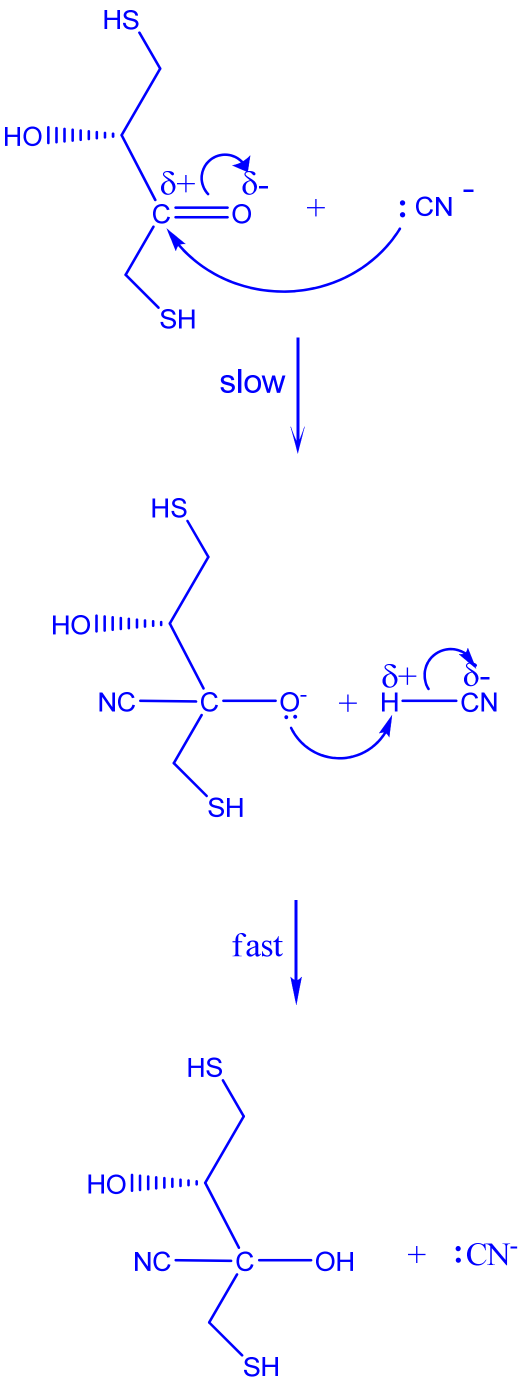
Conditions: Trace amount of NaOH (aq) or NaCN (aq), 10 – 20 °C

$NaOH + HCN \rightarrow Na^+ + CN^- + H_2O$

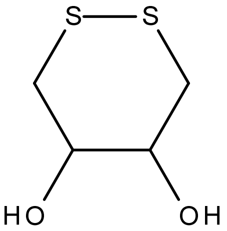
OR

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

12

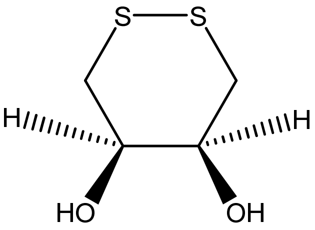


(d) **DTT** can be oxidised to form a stable six-membered ring with an internal disulfide bond as shown in the following structure.

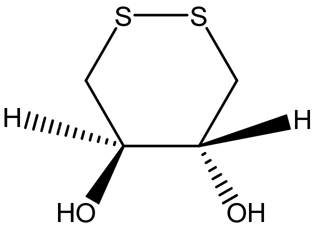


The oxidised form of **DTT** has a restricted rotation about the C-C bond with the two –OH groups hence enabling it to exhibit cis-trans isomerism.
Draw the cis-trans isomers of the oxidised form of **DTT**.

[2]



cis



trans

[Total: 10]

4 Iron salts, usually iron(II) sulfate, catalyses the decomposition of aqueous hydrogen peroxide to water and oxygen. The reaction mechanism involves OH and HO_2 free radicals. The reaction mechanism is given below.

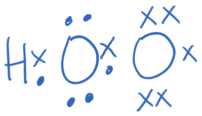
$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO\bullet + OH^-$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HOO\bullet + H^+$$

(a) Define *free radical*. **[1]**

Free radical is an atom or group of atoms having an **unpaired / single / lone / odd electron**.

(b) Draw the dot-and-cross diagram for HO_2 free radical. **[1]**

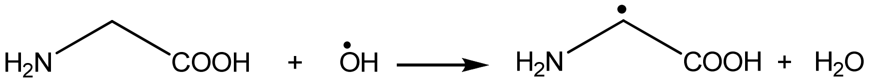


(c) State the type of catalysis that takes place between iron(II) sulfate and hydrogen peroxide and state the property of iron(II) sulfate that allows it to carry out its function as a catalyst in the above decomposition reaction. **[2]**

Homogeneous catalysis.

Iron can exist in **variable oxidation states**.

(d) OH radicals can modify amino acids. They behave similarly to chlorine radicals by abstracting a hydrogen in the propagation step of free radical substitution mechanisms. This is represented using glycine as shown below.

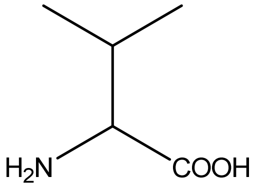


glycine

(i) Suggest why the rate of propagation is slower when glycine exists as an anion. **[1]**

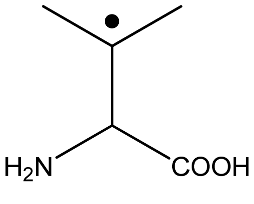
When glycine exists as an anion, the negatively-charged ion and electron on the OH radical will **repel** one another.

(ii) Valine is another amino acid that can react with OH radicals. The structure of valine is as shown below.

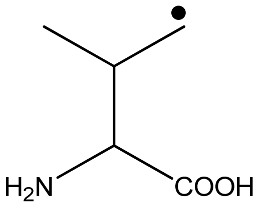


valine

Valine reacts with OH radicals to form three radical products, of which two are shown below.



&

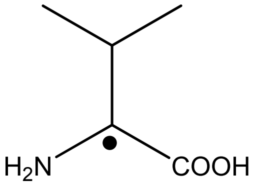


Product A **Product B**

Suggest a reason why product **A** is more stable. **[1]**

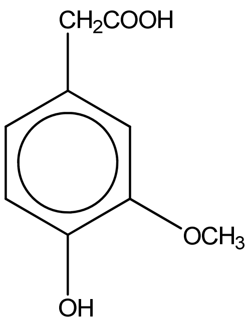
There are more **<u>electron-donating alkyl groups in A</u>** to stabilise the electron deficiency on the carbon with the radical.

(iii) Draw the structural formula of the third radical product for the above reaction in **(ii)**. **[1]**

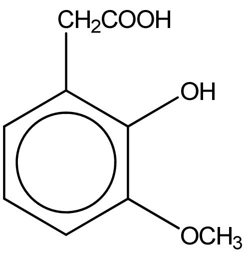


[Total: 7]

5 **(a)** The concentration of hydrogen peroxide can be determined by fluorescence reaction between homovanillic acid (HVA) and hydrogen peroxide. HVA can be found in urine and can be found to exist in two constitutional forms as shown below.



HVA - I



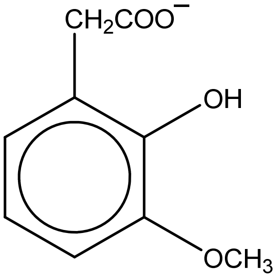
HVA-II

(i) There are two pK_a values associated with **HVA - I**: 3.7 and 5.3. Explain the difference in the pK_a values. **[2]**

The <u>negative charge delocalises over the O-C-O bond of the carboxylate ion</u>, while the <u>negative charge delocalises into the benzene ring of the phenoxide ion</u>. However the <u>resonance effect is greater</u> for carboxylate ion / carboxylate ion is <u>more stable</u>, hence carboxylic acid is a stronger acid / carboxylic acid has a lower pKa.

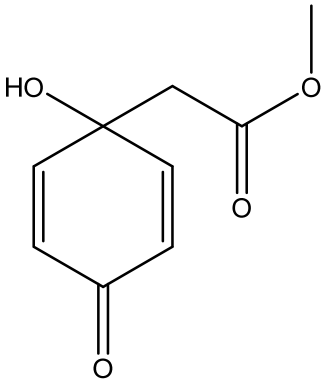
(ii) Draw the structural formula of the monoanion produced from the first dissociation of **HVA – II**.

Hence, explain why the first pK_a value of **HVA – II** is much lower than the first pK_a value of **HVA – I.** **[2]**



The **monoanion formed from HVA-II is more stable than the monoanion from HVA-I** as it is able to **form intramolecular hydrogen bonding / ion-dipole interactions.**

An isomer of HVA is jacaranone which is used in cancer treatments. Its structure is given below.



jacaranone

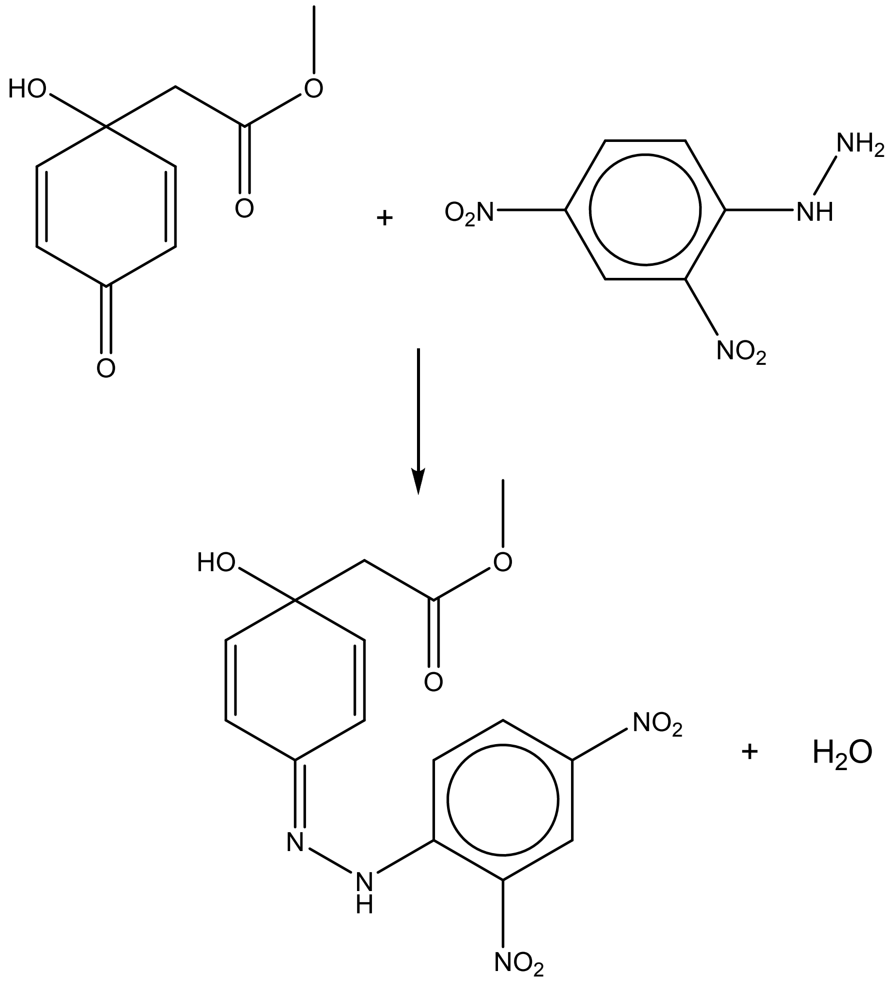
(iii) Identify the functional groups present in jacaranone. **[2]**

Tertiary alcohol, ester, alkene, ketone

(iv) Suggest a simple chemical test which could distinguish between **HVA - I** and jacaranone. Write the balanced equation for the positive test. **[3]**

Add **2,4-dinitrophenylhydrazine** to each compound separately and warm.

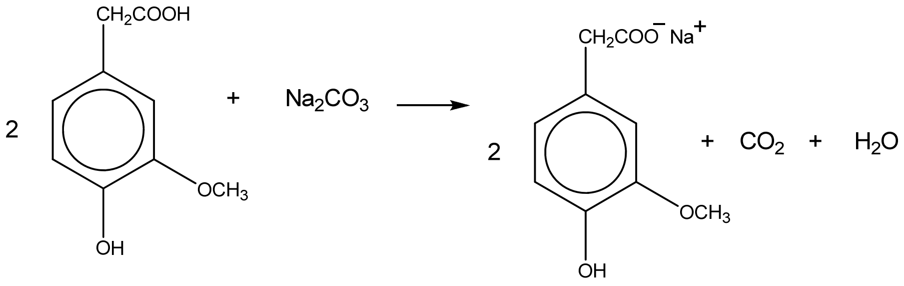
Orange ppt seen with jacaranone.



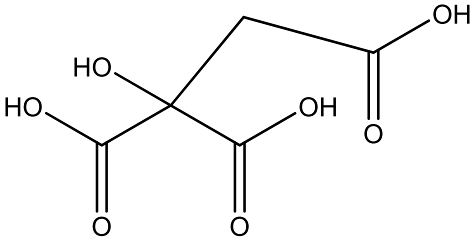
OR

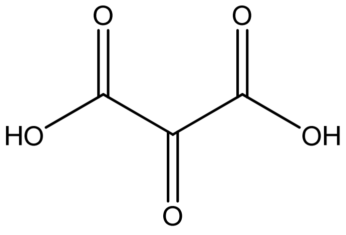
Add **Na_2CO_3** to each compound separately.

Effervescence is seen for HVA-I and gas forms white ppt in limewater.



(v) Draw all the carbon-containing products formed when jacaranone is heated with acidified $KMnO_4$. **[3]**





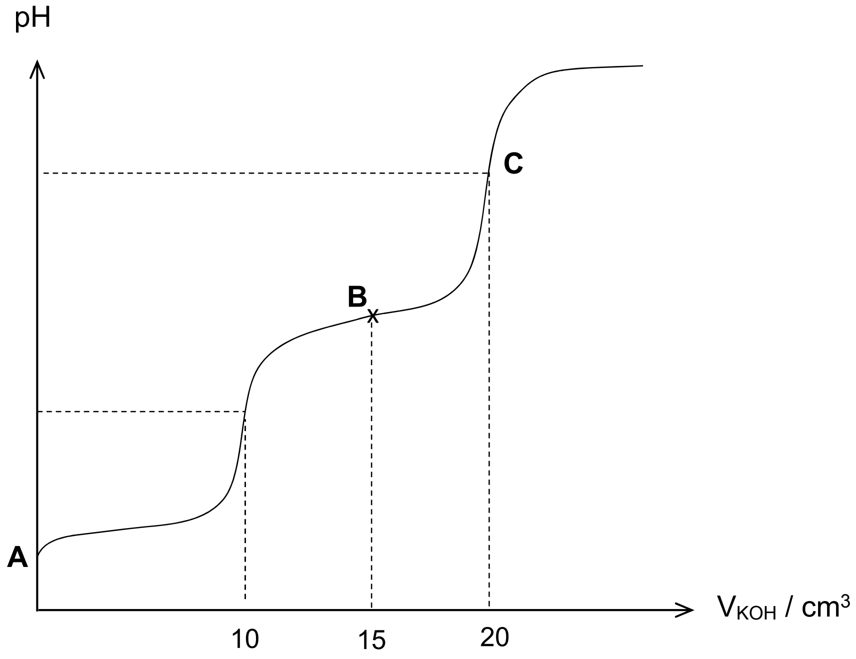
CO_2

(b) **HVA - I**, $C_9H_{10}O_4$, is a weak dibasic acid which dissociates in water as follows:

$$C_9H_{10}O_4 \rightleftharpoons C_9H_9O_4^- + H^+ \qquad pK_{a1} = 3.7$$

$$C_9H_9O_4^- \rightleftharpoons C_9H_8O_4^{2-} + H^+ \qquad pK_{a2} = 5.3$$

A quantitative analysis was performed on a 25.0 cm^3 sample of **HVA - I**. It was titrated against 0.75 mol dm^{-3} of potassium hydroxide. The resulting pH curve was plotted as shown below.



(i) Calculate the concentration of **HVA - I** present in the sample. **[2]**

Amount of KOH = 0.75 x 0.020 = 0.015 mol

Mole ratio of KOH : **HVA - I** = 2 : 1

Amount of **HVA - I** = 0.015 / 2 = 0.0075 mol

[**HVA - I**] = 0.0075 / 0.025 = **0.300** mol dm^{-3}

(ii) Using the first pK_a value, calculate the initial pH at point **A**. **[2]**

$K_a = 10^{-3.7} = 1.995 \times 10^{-4}$

$K_a = [H^+]^2 / [\mathbf{HVA - I}]$

$[H^+] = (1.995 \times 10^{-4} \times 0.300)^{1/2} = 7.736 \times 10^{-3}$ mol dm^{-3}

pH = −lg(7.736 x 10^{-3}) = **2.11**

(iii) State the pH at point **B** and hence, explain the significance of point **B**. **[2]**

pH = 5.3

It has equal concentrations of salt and acid. OR It has equal ability to remove small amount of H^+ and OH^-. OR Maximum buffer capacity.

(iv) Write an equation to show that pH at point **C** is more than 7. **[1]**

$C_9H_8O_4^{2-} + H_2O \rightleftharpoons C_9H_9O_4^- + OH^-$

[Total: 19]

~ END OF PAPER ~

NAME		**Class**	

ST ANDREW'S JUNIOR COLLEGE

JC2 PRELIMINARY EXAMINATIONS

Chemistry (9729) **14 September 2018**

Paper 3 Free Response **2 hours**

Additional Materials: Data Booklet, Writing Paper

READ THESE INSTRUCTIONS:

Write in dark blue or black pen.

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

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

Section A

Answer **all** questions. Marks **[60]**

Section B

Answer **one** question. Marks **[20]**

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

A Data Booklet is provided.

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

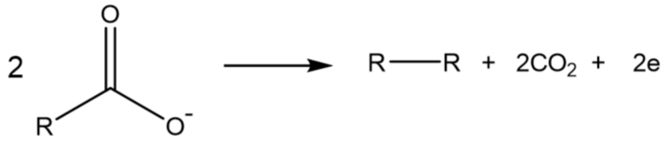
The number of marks is given in brackets [ ] at the end of each question or part question.

This document consists of **16** printed pages including this page.

Section A

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

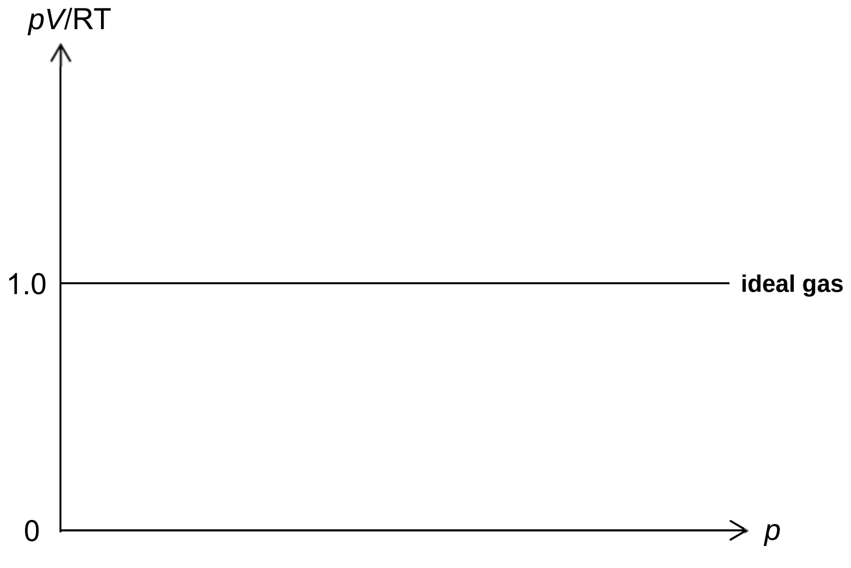
1 Electrosynthesis in organic chemistry is the synthesis of compounds in an electrolytic cell using inert electrodes. One important process is the Kolbe reaction. The Kolbe reaction is the decarboxylative dimerization of two carboxylate ions. Alkanes can be formed at the anode by the following reaction.



(a) Explain why alkanes are generally unreactive. **[1]**

(b) **(i)** Calculate the volume of carbon dioxide produced when a steady current of 5A is passed through the electrolyte for 32 minutes at standard temperature and pressure. **[2]**

(ii) Methanoate ions undergo the Kolbe reaction to form only 2 gases. Using the axes given below, sketch the variation of pV/RT against p for one mole of **each** gas at the same temperature. Briefly explain your answer. **[2]**



1 **(c)** The cathodic reaction for the Kolbe reaction can be represented by the following half equation: $2H_2O + 2e \rightarrow H_2 + 2OH^-$.

Write an overall equation for the Kolbe reaction involving ethanoate ions. Hence, calculate $\Delta G^\ominus$ for the Kolbe reaction given that the $E^\ominus_{cell}$ value for the reaction is +2.28 V.

[2]

(d) The reaction mechanism of the Kolbe reaction involves a 4-step reaction mechanism as described below:

Step 1: Dissociation of carboxylic acid to form a carboxylate ion.

Step 2: Oxidation of carboxylate ion to form a carboxyl radical, RCOO•.

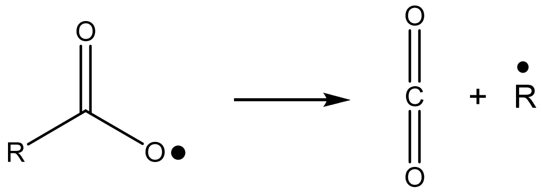
Step 3: Decomposition of the carboxyl radical to form carbon dioxide gas and an alkyl radical, R•.

Step 4: Formation of a covalent bond between two alkyl radicals.

(i) Using ethanoic acid as a starting reagent, suggest suitable equations for **Steps 1, 2** and **4** on how ethane can be produced using the Kolbe reaction. **[3]**

(ii) The decomposition of the carboxyl radical to form carbon dioxide gas and an alkyl radical, R•, in **Step 3** can be represented by the following equation: $RCOO\bullet \rightarrow CO_2 + R\bullet$

Outline the mechanism of this step by copying the diagram below and include relevant curly half arrows.



[1]

(e) In another separate experiment, a new alkane **A**, C_6H_{12}, was produced. When reacted with bromine under ultraviolet light, **A** produced only **one isomeric monobromo** compound, **B**, which does not have a chiral centre. Draw the skeletal formulae of **A** and **B**. **[2]**

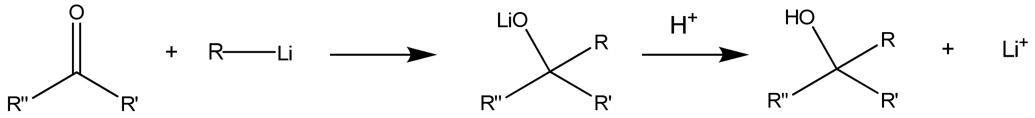
1 **(f)** **(i)** Using monohalogenoethane, C_2H_5X, as examples, describe and explain the relative reactivities of chloro- and bromo-compounds in hydrolysis reactions. **[2]**

(ii) Halogenoalkanes such as chlorofluoroalkanes, CFCs, were once used as refrigerant fluids and aerosol propellants. In many applications, they have now been replaced by alkanes. This is because CFCs contribute to the destruction of the ozone layer. Explain how CFCs destroy the ozone layer and suggest one potential hazard of using alkanes instead of CFCs. **[2]**

(iii) Halogenoalkanes can react with lithium to give organolithium compounds.

$$\text{R-Br} + 2\text{Li} \rightarrow \text{R-Li} + \text{LiBr}$$

These organolithium compounds can react with carbonyl compounds to form alcohols.



(R is alkyl, R’ and R’’ are either alkyl or H)

Using the above reaction sequence, deduce the structure of a suitable bromoalkane, R-Br, and a suitable carbonyl compound to synthesise hexan-2-ol. **[2]**

[Total: 19]

2 Wastewater has to be treated carefully to remove all harmful contaminants before it can be released into water bodies.

(a) Industrial wastewater contains high levels of heavy metal ions. Electrocoagulation is used to remove heavy metal ions from wastewater. In this method, heavy metal ions are oxidised to form hydroxides, so that they can coagulate easily and be removed easily in subsequent steps.

A sample of wastewater containing Fe^{2+} is treated by electrocoagulation.

$$4Fe^{2+}\,(aq) + 10H_2O\,(l) + O_2\,(g) \rightleftharpoons 4Fe(OH)_3\,(s) + 8H^+\,(aq)$$

(i) By considering the interaction it forms with water, explain why Fe^{2+} cannot be easily removed from wastewater. **[1]**

(ii) State a suitable physical method to remove $Fe(OH)_3$ from the wastewater. **[1]**

(iii) Using *Le Chatelier's Principle*, suggest why the wastewater has to be kept alkaline for a more effective removal of Fe^{2+}. **[1]**

(iv) With an appropriate sketch of the Boltzmann distribution, explain how an increase in temperature would affect the rate of the electrocoagulation process. **[3]**

(b) Ammonia is a toxic substance present in wastewater from the mining industry. Nitrification is a common biological treatment method to convert ammonia into less toxic nitrate.

$$NH_3\,(aq) + 2O_2\,(g) \rightleftharpoons NO_3^-\,(aq) + H^+\,(aq) + H_2O\,(l)$$

(i) Write the expression for the equilibrium constant, K_c, for this reaction given that K_c has units of $mol^{-1}\,dm^3$. **[1]**

(ii) 12 mol of oxygen gas was pumped into 1000 dm^3 of wastewater containing 5 mol of NH_3. After nitrification, the resulting treated wastewater had a pH of 4.2.

Calculate the value of K_c. Leave your answer to 3 significant figures. **[3]**

(iii) State how the K_c in **(ii)** would change when the amount of NH_3 in wastewater is increased to 10 mol. **[1]**

(iv) The nitrification process was carried out at room temperature. It was observed that the outer surface of the reaction vessel was cold after some time.

By considering the effect of temperature on the equilibrium, suggest and explain how you can change the reaction temperature to increase the conversion of ammonia. **[2]**

2 **(b)** **(v)** Construct a suitable energy cycle using the following equations to show how the enthalpy change of reaction, ΔH_r, can be determined.

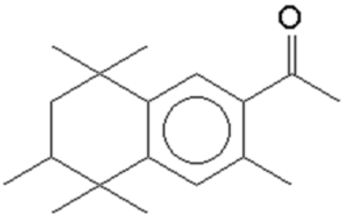
$NH_3\,(aq) + 2O_2\,(g) \longrightarrow NO_3^-\,(aq) + H^+\,(aq) + H_2O\,(l)$ ΔH_r

$NH_3(aq) + O_2(g) + H_2(g) \longrightarrow NH_2OH(aq) + H_2O(l)$ ΔH_1

$NH_2OH(aq) + H_2O(l) + \frac{1}{2}O_2(g) \longrightarrow NO_3^-(aq) + 2H_2(g) + H^+(aq)$ ΔH_2

$2H_2O(l) \longrightarrow 2H_2(g) + O_2(g)$ ΔH_3 **[3]**

(c) Wastewater treatment plants that treat pharmaceutical wastewater produces sludge that contains a high amount of organic substances. These organic substances can be combusted to harness energy for other processes. Tonalide, $C_{18}H_{26}O$, is one such organic compound found commonly in sludge. It has a melting point of 54.5°C.



tonalide

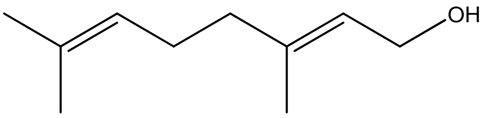
(i) Write an equation which describes the standard enthalpy change of combustion of tonalide. **[1]**

(ii) The enthalpy change of combustion of tonalide is −865 kJ mol^{-1}.
Given that the combustion is 70% efficient, determine the amount of energy that can be harnessed from the combustion of sludge, which contains 900 g of tonalide. **[2]**

(iii) The sign of the entropy change of combustion of tonalide is positive. Briefly explain the effect of temperature on the spontaneity of combustion of tonalide. **[1]**

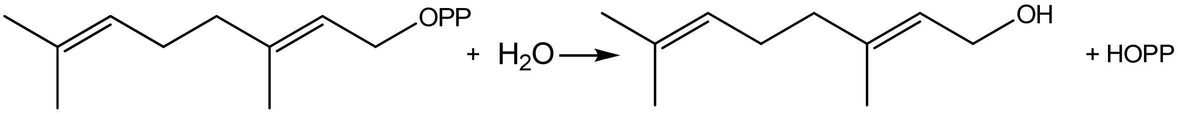
[Total: 20]

3 Geraniol, $C_{10}H_{18}O$, is commonly used in perfumes and food flavourings.



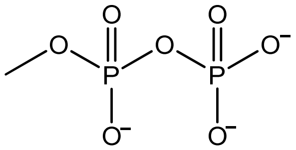
Geraniol

It is produced from geranyl diphosphate as shown in the following equation.



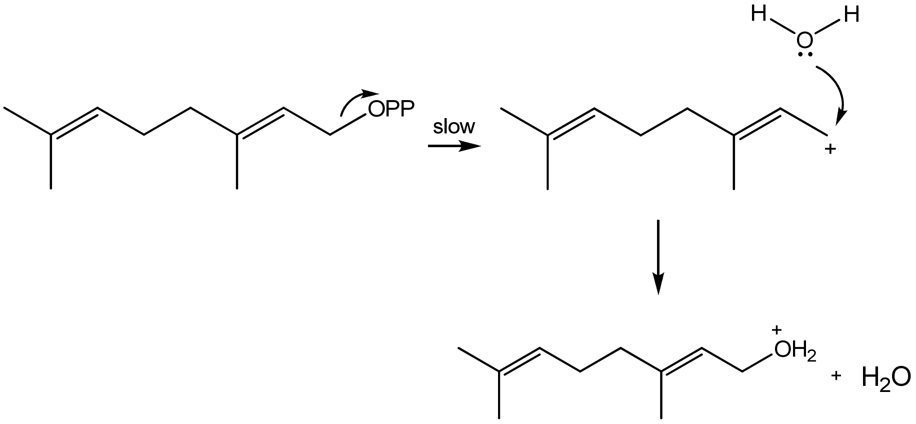
Geranyl diphosphate

where OPP :

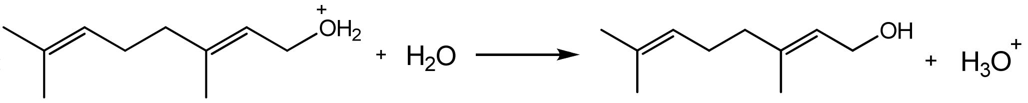


(a) The mechanism of this reaction consists of the following:

Reaction I:



Reaction II:

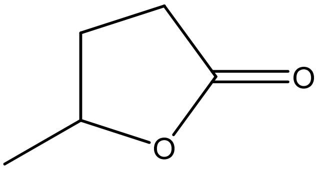


(i) State the mechanism in reaction **I**. **[1]**

(ii) Explain why the mechanism in reaction **I** takes place in two steps instead of one step. **[1]**

(iii) State the role of water in reaction **II**. **[1]**

3 **(a)** **(iv)** The following compound can be synthesised from geraniol.



Propose a reaction scheme for this synthesis. **[4]**

(v) Explain what is meant by constitutional isomers and draw a constitutional isomer of geraniol that will form a yellow precipitate with alkaline aqueous iodine. **[2]**

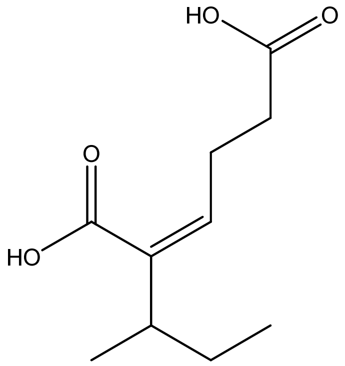
(b) Geranyl diphosphate can be synthesised using P_4O_{10}.

(i) Write an equation for the reaction of P_4O_{10} in water and describe the effect of the resulting solution on universal indicator solution. **[2]**

(ii) Naturally occurring phosphorus contains the isotopes ^{31}P, ^{32}P and ^{33}P. Explain the term isotopes and calculate the relative atomic mass of phosphorus given that the relative abundance of each isotope is 91.1 %, 7.9% and 1.0 % respectively. **[2]**

(c) Geraniol is a by-product of the metabolism of sorbic acid, C_5H_7COOH. Sorbic acid and its salt are used to prevent growth of mould and fungi and to regulate the pH in food and drinks. With the aid of relevant equations, explain how the pH of food and drinks can be regulated through the use of sorbic acid and its salt. **[3]**

3 **(d)** Another constitutional isomer of geraniol is compound **X**. **X** does not react with 2,4-dinitrophenylhydrazine. **X** produces effervescence when sodium metal is added to it. When hot acidified $K_2Cr_2O_7$ is added to **X**, orange solution remains. On addition of aqueous bromine to **X**, the orange solution decolourises and compound **Y** is formed. **X** reacts with hot acidified $KMnO_4$ to form compound **Z** only. When **Z** is reacted with excess concentrated H_2SO_4 at 170 °C, the following product is obtained.



X, **Y** and **Z** are all able to rotate the plane of polarised light. Suggest the identities of **X**, **Y** and **Z**, explaining your reasoning.

[5]

[Total: 21]

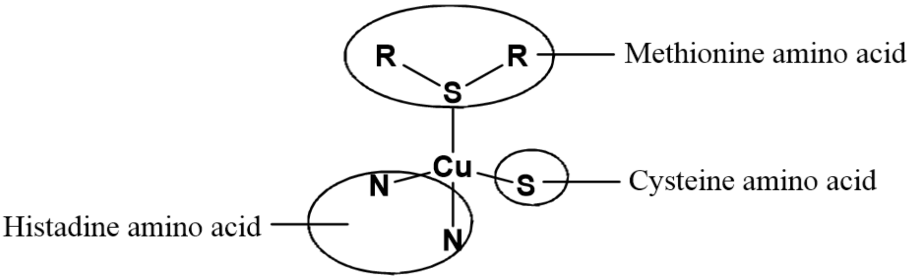
Section B

Answer **one** question in this section.

4 Transition elements and its compounds have various applications, such as in materials, catalysis and even in nature. An example of a transition element which has many uses and is widely researched on is copper.

(a) Explain what is meant by the term *transition element*. **[1]**

(b) **(i)** Plastocyanin is a copper-containing protein found in vascular plants. The shape around Cu^{2+} in plastocyanin is tetrahedral and can be represented by the following simplified structure. The amino acids found around Cu^{2+} act as ligands.



Define the term *ligand*. **[1]**

(ii) Plastocyanin is commonly involved in electron transfer and this results in the formation of Cu^+ complex which has a deep blue colour.

State the electronic configuration of Cu^+. **[1]**

(iii) The deep blue colour seen is considered to be unusual.

Suggest a reason why this is so. **[1]**

(c) Azurite is a copper containing mineral that is deep blue in colour. The formula of azurite is $Cu_3(CO_3)_2(OH)_2$ and it can be inferred that azurite contained copper(II) carbonate and copper(II) hydroxide, which are sparingly soluble salts.

(i) To prepare small crystals of azurite in the lab, a few drops of copper(II) sulfate solution can be added into a saturated solution of sodium carbonate and leave to stand overnight.

With reference to the preparation method as described, write an equation to suggest how OH^- may be produced from a saturated solution of sodium carbonate. **[1]**

(ii) A student wishes to determine the percentage of azurite in a rock sample. He proposes to do so by performing a direct titration with dilute sulfuric acid.

Suggest an explanation why the proposed method is not ideal. **[1]**

4 **(c)** **(iii)** Another student proposed the following method which is ideal in determining the percentage of azurite in a rock sample.

Step 1: Add 7.00 g of the rock sample to 130 cm^3 of 0.550 mol dm^{-3} sulfuric acid. The resulting solution was topped up to 250 cm^3 using deionised water.

Step 2: 25.0 cm^3 of the solution required 15.55 cm^3 of 0.200 mol dm^{-3} sodium hydroxide for complete reaction.

Azurite reacts with sulfuric acid according to the following equation.

$$Cu_3(CO_3)_2(OH)_2 + \boldsymbol{a}\ H_2SO_4 \rightarrow \boldsymbol{a}\ CuSO_4 + \boldsymbol{b}\ H_2O + \boldsymbol{c}\ CO_2$$

Complete the balancing of the above equation by deducing values for ***a***, ***b*** and ***c***. Hence, calculate the percentage of azurite in the rock sample. **[3]**

(iv) Using your knowledge on the thermal decomposition of carbonates and given that $Cu(OH)_2$ thermally decomposes to form CuO and H_2O, write an equation for the thermal decomposition of azurite.

Using the equation written and appropriate molar mass values, calculate the percentage loss in mass upon strongly heating a sample of azurite until no further changes. **[3]**

(v) In another instance, a student tried to synthesise azurite by adding copper(II) nitrate solution slowly to a solution containing 0.100 mol dm^{-3} sodium carbonate solution and 0.100 mol dm^{-3} potassium hydroxide solution. Calculate the concentration of Cu^{2+} required to begin precipitating $CuCO_3$ and $Cu(OH)_2$ respectively. Hence, state which compound precipitates first assuming that there is a negligible change in volume.

K_{sp} of $CuCO_3$ = 7.08×10^{-9} $mol^2\ dm^{-6}$
K_{sp} of $Cu(OH)_2$ = 4.8×10^{-20} $mol^3\ dm^{-9}$

[3]

(vi) When sufficient ammonia is added to copper(II) hydroxide precipitate, the precipitate dissolves. Explain this observation with the aid of relevant equations. **[2]**

(d) Copper metal is obtained from copper ore and is widely used in electrical wiring. To prevent short circuit, the metal used must have high purity. Outline how the impure copper ore is purified industrially to remove impurities such as zinc and silver metals.

[3]

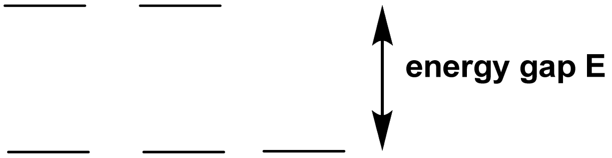
[Total: 20]

5 Iron is an important transition element and the second most abundant metal in Earth's crust. Iron containing compounds have various uses and the element itself can also be found in a number of proteins within living things. Iron and its compounds have been widely researched on as they are relatively cheap and non-toxic.

(a) Haemoglobin is a protein found in red blood cells. Within haemoglobin, it contains an Fe^{2+} ion which has an octahedral shape as it is surrounded by five nitrogen-containing ligands and one oxygen-containing ligand, which is H_2O in deoxyhaemoglobin and O_2 in oxyhaemoglobin.

(i) A species with unpaired electrons is paramagnetic and can be attracted by an externally applied magnetic field. On the other hand, a species with no unpaired electrons is diamagnetic and is unaffected by a magnetic field.

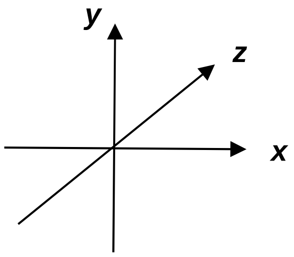
Oxyhaemoglobin is found to be diamagnetic. Based on the information provided and using the diagram below, show the electronic distribution of the 3d electrons of Fe^{2+} in oxyhaemoglobin.



[1]

(ii) In both oxyhaemoglobin and deoxyhaemoglobin, the 3d orbitals are no longer degenerate as they are split into two different energy levels.

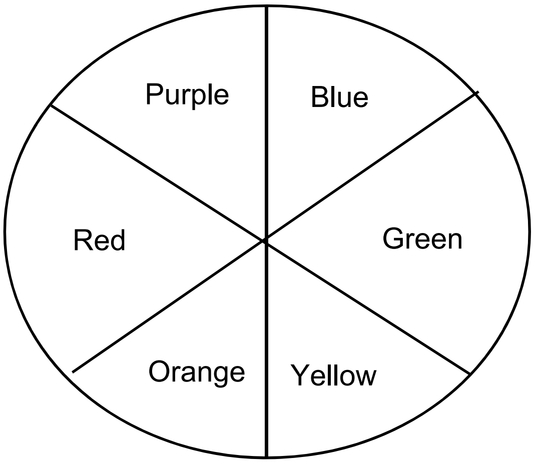
Explain this observation. Using the Cartesian axes like those shown below, draw a fully labelled diagram of one of the 3d orbitals which has a lower energy level.



[3]

5 (a) (iii) Explain why oxyhaemoglobin is red. **[2]**

(iv) The complementary colours are shown using the following colour wheel.



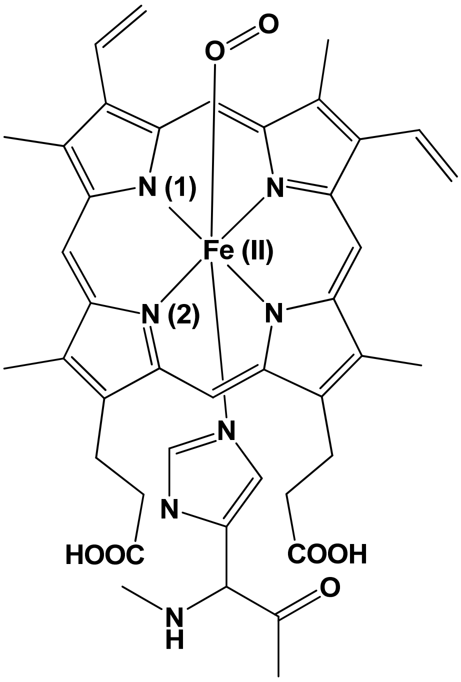
The wavelength of each colour component in visible light is as provided.

Colour	**Purple**	**Blue**	**Green**	**Yellow**	**Orange**	**Red**
Wavelength / nm	380 - 450	450 - 495	495 - 570	570 - 590	590 - 620	620 – 750

Oxyhaemoglobin is bright red while deoxyhaemoglobin is blue. Given that the wavelength of light is inversely proportional to energy, state and explain if water or oxygen causes a larger energy gap between the 3d orbitals.

[2]

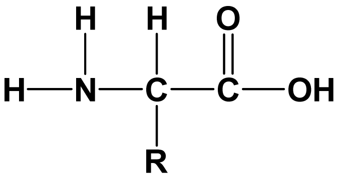
5 **(a)** **(v)** Fe^{2+} complex in oxyhaemoglobin does not have an overall charge. The structure is as shown.



State the charge around the N atom labelled **(1)** and the bond angle around the N atom labelled **(2)**. **[2]**

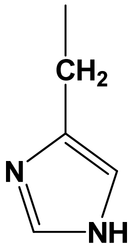
(vi) Besides Fe^{2+}, Fe^{3+} may also exist in haemoglobin. Explain why Fe can have variable oxidation states in haemoglobin. **[1]**

5 **(a)** **(vii)** Each polypeptide chain in haemoglobin is made up of more than 100 amino acid residues. The general structure of an amino acid is as shown below.



$$H_2N-CH(R)-COOH$$

In each chain, histidine, leucine and glycine amino acids can be found.

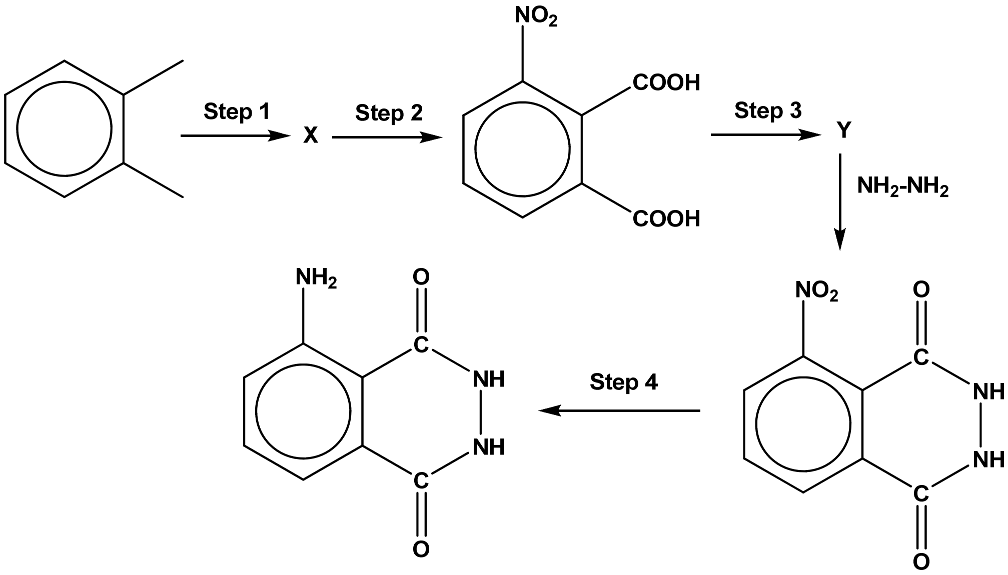
Amino acid	**R group**
Histidine	
Leucine	$-CH_2CH(CH_3)_2$
Glycine	-H

Draw the structural formula of a tripeptide with the sequence histidine-leucine-glycine at pH 2. **[2]**

(viii) Haemoglobin can undergo complete hydrolysis non-enzymatically. State the reagents and condition for this to occur. **[1]**

5 (b) To detect for the presence of blood in a crime scene, an organic compound named luminol may be used. Luminol uses iron in haemoglobin to catalyse the decomposition of hydrogen peroxide, which eventually leads to a blue glow to indicate the presence of blood.

The synthetic route for luminol is as shown.



Luminol

(i) State the reagents and conditions for **steps 1** to **3**. **[3]**

(ii) Draw the structures for intermediate products **X** and **Y**. **[2]**

(iii) For **Step 4**, $Na_2S_2O_4$ is commonly used as the reagent.

State the role of $Na_2S_2O_4$. **[1]**

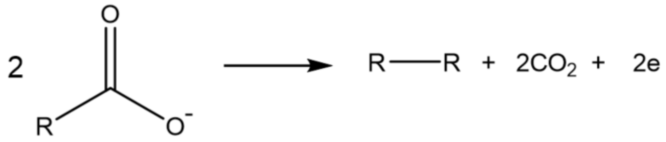
[Total: 20]

END OF PAPER

Section A

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

1 Electrosynthesis in organic chemistry is the synthesis of compounds in an electrolytic cell using inert electrodes. One important process is the Kolbe reaction. The Kolbe reaction is the decarboxylative dimerization of two carboxylate ions. Alkanes can be formed at the anode by the following reaction.



(a) Explain why alkanes are generally unreactive. **[1]**

Alkanes have C-C and C-H bonds which are strong and non-polar.

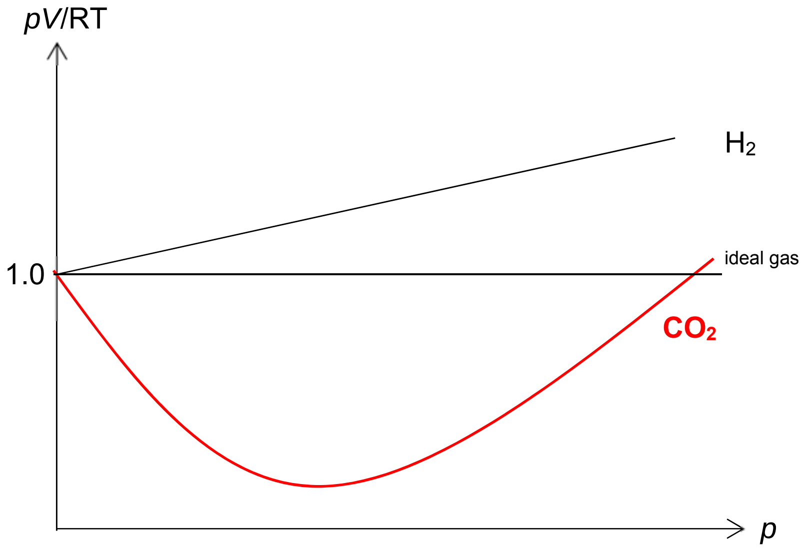
(b) **(i)** Calculate the volume of carbon dioxide produced when a steady current of 5A is passed through the electrolyte for 32 minutes at standard temperature and pressure. **[2]**

Q = It = 32 x 60 x 5 = 9600 C

Amt of CO_2 = Amt of e = Q/F = 9600/(96500) = 0.09948 mol

Vol of CO_2 collected = 0.09948 x 22.7 = 2.26 dm^3

(ii) Methanoate ions undergo the Kolbe reaction to form only 2 gases. Using the axes given below, sketch the variation of *pV*/RT against *p* for one mole of **each** gas at the same temperature. Briefly explain your answer. **[2]**



CO_2 deviates more from ideal behaviour because it experiences <u>stronger instantaneous dipole-induced dipole interactions / intermolecular forces</u> between the molecules compared to H_2 which has a smaller electron cloud.

(c) The cathodic reaction for the Kolbe reaction can be represented by the following half equation: $2H_2O + 2e \rightarrow H_2 + 2OH^-$.

Write an overall equation for the Kolbe reaction involving ethanoate ions. Hence, calculate $\Delta G^\ominus$ for the Kolbe reaction given that the $E^\ominus_{cell}$ value for the reaction is +2.28 V. **[2]**

$2CH_3COO^- \rightarrow CH_3\text{-}CH_3 + 2CO_2 + 2e$

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

Overall: $2CH_3COO^- + 2H_2O \rightarrow CH_3\text{-}CH_3 + 2CO_2 + H_2 + 2OH^-$

$\Delta G^\ominus = -nFE = -(2)(96500)(2.28) = -440 \text{ kJ mol}^{-1}$

(d) The reaction mechanism of the Kolbe reaction involves a 4-step reaction mechanism as described below:

Step 1: Dissociation of carboxylic acid to form a carboxylate ion.

Step 2: Oxidation of carboxylate ion to form a carboxyl radical, RCOO•.

Step 3: Decomposition of the carboxyl radical to form carbon dioxide gas and an alkyl radical, R•.

Step 4: Formation of a covalent bond between two alkyl radicals.

(i) Using ethanoic acid as a starting reagent, suggest suitable equations for **Steps 1, 2** and **4** on how ethane can be produced using the Kolbe reaction. **[3]**

Step 1: $CH_3COOH \rightarrow CH_3COO^- + H^+$

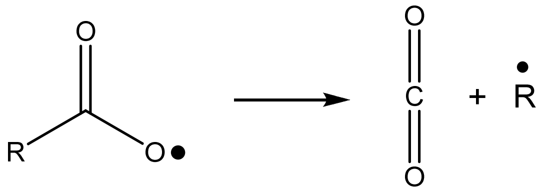
Also accept "$CH_3COOH + H_2O \rightarrow CH_3COO^- + H_3O^+$".

Step 2: $CH_3COO^- \rightarrow CH_3COO\bullet + e$

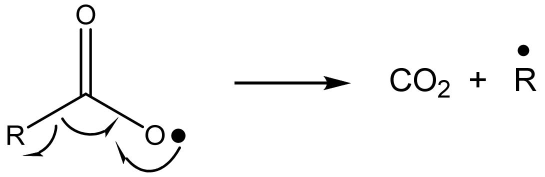
Step 4: $CH_3\bullet + CH_3\bullet \rightarrow CH_3CH_3$ (accept C_2H_6 also)

(ii) The decomposition of the carboxyl radical to form carbon dioxide gas and an alkyl radical, R•, in **Step 3** can be represented by the following equation: $RCOO\bullet \rightarrow CO_2 + R\bullet$

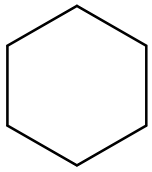
Outline the mechanism of this step by copying the diagram below and include relevant curly half arrows.

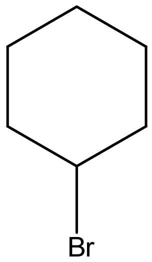


[1]



(e) In another separate experiment, a new alkane **A**, C_6H_{12}, was produced. When reacted with bromine under ultraviolet light, **A** produced only **one isomeric monobromo** compound, **B**, which does not have a chiral centre. Draw the skeletal formulae of **A** and **B**. **[2]**





(f) **(i)** Using monohalogenoethane, C_2H_5X, as examples, describe and explain the relative reactivities of chloro- and bromo-compounds in hydrolysis reactions. **[2]**

The hydrolysis of C_2H_5X will increases in reactivity ($C_2H_5Cl < C_2H_5Br$) . This is because the bond length / bond energy of C-C*l* <C-Br, hence, it is most difficult to overcome C-C*l* bond > C-Br bond.

(ii) Halogenoalkanes such as chlorofluoroalkanes, CFCs, were once used as refrigerant fluids and aerosol propellants. In many applications, they have now been replaced by alkanes. This is because CFCs contribute to the destruction of the ozone layer. Explain how CFCs destroy the ozone layer and suggest one potential hazard of using alkanes instead of CFCs. **[2]**

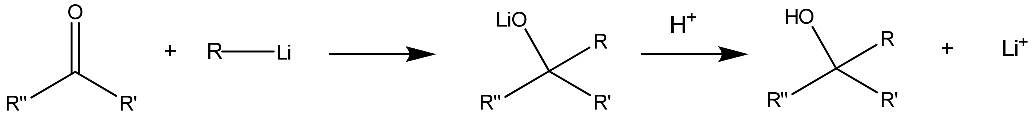
CFCs produce chlorine radicals, which in turn initiate the chain reaction breaking down ozone molecules, O_3 to O_2.

Alkanes are flammable.

(iii) Halogenoalkanes can react with lithium to give organolithium compounds.

$$R\text{-}Br + 2Li \rightarrow R\text{-}Li + LiBr$$

These organolithium compounds can react with carbonyl compounds to form alcohols.



(R is alkyl, R' and R'' are either alkyl or H)

Using the above reaction sequence, deduce the structure of a suitable bromoalkane, R-Br, and a suitable carbonyl compound to synthesise hexan-2-ol. **[2]**

Ethanal, 1-bromobutane

OR Bromomethane, Pentanal

[Total: 19]

2 Wastewater has to be treated carefully to remove all harmful contaminants before it can be released into water bodies.

(a) Industrial wastewater contains high levels of heavy metal ions. Electrocoagulation is used to remove heavy metal ions from wastewater. In this method, heavy metal ions are oxidised to form hydroxides, so that they can coagulate easily and be removed easily in subsequent steps.

A sample of wastewater containing Fe^{2+} is treated by electrocoagulation.

$$4Fe^{2+}\ (aq) + 10H_2O\ (l) + O_2\ (g) \qquad 4Fe(OH)_3\ (s) + 8H^+\ (aq)$$

(i) By considering the interaction it forms with water, explain why Fe^{2+} cannot be easily removed from wastewater. **[1]**

It forms ion-dipole interaction with water. Hence, it is soluble in water and cannot be easily removed.

OR

It forms dative bond with water to form a soluble complex of $[Fe(H_2O)_6]^{2+}$. Hence it cannot be easily removed.

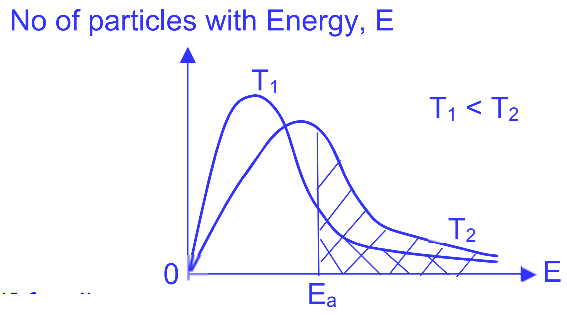
(ii) State a suitable physical method to remove $Fe(OH)_3$ from the wastewater. **[1]**

filtration

(iii) Using *Le Chatelier's Principle*, suggest why the wastewater has to be kept alkaline for a more effective removal of Fe^{2+}. **[1]**

As $[OH^-]$ is high / $[H^+]$ is low, the position of the equilibrium shifts right to increase $[H^+]$. Hence, more Fe^{2+} would be oxidised/removed as $Fe(OH)_3$.

(iv) With an appropriate sketch of the Boltzmann distribution, explain how an increase in temperature would affect the rate of removal of Fe^{2+}. **[3]**



When T increases, the KE of the reacting particles increases. Hence, there are more particles with $E \geq E_a$ and the frequency of effective collision increases. The rate of removal of Fe^{2+} would increase.

(b) Ammonia is a toxic substance present in wastewater from the mining industry. Nitrification is a common biological treatment method to convert ammonia into less toxic nitrate.

$$NH_3\,(aq) + 2O_2\,(g) \rightleftharpoons NO_3^-\,(aq) + H^+\,(aq) + H_2O\,(l)$$

(i) Write the expression for the equilibrium constant, K_c, for this reaction given that K_c has units of $mol^{-1}\ dm^3$. **[1]**

$K_c = [NO_3^-][H^+] / [NH_3]\,[O_2]^2$

(ii) 12 mol of oxygen gas was pumped into 1000 dm^3 of wastewater containing 5 mol of NH_3. After nitrification, the resulting treated wastewater had a pH of 4.2. Calculate the value of K_c. Leave your answer to 3 significant figures. **[3]**

	$NH_3(aq)$	$+ 2O_2$	$\rightleftharpoons$	$NO_3^-(aq)$	$H^+(aq)$	H_2O
Initial conc / $mol\ dm^{-3}$	0.005	0.012		0	0	
Eqm conc / $mol\ dm^{-3}$	$0.005 - 10^{-4.2}$ $= 0.0049369$	$0.012 - 2 \times 10^{-4.2}$ $= 0.011873$		$10^{-4.2}$	$10^{-4.2}$	

$$K_c = \frac{(10^{-4.2})^2}{(4.9369 \times 10^{-3})(1.1873 \times 10^{-2})^2} = 5.72 \times 10^{-3}\ mol^{-1}\ dm^3\ (3sf)$$

(iii) State how the K_c in **(ii)** would change when the amount of NH_3 in wastewater is increased to 10 mol. **[1]**

K_c would remain the same.

(iv) The nitrification process was carried out at room temperature. It was observed that the outer surface of the reaction vessel was cold after some time. **[2]**

By considering the effect of temperature on the equilibrium, suggest and explain how you can change the reaction temperature to increase the conversion of ammonia.

The (forward) reaction is endothermic. Hence, we can increase the temperature to shift the equilibrium position right, so as to absorb the excess heat, which allows more NH_3 to be converted.

(v) Construct a suitable energy cycle using the following equations to show how the enthalpy change of reaction, ΔH_r, can be determined. **[3]**

$NH_3\ (aq) + 2O_2\ (g) \qquad NO_3^-\ (aq) + H^+\ (aq) + H_2O\ (l)$ $\qquad \Delta H_r$

$NH_3(aq) + O_2(g) + H_2(g) \qquad NH_2OH(aq) + H_2O(l)$ $\qquad \Delta H_1$

$NH_2OH(aq) + H_2O(l) + \frac{1}{2}O_2(g) \qquad NO_3^-(aq) + 2H_2(g) + H^+(aq)$ $\qquad \Delta H_2$

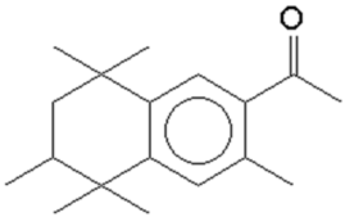
$2H_2O(l) \qquad 2H_2(g) + O_2(g)$ $\qquad \Delta H_3$

$$\begin{tikzcd}
NH_3(aq) + 2O_2(g) + H_2(g) \arrow[d, "\Delta H_1"] \arrow[r, phantom, "\Delta H_r"] & NO_3^-\ (aq) + H^+\ (aq) + H_2O\ (l) + H_2\ (g) \arrow[ddl, "\frac{1}{2}\Delta H_3"'] & \\
NH_2OH\ (aq) + H_2O\ (l) + O_2\ (g) \arrow[d, "\Delta H_2"] & & \Delta H_3 \\
NO_3^-\ (aq) + 2H_2\ (g) + H^+\ (aq) + \frac{1}{2}\ O_2\ (g) & &
\end{tikzcd}$$

$\Delta H_r + \frac{1}{2}\ \Delta H_3 = \Delta H_1 + \Delta H_2$

$\Delta H_r = \Delta H_1 + \Delta H_2 - \frac{1}{2}\ \Delta H_3$

(c) Wastewater treatment plants that treat pharmaceutical wastewater produces sludge that contains a high amount of organic substances. These organic substances can be combusted to harness energy for other processes. Tonalide, $C_{18}H_{26}O$, is one such organic compound found commonly in sludge. It has a melting point of 54.5°C.



tonalide

(i) Write an equation which describes the standard enthalpy change of combustion of tonalide. **[1]**

$C_{18}H_{26}O\ (s) + 24O_2\ (g) \rightarrow 18CO_2\ (g) + 13H_2O\ (l)$

(ii) The enthalpy change of combustion of tonalide is −865 kJ mol^{-1}. **[2]**

Given that the combustion is 70% efficient, determine the amount of energy that can be harnessed from the combustion of sludge, which contains 900 g of tonalide.

Amt of tonalide = 900 / (18 X 12.0 + 26 X 1.0 + 16.0) = 3.4883 mol

Amt of heat released (100%) = 865 X 3.4883 = 3017.4 kJ

Amt of energy harnessed (70%) = 3017.4 X 0.7 = 2110 kJ (3sf)

(iii) The sign of the entropy change of combustion of tonalide is positive. Briefly explain the effect of temperature on the spontaneity of combustion of tonalide. **[1]**

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

$T\Delta S > 0$

$\Delta H < 0$

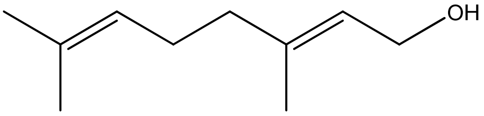
ΔG becomes more negative at higher temperatures. Hence, the combustion is more feasible.

OR

ΔG is always negative at all temperatures. Hence, the combustion is feasible at all temperatures.

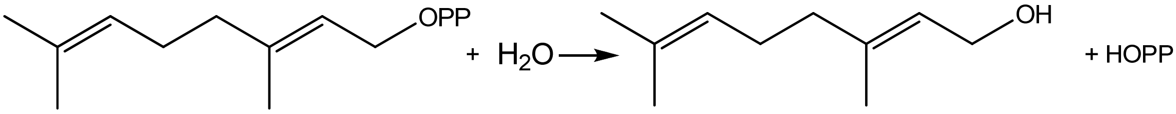
[Total: 20]

3 Geraniol, $C_{10}H_{18}O$, is commonly used in perfumes and food flavourings.



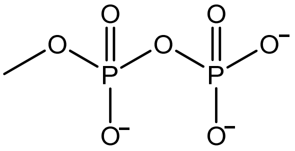
Geraniol

It is produced from geranyl diphosphate as shown in the following equation.



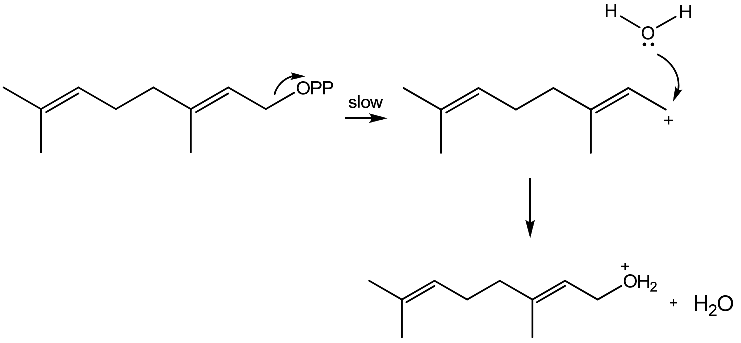
Geranyl diphosphate

where OPP :

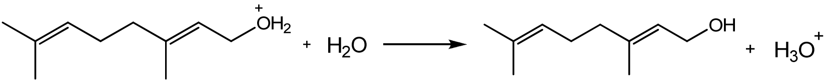


(a) The mechanism of this reaction consists of the following:

Reaction I:



Reaction II:



(i) State the mechanism in reaction I. **[1]**

Nucleophilic substitution

(ii) Explain why the mechanism in reaction **I** takes place in two steps instead of one step.

OPP is a **bulky group** which creates **steric hindrance** for the nucleophile to attack the carbon bonded to OPP / **transition state is unstable**.

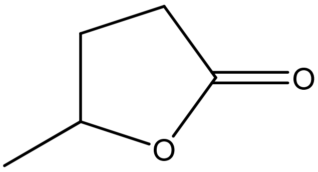
OR

OPP is negatively charged so it repels the approaching nucleophile (H_2O).

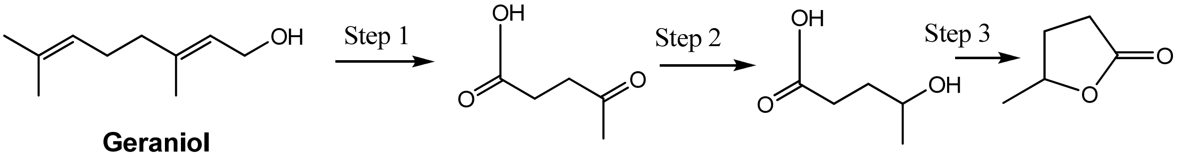
(iii) State the role of water in reaction **II**. **[1]**

It acts as a **Bronsted-Lowry / Lewis base** (as it accepts H^+ to form H_3O^+) or **nucleophile**.

(iv) The following compound can be synthesised from geraniol. **[4]**



Propose a reaction scheme for this synthesis.



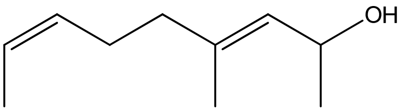
Step 1: $KMnO_4$, H_2SO_4 (aq), heat

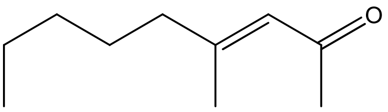
Step 2: $NaBH_4$ or Hydrogen / Nickel, heat

Step 3: concentrated sulfuric acid, heat

(v) Explain what is meant by constitutional isomers and draw a constitutional isomer of geraniol that will form a yellow precipitate with alkaline aqueous iodine. **[2]**

They are compounds with the same molecular formula but different structural formulae





OR Any other structure with same molecular formula with R-CO(CH_3) or R-CH(OH)CH_3

(b) Geranyl diphosphate can be synthesised using P_4O_{10}.

(i) Write an equation for the reaction of P_4O_{10} in water and describe the effect of the resulting solution on universal indicator solution. **[2]**

$P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4$

Universal indicator will turn red / orange.

(ii) Naturally occurring phosphorus contains the isotopes ^{31}P, ^{32}P and ^{33}P. Explain the term isotopes and calculate the relative atomic mass of phosphorus given that the relative abundance of each isotope is 91.1 %, 7.9% and 1.0 % respectively. **[2]**

Isotopes are elements with the same atomic number / same number of protons but different mass number / due to different number of neutrons.

relative atomic mass = (0.911 x 31) + (0.079 x 32) + (0.01 x 33) = 31.1

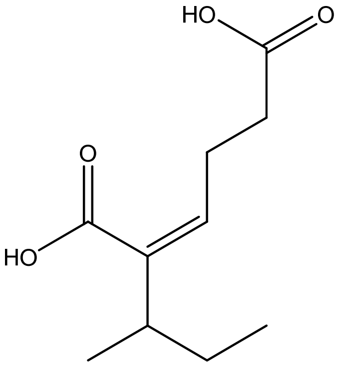
(c) Geraniol is a by-product of the metabolism of sorbic acid, C_5H_7COOH. Sorbic acid and its salt are used to prevent growth of mould and fungi and to regulate the pH in food and drinks. With the aid of relevant equations, explain how the pH of food and drinks can be regulated through the use of sorbic acid and its salt. **[3]**

$C_5H_7COOH + OH^- \rightarrow C_5H_7COO^- + H_2O$

$C_5H_7COO^- + H^+ \rightarrow C_5H_7COOH$

A large reservoir of acid and salt will help to remove a small amount of base and acid respectively to ensure that the pH remains **relatively/almost** constant/resists pH changes.

(d) Another constitutional isomer of geraniol is compound **X**. **X** does not react with 2,4-dinitrophenylhydrazine. **X** produces effervescence when sodium metal is added to it. When hot acidified $K_2Cr_2O_7$ is added to **X**, orange solution remains. On addition of aqueous bromine to **X**, the orange solution decolourises and compound **Y** is formed. **X** reacts with hot acidified $KMnO_4$ to form compound **Z** only. When **Z** is reacted with excess concentrated H_2SO_4 at 170 °C, the following product is obtained. **[5]**

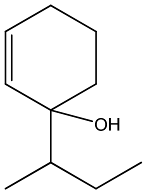


X, **Y** and **Z** are all able to rotate the plane of polarised light. Suggest the identities of **X**, **Y** and **Z**, explaining your reasoning.

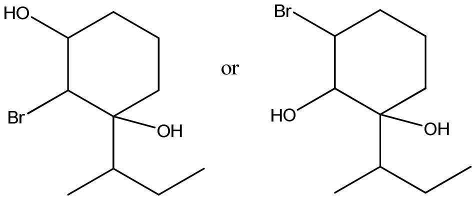
Observations	**Deductions**
X does not react with 2,4-DNPH.	**X** is not an aldehyde or ketone / not a carbonyl compound.
X produces effervescence when Na added.	Redox. Gas is H_2. **X** contains hydroxyl group (or –OH group or alcohol).
Orange solution remains when hot $K_2Cr_2O_7$ added to **X**.	**X** contains tertiary alcohol.
On addition of aqueous bromine to **X**, the orange solution turns colourless.	**X** undergoes electrophilic addition. **X** contains C=C (or alkene).
X reacts with hot acidified $KMnO_4$ to produce **Z** only.	Oxidation **X** is a cyclic compound
Z reacts with excess concentrated H_2SO_4 at 170 °C.	Elimination
X, **Y** and **Z** are all able to rotate the plane of polarised light.	All 3 compounds have chiral carbon.

Structures

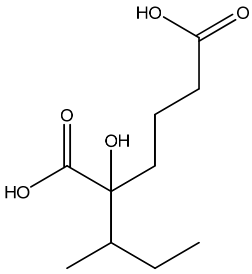
X:



Y:



Z:



[Total: 21]

Section B

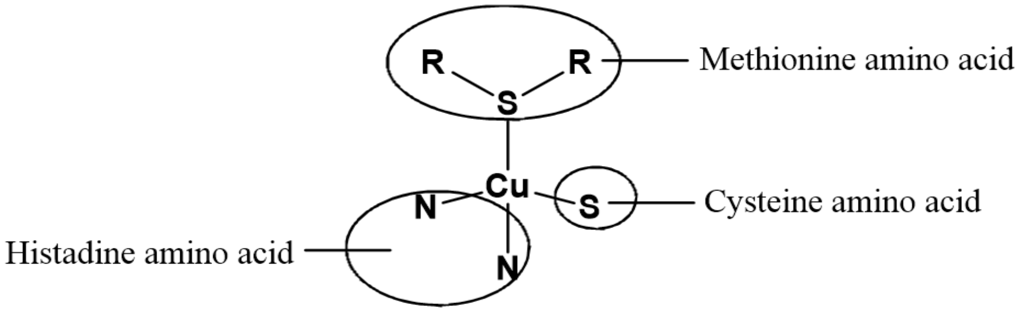
Answer **one** question in this section.

4 Transition elements and its compounds have various applications, such as in materials, catalysis and even in nature. An example of a transition element which has many uses and is widely researched on is copper.

(a) Explain what is meant by the term *transition element*. **[1]**

It is a **d-block element** which forms **one or more stable ions** with **partially filled d subshells**.

(b) **(i)** Plastocyanin is a copper-containing protein found in vascular plants. The shape around Cu^{2+} in plastocyanin is tetrahedral and can be represented by the following simplified structure. The amino acids found around Cu^{2+} act as ligands.



Define the term *ligand*. **[1]**

It is an **ion or molecule** which contains **at least 1 atom bearing a lone pair of electrons** which can be **donated into a low-lying vacant orbital of a central metal atom or ion** by forming a **dative bond**.

(ii) Plastocyanin is commonly involved in electron transfer and this results in the formation of Cu^+ complex which has a deep blue colour.

State the electronic configuration of Cu^+. **[1]**

$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$

(iii) The deep blue colour seen is considered to be unusual.

Suggest a reason why this is so. **[1]**

The **d orbitals in Cu^+ are completely filled** and therefore, **no d-d transition** can occur and the complex should not be coloured.

(c) Azurite is a copper containing mineral that is deep blue in colour. The formula of azurite is $Cu_3(CO_3)_2(OH)_2$ and it can be inferred that azurite contained copper(II) carbonate and copper(II) hydroxide, which are sparingly soluble salts.

(i) To prepare small crystals of azurite in the lab, a few drops of copper(II) sulfate solution can be added into a saturated solution of sodium carbonate and leave to stand overnight.

With reference to the preparation method as described, write an equation to suggest how OH^- may be produced from a saturated solution of sodium carbonate. **[1]**

$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^-$

(ii) A student wishes to determine the percentage of azurite in a rock sample. He proposes to do so by performing a direct titration with dilute sulfuric acid.

Suggest an explanation why the proposed method is not ideal. **[1]**

The solid is **insoluble** and **cannot be directly titrated**.

OR

The solid hydroxide and carbonate (especially) will be **too slow to react** with the sulfuric acid.

OR

The **end-point will not be accurately determined**.

(iii) Another student proposed the following method which is ideal in determining the percentage of azurite in a rock sample.

Step 1: Add 7.00 g of the rock sample to 130 cm^3 of 0.550 mol dm^{-3} sulfuric acid. The resulting solution was topped up to 250 cm^3 using deionised water.

Step 2: 25.0 cm^3 of the solution required 15.55 cm^3 of 0.200 mol dm^{-3} sodium hydroxide for complete reaction.

Azurite reacts with sulfuric acid according to the following equation.

$$Cu_3(CO_3)_2(OH)_2 + \boldsymbol{a}\ H_2SO_4 \rightarrow \boldsymbol{a}\ CuSO_4 + \boldsymbol{b}\ H_2O + \boldsymbol{c}\ CO_2$$

Complete the balancing of the above equation by deducing values for ***a***, ***b*** and ***c***. Hence, calculate the percentage of azurite in the rock sample. **[3]**

$Cu_3(CO_3)_2(OH)_2 + 3\ H_2SO_4 \rightarrow 3\ CuSO_4 + 4\ H_2O + 2\ CO_2$

Amount of NaOH = Amount of excess H_2SO_4 = ½ x 15.55/1000 x 0.2 = 1.55×10^{-3} mol

Amount of excess H_2SO_4 in 250 cm^3 = 10 x 1.55×10^{-3} = 0.0155 mol

Amount of H_2SO_4 reacted with azurite = (130/1000 x 0.55) – 0.0155 = 0.05595 mol

Amount of azurite = 0.05595 / 3 = 0.01865 mol

Mass of azurite = 0.01865 x 344.5 = 6.42 g

% azurite in rock sample = 6.425 / 7 x 100% = 91.8% (to 3 sf)

(iv) Using your knowledge on the thermal decomposition of carbonates and given that $Cu(OH)_2$ thermally decomposes to form CuO and H_2O, write an equation for the thermal decomposition of azurite.

Using the equation written and appropriate molar mass values, calculate the percentage loss in mass upon strongly heating a sample of azurite until no further changes. **[3]**

$Cu_3(CO_3)_2(OH)_2 \rightarrow 3\ CuO + H_2O + 2\ CO_2$

Mass of azurite in 1 mol = 344.5 g

Mass of H_2O in 1 mol = 18 g

Mass of CO_2 in 2 mol = 2 x 44 = 88 g

% loss in mass = (18+88) / 344.5 x 100% = 30.76% ≈ 30.8% (to 3 sf)

(v) In another instance, a student tried to synthesise azurite by adding copper(II) nitrate solution slowly to a solution containing 0.100 mol dm^{-3} sodium carbonate solution and 0.100 mol dm^{-3} potassium hydroxide solution. Calculate the concentration of Cu^{2+} required to begin precipitating $CuCO_3$ and $Cu(OH)_2$ respectively. Hence, state which compound precipitates first assuming that there is a negligible change in volume.

K_{sp} of $CuCO_3$ = 7.08 x 10^{-9} $mol^2\ dm^{-6}$

K_{sp} of $Cu(OH)_2$ = 4.8 x 10^{-20} $mol^3\ dm^{-9}$

[3]

When $Cu(OH)_2$ first precipitates,

$[Cu^{2+}]$ = 4.8 x 10^{-20} / $(0.1)^2$ = **4.8 x 10^{-18} mol dm^{-3}**

When $CuCO_3$ first precipitates,

$[Cu^{2+}]$ = 7.08 x 10^{-9} / 0.1 = **7.08 x 10^{-8} mol dm^{-3}**

$Cu(OH)_2$ will precipitate first.

(vi) When sufficient ammonia is added to copper(II) hydroxide precipitate, the precipitate dissolves. Explain this observation with the aid of relevant equations.

[2]

$[Cu(H_2O)_6]^{2+}(aq) + 2OH^-(aq) \rightleftharpoons \mathbf{Cu(OH)_2(s)} + 6H_2O\,(l)$ **---- eqm (1)**

blue solution **blue precipitate**

When <u>excess</u> aqueous NH_3 is added, **<u>ligand exchange</u>** occurs to form a deep blue solution.

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

deep blue solution

The formation of $[Cu(NH_3)_4(H_2O)_2]^{2+}$ decreases the concentration of $[Cu(H_2O)_6]^{2+}$ causing **<u>position of equilibrium (1) to shift to the left in order to replenish $[Cu(H_2O)_6]^{2+}$</u>**. Hence, blue ppt of $Cu(OH)_2$ dissolves, forming the deep blue solution.

(d) Copper metal is obtained from copper ore and is widely used in electrical wiring. To prevent short circuit, the metal used must have high purity. Outline how the impure copper ore is purified industrially to remove impurities such as zinc and silver metals.

[3]

Impure copper ore can be purified using electrolysis. The impure copper is placed at the anode, while pure copper is used as the cathode. The electrolyte used is aqueous $CuSO_4$.

When an electric current is applied, copper at the **anode (+)**, together with Zn are oxidised to their ions owing to their relatively less positive $E^\ominus$ values. Hence, Cu^{2+} and Zn^{2+} then migrate to the cathode / remain in solution.

Ag will not be oxidised as it has a relatively positive $E^\ominus$ values and it falls off the electrode and accumulate at the bottom as anodic sludge.

At the cathode, only Cu^{2+} ions are reduced to Cu, which is deposited on the pure copper electrode, due to its more positive $E^\ominus$.

Zn^{2+} remain as ions in the solution as they do not reduce to metals easily.

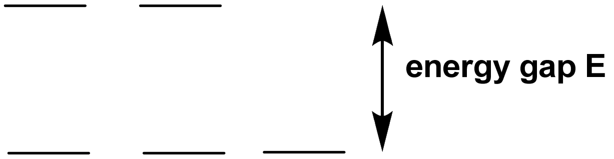
[Total: 20]

5 Iron is an important transition element and the second most abundant metal in Earth's crust. Iron containing compounds have various uses and the element itself can also be found in a number of proteins within living things. Iron and its compounds have been widely researched on as they are relatively cheap and non-toxic.

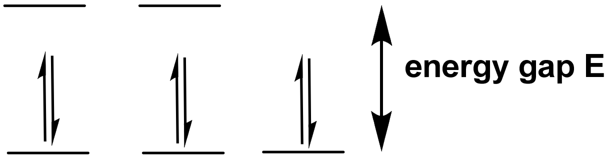
(a) Haemoglobin is a protein found in red blood cells. Within haemoglobin, it contains an Fe^{2+} ion which has an octahedral shape as it is surrounded by five nitrogen-containing ligands and one oxygen-containing ligand, which is H_2O in deoxyhaemoglobin and O_2 in oxyhaemoglobin.

(i) A species with unpaired electrons is paramagnetic and can be attracted by an externally applied magnetic field. On the other hand, a species with no unpaired electrons is diamagnetic and is unaffected by a magnetic field.

Oxyhaemoglobin is found to be diamagnetic. Based on the information provided and using the diagram below, show the electronic distribution of the 3d electrons of Fe^{2+} in oxyhaemoglobin.

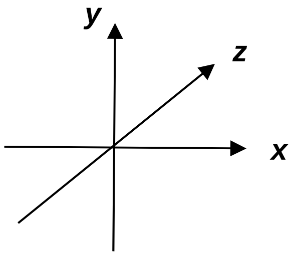


[1]



(ii) In both oxyhaemoglobin and deoxyhaemoglobin, the 3d orbitals are no longer degenerate as they are split into two different energy levels.

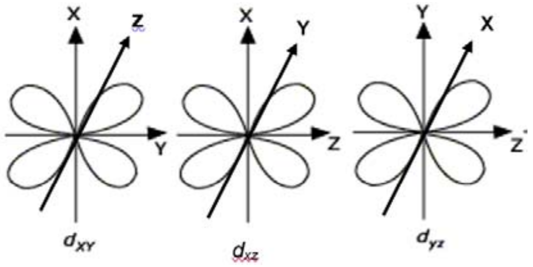
Explain this observation. Using the Cartesian axes like those shown below, draw a fully labelled diagram of one of the 3d orbitals which has a lower energy level.



[3]

In octahedral complexes, the lone pair of electrons on the 6 ligands **approach Fe^{2+} along the axes**. This results in **electronic repulsion**, which causes the energy level of $3d_{x2-y2}$ and $3d_{z2}$ to be higher.

Either one:

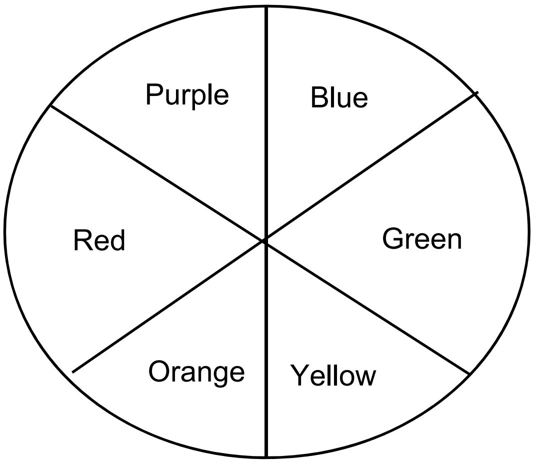


(iii) Explain why oxyhaemoglobin is red. **[2]**

When a **d electron from the lower energy d orbital absorbs light energy (visible light with wavelength corresponding to this energy gap)**, it is **promoted to the higher energy d orbital** and this is d-d transition.

The **red colour seen is complementary to the colour absorbed / red colour is not absorbed**.

(iv) The complementary colours are shown using the following colour wheel.



The wavelength of each colour component in visible light is as provided.

Colour	**Purple**	**Blue**	**Green**	**Yellow**	**Orange**	**Red**
Wavelength / nm	380 - 450	450 - 495	495 - 570	570 - 590	590 - 620	620 – 750

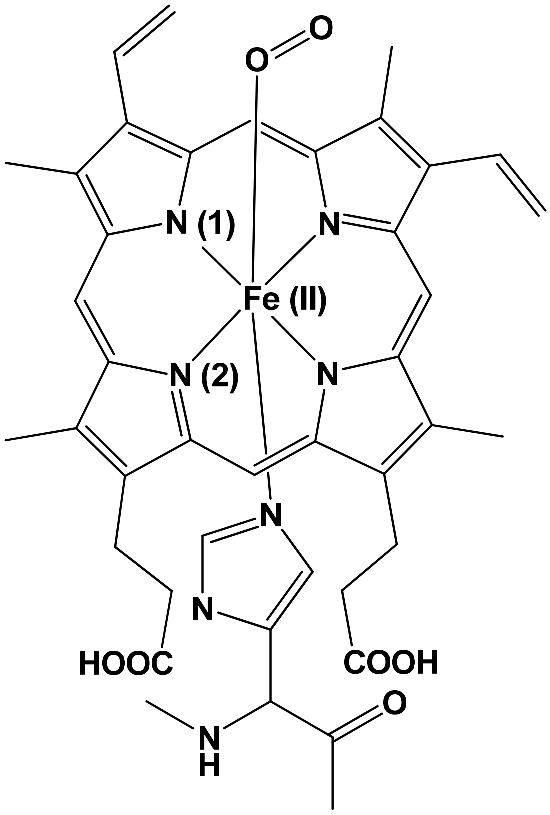
Oxyhaemoglobin is bright red while deoxyhaemoglobin is blue. Given that the wavelength of light is inversely proportional to energy, state and explain if water or oxygen causes a larger energy gap between the 3d orbitals.

[2]

O_2 causes a larger energy gap between the 3d orbitals.

Oxyhaemoglobin absorbs **green colour which is of lower wavelength / higher energy than the orange colour** that deoxyhaemoglobin absorbs.

(v) Fe^{2+} complex in oxyhaemoglobin does not have an overall charge. The structure is as shown.



State the charge around the N atom labelled **(1)** and the bond angle around the N atom labelled **(2)**.

[2]

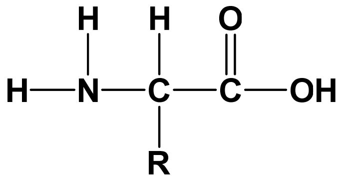
Charge around N(1): 1−

Bond angle around N(2): 120□

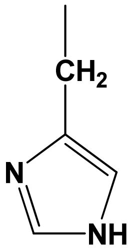
(vi) Besides Fe^{2+}, Fe^{3+} may also exist in haemoglobin. Explain why Fe can have variable oxidation states in haemoglobin. **[1]**

The **energy of 3d and 4s electrons are close in proximity**. Hence, the electrons in 3d and 4s orbitals may be shared or lost to give variable oxidation states.

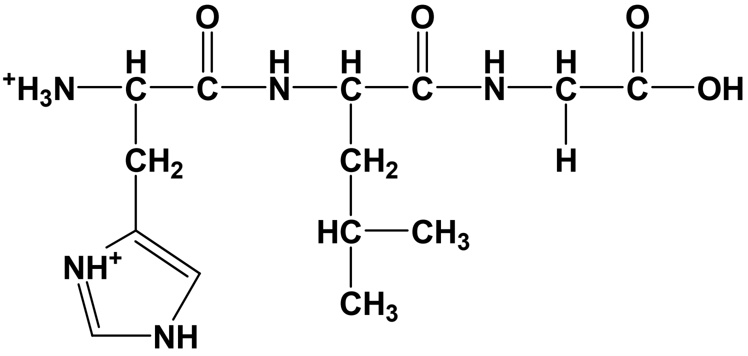
(vii) Each polypeptide chain in haemoglobin is made up of more than 100 amino acid residues. The general structure of an amino acid is as shown below.



In each chain, histidine, leucine and glycine amino acids can be found.

Amino acid	**R group**
Histidine	
Leucine	-CH$_2$CH(CH$_3$)$_2$
Glycine	-H

Draw the structural formula of a tripeptide with the sequence histidine-leucine-glycine at pH 2. **[2]**

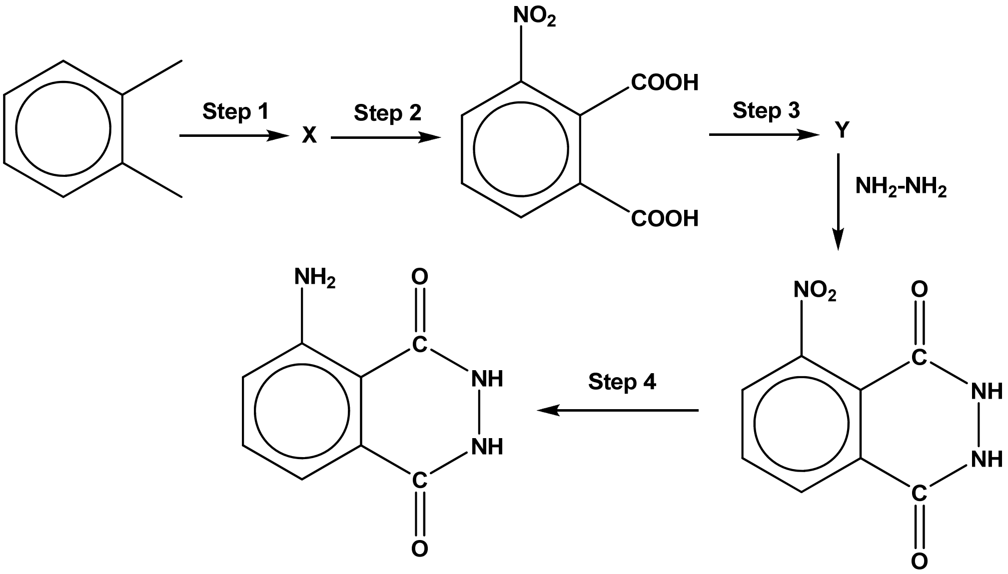


(viii) Haemoglobin can undergo complete hydrolysis non-enzymatically. State the reagents and condition for this to occur. **[1]**

(6 mol dm^{-3}) **concentrated** HC*l* (Any mineral acid), **prolonged heating** / several hours (for 24h)

(b) To detect for the presence of blood in a crime scene, an organic compound named luminol may be used. Luminol uses iron in haemoglobin to catalyse the decomposition of hydrogen peroxide, which eventually leads to a blue glow to indicate the presence of blood.

The synthetic route for luminol is as shown.



Luminol

(i) State the reagents and conditions for **steps 1** to **3**. **[3]**

Step 1: Concentrated sulfuric acid, concentrated nitric acid, < 55 □C

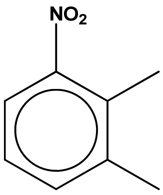
Step 2: $KMnO_4$, H_2SO_4 (aq), heat

Step 3: PCl_5 or $SOCl_2$

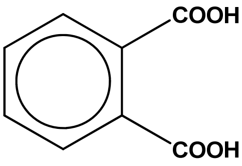
Note: Steps 1 and 2 can be interchangable but temperature > 55°C

(ii) Draw the structures for intermediate products **X** and **Y**. **[2]**

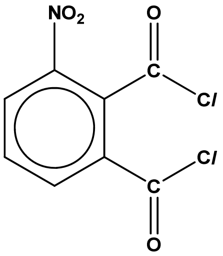
X:



or



Y:



(iii) For **Step 4**, $Na_2S_2O_4$ is commonly used as the reagent.

State the role of $Na_2S_2O_4$. **[1]**

Reducing agent

[Total: 20]