HWA CHONG INSTITUTION
C2 Preliminary Examinations
Higher 2

CANDIDATE NAME		CT GROUP	18S
CENTRE NUMBER		INDEX NUMBER	

CHEMISTRY

Paper 1 Multiple Choice

9729/01

25 September 2019

1 hour

Additional Materials: Multiple Choice Answer Sheet
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write in soft pencil.

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

Complete the information on the Answer Sheet as shown below.

1. Enter your **NAME** (as in NRIC).

2. Enter the **PAPER NUMBER**.

3. Enter your **CT GROUP**.

4. Enter your **NRIC NUMBER** or **FIN Number**

5. Now **SHADE** the corresponding circles in the grid for **EACH DIGIT** or **LETTER**

USE PENCIL ONLY
FOR ALL ENTRIES ON THIS SHEET
0 1 2 3 4 5 6 7

NRIC / FIN

There are **30** 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 Answer Sheet.
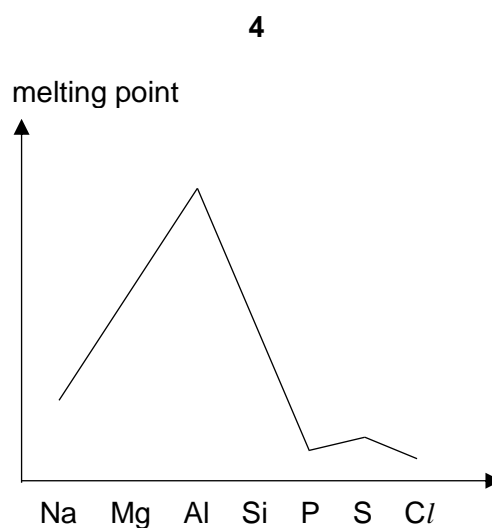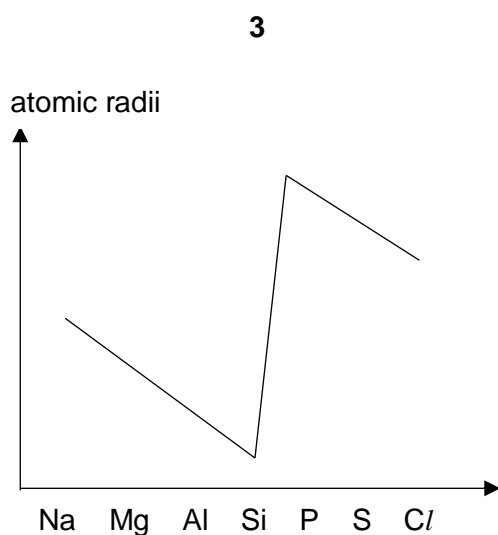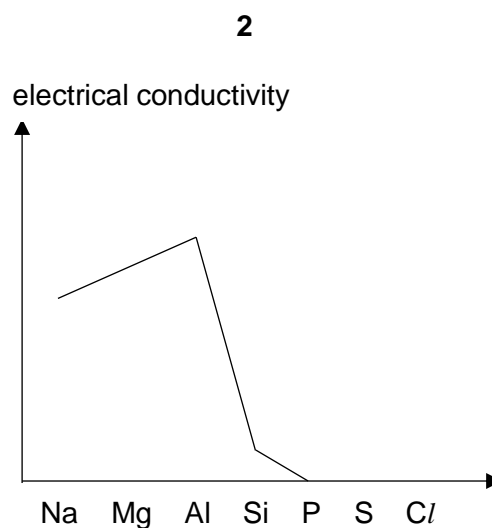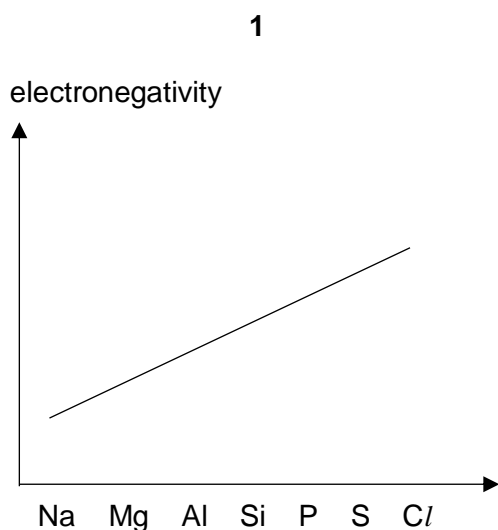
Read the instructions on the Answer Sheet very carefully.

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

Any rough working should be done in this booklet.

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

This document consists of **12** printed pages.

1   Which statement about relative atomic mass is correct?

   A   It is the average of the masses of all the isotopes of that element.

   B   It is the sum of the relative masses of the neutrons and protons in each atom.

   C   It is the ratio of the average mass of one atom of an element to the mass of one ^1H atom.

   D   It is the ratio of the mass of one mole of atoms of an element to one-twelfth the mass of one mole of ^{12}C atoms.

2   Which of the graphs correctly represent the trends in some properties of the Period 3 elements?

1

electronegativity

Na   Mg   Al   Si   P   S   C*l*

2

electrical conductivity

Na   Mg   Al   Si   P   S   C*l*

3

atomic radii

Na   Mg   Al   Si   P   S   C*l*

4

melting point

Na   Mg   Al   Si   P   S   C*l*

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

3   Which of the following correctly describes the structure and bonding present in the solid lattice of the substances given?

	substance	structure	bonding
A	ice	giant covalent	covalent bonding + hydrogen bonding
B	iodine	simple covalent	covalent bonding + permanent dipoles
C	aluminium chloride	giant ionic	ionic bonding + permanent dipoles
D	graphite	giant covalent	covalent bonding + dispersion forces

4   In which of the following pairs is the bond angle in the first species smaller than that in the second species?

   A NH_4^+ XeF_4

   B NF_3 NH_3

   C NO_2^+ SO_2

   D BCl_3 PCl_3

5   A container with a volume of 420 m³ with an internal pressure of 1 bar at 293 K was joined to two containers as shown below. One of them has a volume of 13 m³ with a vacuum within, while the other has a volume of 75.5 m³ with an internal pressure of 2 bar and a temperature of 273 K.
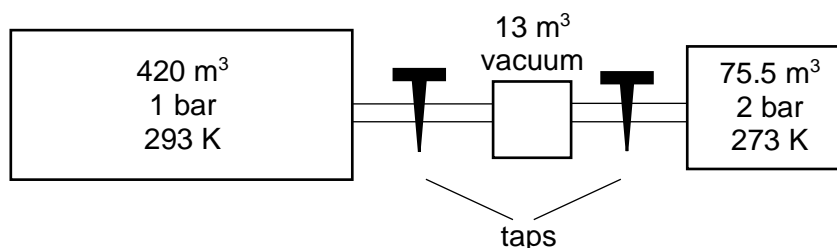
   What is the final pressure, in bar, in the combined containers when the taps were opened and the temperature allowed to equilibrate to 298 K?

   A   0.84   **B**   1.12   **C**   1.16   **D**   1.19

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

Sodium percarbonate, $(Na_2CO_3)_x \cdot y(H_2O_2)$, is an oxidising agent in some home and laundry cleaning products.

10.0 cm³ of 0.100 mol dm⁻³ sodium percarbonate releases 45.4 cm³ of carbon dioxide at s.t.p. on acidification.

An identical sample, on titration with 0.05 mol dm⁻³ $KMnO_4$, requires 24.0 cm³ before the first pink colour appears. $KMnO_4$ reacts with H_2O_2 in the mole ratio 2 : 5.

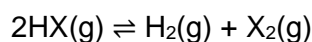What is the ratio $\dfrac{y}{x}$?

**A** $\dfrac{1}{3}$ **B** $\dfrac{2}{3}$ **C** $\dfrac{3}{2}$ **D** $\dfrac{3}{1}$

7 Which statement correctly explains why the change in Gibbs' free energy of the reaction below is relatively constant when the temperature changes?

$$2HX(g) \rightleftharpoons H_2(g) + X_2(g)$$

A ΔS is almost zero for all temperatures in which the reactants and products are gases.

B The equilibrium constant is not affected by a temperature change.

C ΔH and ΔS do not change with temperature, hence ΔG remains constant.

D The equilibrium position will shift in such a way to offset the changes in temperature.

8 The conversion of diamond into graphite is an exothermic reaction.

$$C(\text{diamond}) \rightarrow C(\text{graphite}) \qquad \begin{array}{l} \Delta H < 0 \\ \Delta G < 0 \end{array}$$
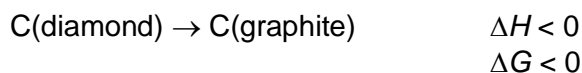
Which statements are correct?

1 The magnitude of the enthalpy change of atomisation of graphite is greater than that for diamond.

2 The magnitude of the enthalpy change of combustion of graphite is greater than that for diamond.

3 The bond energy of the C–C bonds in graphite is greater than that for diamond.

4 The conversion of diamond to graphite does not take place readily due to the high activation energy.

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

9 Thorium-234 undergoes radioactive decay to form protactinium-234 by emitting a beta particle. This radioactive decay is a first order reaction with a half-life of 24.1 hours.

A rock sample contains a 2 : 3 molar proportion of thorium-234 to protactinium-234. How many hours has the radioactive decay taken place if the sample was initially protactinium-234 free?

A 14.1 **B** 24.1 **C** 31.9 **D** 60.3

10 Which suggested mechanism is consistent with the experimentally determined rate equation?

|	rate equation	suggested mechanism	
1	rate = k[NO]^2[H$_2$]	2NO + H$_2 \rightarrow$ N$_2$O + H$_2$O	slow
		N$_2$O + H$_2 \rightarrow$ N$_2$ + H$_2$O	fast
2	rate = k[O$_2$][N$_2$O$_2$]	2NO $\rightarrow$ N$_2$O$_2$	fast
		N$_2$O$_2$ + O$_2 \rightarrow$ 2NO$_2$	slow
3	rate = k[O$_3$][Cl]	Cl + O$_3 \rightarrow$ OCl + O$_2$	slow
		OCl + O$_3 \rightarrow$ 2O$_2$ + Cl	fast

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

11 The key stage in the manufacture of sulfuric acid is the reaction between sulfur dioxide and oxygen to form sulfur trioxide.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$
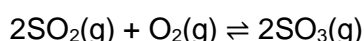
When 0.50 mol of SO$_2$ and 1.00 mol of O$_2$ were reacted together in a container of volume 0.5 dm^3, 0.30 mol of SO$_3$ was present in the equilibrium mixture.

What is the numerical value of the equilibrium constant, K_c, for the equilibrium reaction below?

$$SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons SO_3(g)$$
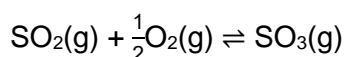
**A** 0.66 **B** 1.15 **C** 1.32 **D** 1.63

12 Which statement about the effect of adding a catalyst to a reversible reaction is correct?

A It increases the yield of product in the reaction.

B It increases the rate constant for the forward reaction.

C It increases the equilibrium constant of the forward reaction.

D It increases the activation energy of the reverse reaction.

13 Which graphs correctly show how the values of pH, α (degree of dissociation) and K_a for a weak acid vary with dilution at constant temperature?

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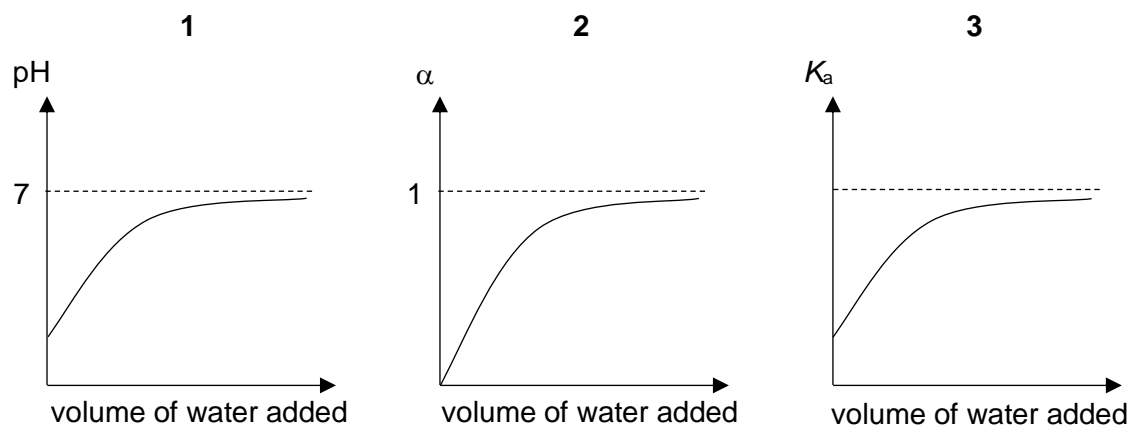
A 1 only	**B** 1 and 2	**C** 2 and 3	**D** 1, 2 and 3

14 Aluminium objects are surface treated by means of anodisation to increase the thickness of the corrosion resistant oxide layer.

Which factor will affect the mass of the oxide coating in the anodisation process?

A size of the current

B size of the cathode

C concentration of electrolyte

D surface area of the aluminium object

15 Compound V has the molecular formula $C_6H_{14}O$. V has an aliphatic carbon skeleton that is branched and contains a secondary alcohol functional group.

How many constitutional isomers fit this description of V?

A 2	**B** 3	**C** 4	**D** 5

16 Tamoxifen is an important drug used in the prevention of breast cancer. The first two steps in the synthesis of Tamoxifen is shown below.
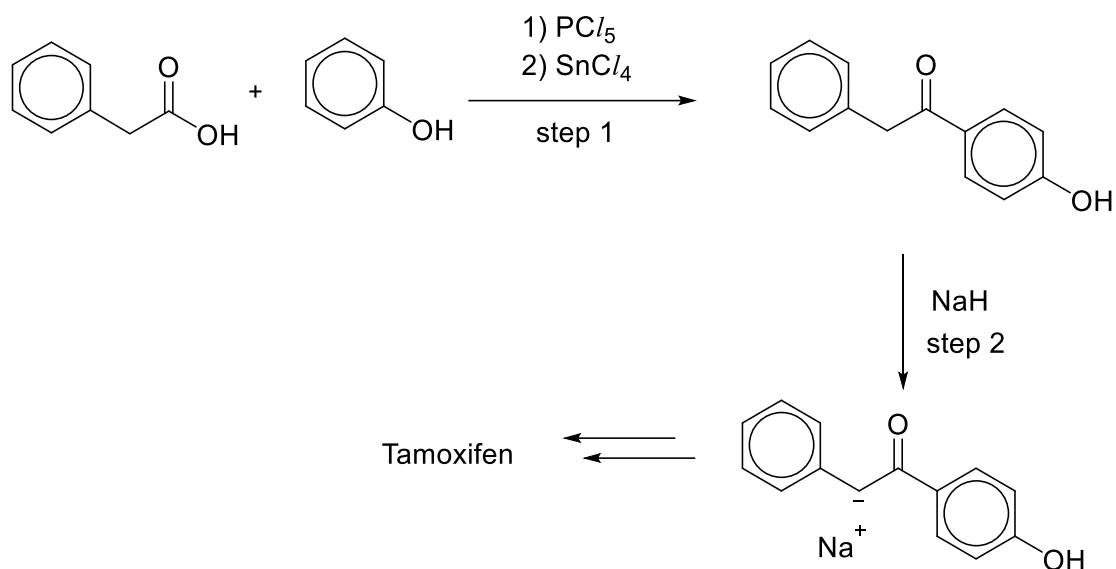
Which of the following correctly describes the type of reaction in each step in the above synthetic pathway?

	step 1	step 2
A	nucleophilic addition	acid-base
B	condensation	elimination
C	electrophilic substitution	elimination
D	electrophilic substitution	acid-base

17 Compound W is a cyclic oligopeptide.

W
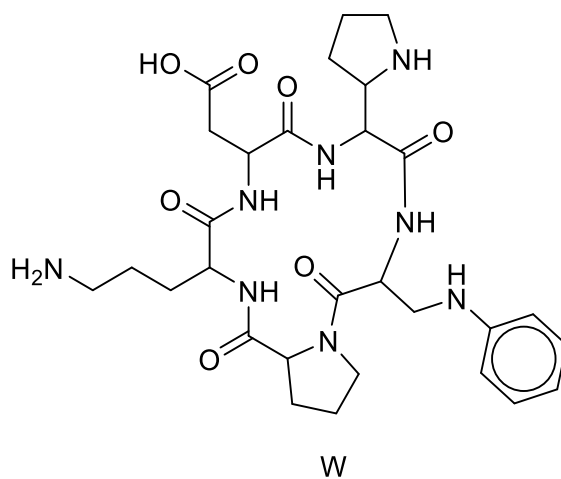
How many amide linkages exist in compound W?

A 5 **B** 6 **C** 7 **D** 8

18 When heated with chlorine, 2,2-dimethylbutane undergoes free radical substitution. In a propagation step, the free radical X• is formed by the loss of one hydrogen atom.
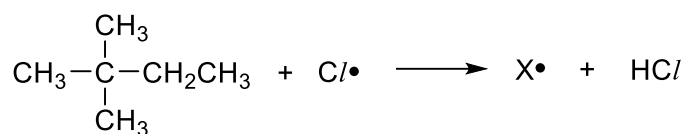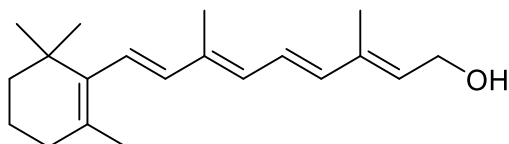
$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2CH_3 \ + \ Cl• \ \longrightarrow \ X• \ + \ HCl$$

How many different forms of X• are theoretically possible?

A 2 **B** 3 **C** 4 **D** 5

19 When retinol reacts completely with cold alkaline $KMnO_4$, it forms product Y. How many stereoisomers do retinol and Y have?

retinol

	retinol	Y
A	2^4	2^8
B	2^5	2^8
C	2^4	2^{10}
D	2^5	2^{10}

20 Which compounds may be a possible product of the reaction of $C_6H_5OCOCHBrCH_3$ with sodium hydroxide under different conditions?

1 $C_6H_5CO_2Na$

2 $CH_3CH(OH)CO_2Na$

3 $C_6H_5OCOCH=CH_2$

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

21 3-methylbutan-2-ol is treated with alkaline aqueous iodine. The mixture of products is then acidified.

Which compound is present in the final mixture of the products?

A propanoic acid

B butanoic acid

C 3-methylbutanoic acid

D 2-methylpropanoic acid

22 1 mol of compound Z reacts with sodium hydroxide to produce 2 mol of water.

Which compound could Z be?

A HO⌒⌒OH

B

C

D
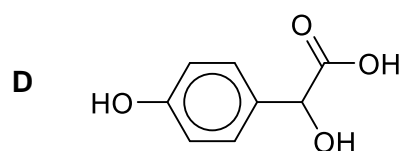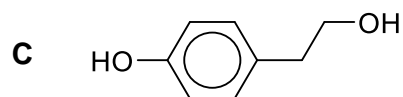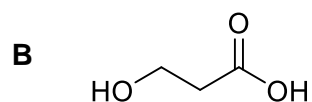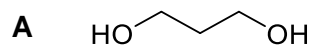
23 Acetoacetic acid can be synthesised in a two-step process starting from R.

R ⟶ S ⟶

acetoacetic acid
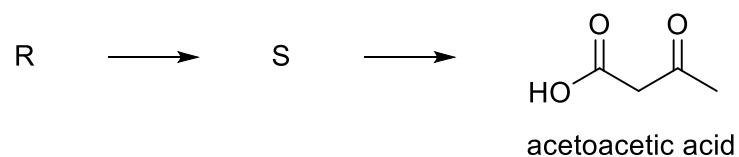
What could be the structure of R?

1 HO⌒⌒

2

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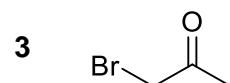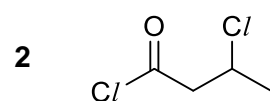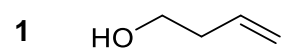
| **A** | 1 only | **B** | 1 and 2 | **C** | 2 and 3 | **D** | 1, 2 and 3 |

24   Which is the correct product formed when P undergoes reduction using excess hydrogen gas and nickel as catalyst?

P

A

B

C

D
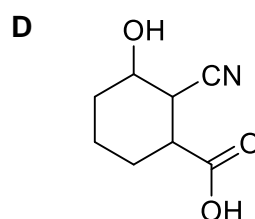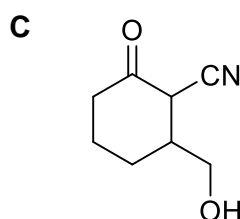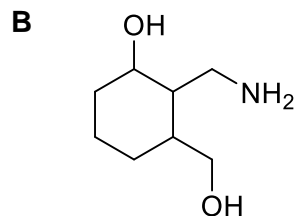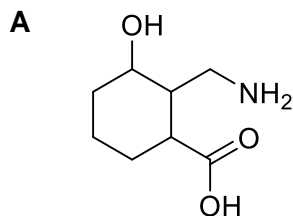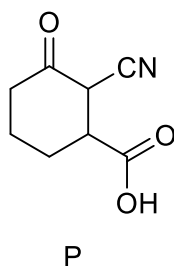
25   Esters can be reduced by $LiAlH_4$ in dry ether to give two alcohols as shown below.
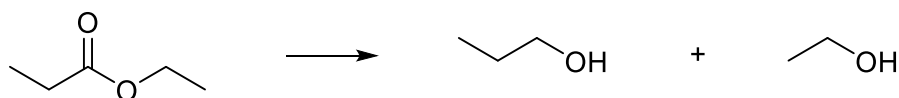
What are the possible products formed when the following compound is reacted with $LiAlH_4$ in dry ether?

1

2

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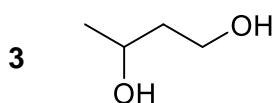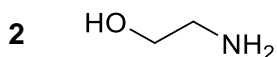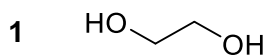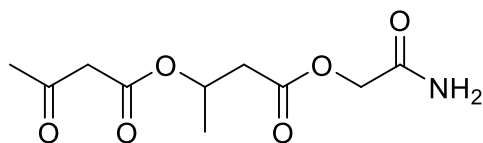
A   3 only   B   1 and 2   C   2 and 3   D   1, 2 and 3

26 Asparagine is required for the development and function of the brain.
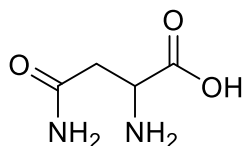
asparagine

Which statements about its structure are correct?

1 Asparagine exists in aqueous solution as a zwitterion.

2 The side chain ($-CH_2CONH_2$) of asparagine is neutral.

3 When hot dilute H_2SO_4 is added to asparagine, a gas which turns damp red litmus paper blue is evolved.

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

27 What is the correct order of the pH of the resulting solutions when the oxides below are added to water?

lowest pH ⟶ highest pH

A	SO_3	SiO_2	MgO	Na_2O
B	Na_2O	MgO	SiO_2	SO_3
C	MgO	SiO_2	SO_3	Na_2O
D	SO_3	Na_2O	MgO	SiO_2

28 The electrical conductivities of two compounds, T and U, are shown in the table below.

	T	U
conductivity of the compound in the liquid state	good	does not conduct
conductivity of the mixture obtained by adding the compound to water	good	good

What could compounds T and U be?

	T	U
A	Al_2O_3	$SiCl_4$
B	NaF	Al_2O_3
C	NaF	$SiCl_4$
D	$SiCl_4$	Al_2O_3

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

$Na_4Fe(CN)_6$ can be oxidised to $Na_3Fe(CN)_6$.

Which reagent can be used to carry out this oxidation?

    A $SO_2(g)$

    B $NO_2(g)$

    C $Cu^{2+}(aq)$

    D $I_2(aq)$

30   The rate of reaction between iodide and peroxodisulfate(VI) ions is increased by the presence of small concentrations of $Fe^{2+}(aq)$.

$$S_2O_8{}^{2-}(aq) + 2I^-(aq) \rightarrow 2SO_4{}^{2-}(aq) + I_2(aq)$$
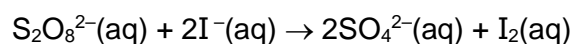
Which property of iron allows it to act as a homogeneous catalyst?

    A   high charge density

    B   partially filled d subshell

    C   variable oxidation states

    D   ability to form complex ions

END OF PAPER

Paper 1

ANSWERS:

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

Comments

1   D

The definition for atomic mass is the ratio of the average mass of one atom of an element to one-twelfth the mass of one atom of ^{12}C. In option **D**, the mass of one mole of atoms of an element has already taken into account all the isotopes and their relative abundances.

2   A

The electronegativity increases across Period 3 as the effective nuclear charge increases.

The electrical conductivity of the metals Na to Al increases while Si is a semiconductor and the non-metals P, S and Cl are non-conductors.

The atomic radii across Period 3 shows a generally decreasing trend due to the increase in effective nuclear charge across the period.

The melting point increases from Na to Al on account of the increasing metallic bonding strength; the trend peaks at Si which has a giant covalent structure with extensive strong covalent bonding, before showing a decreasing trend for the simple covalent compounds which only have weak dispersion forces between molecules.

3   D

Ice has a simple covalent structure. There is hydrogen bonding between water molecules, and covalent bonding between atoms of H and O in each molecule of water.

Iodine has a simple covalent structure. There are dispersion forces between iodine molecules, and covalent bonding between atoms of iodine in each molecule of iodine.

Aluminium chloride has an ionic lattice structure with a large amount of covalency in the solid state at room temperature. Its structure becomes simple covalent just below its melting point resulting in dispersion forces between Al_2Cl_6 molecules. Hence permanent dipole interactions are not found in the solid state.

Graphite has a giant covalent structure with dispersion forces holding the sheets of carbon atoms together.

4   B

Species	NH_4^+	XeF_4
Shape	Tetrahedral	Square planar
Bond Angle	109.5º	90º
Species	NF_3	NH_3
Shape	Trigonal pyramidal	Trigonal pyramidal
Bond Angle	102º	107º
	F is more electronegative than N and so the electron cloud of the N–F bond is distorted towards F. This causes the electron density about N to decrease. Thus, bond pair-bond pair repulsion is weaker around the central N atom in NF_3 than in NH_3. Hence, bond angle in NF_3 is smaller.	
Species	NO_2^+	SO_2
Shape	Linear	Bent
Bond Angle	180º	<120º
Species	BCl_3	PCl_3
Shape	Trigonal planar	Trigonal pyramidal
Bond Angle	120º	107º

5   C

Since the number of moles of gas in the three containers did not change before and after the taps are opened, the number of moles of gas found in the individual containers before and after the taps are opened should be the same.

$n_{\text{gas in first container}} + n_{\text{gas in second container}} + n_{\text{gas in third container}} = n_{\text{gas in overall container}}$

Note that there is no gas in the second container since it contains a vacuum. Thus it is not included in the calculation of the total number of moles of gas.

$$\frac{P_1V_1}{T_1} + \frac{P_2V_2}{T_2} = \frac{P_{final} \times V_{final}}{T_{final}}$$

$$\frac{1 \times 420}{293} + \frac{2 \times 75.5}{273} = \frac{P_{final} \times (420 + 75.5 + 13)}{298}$$

$$P_{final} = 1.16 \text{ bar}$$

6   C

No. of moles of sodium percarbonate = $10.0 \times 10^{-3} \times 0.100 = 0.00100$

1 mole of sodium percarbonate produces x moles of CO_2.
No. of moles of carbon dioxide = $48 \div 24000 = 0.00200$

$$x = \frac{0.00200}{0.00100} = 2$$

No. of moles of $KMnO_4$ = $0.0500 \times 24.0 \times 10^{-3} = 0.00120$
No. of moles of H_2O_2 = $0.00120 \times 5 \div 2 = 0.00300$

1 mole of sodium percarbonate produces y moles of H_2O_2.

$$y = \frac{0.00300}{0.00100} = 3$$

Ratio of $y : x = 3 : 2$

7   A

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

In general, ΔH & ΔS hardly changes with temperature unless there is a change in the physical state of the reactants or products. Normally, ΔG is dependent on the temperature as seen from the equation above.

For this particular reaction, ΔS is almost 0 regardless of the temperature since there are equal number of moles of gas on both sides of the arrow. Since $\Delta S \approx 0$, therefore $T\Delta S \approx 0$ and so $\Delta G \approx \Delta H$. Thus the ΔG of the reaction becomes relatively independent of temperature.

Note also that the equilibrium constant, K, is always affected by temperature unless $\Delta H = 0$.

8   B

The diagram below shows that the magnitude of the ΔH_{atom} for graphite is larger than that for diamond but the magnitude of ΔH_c for graphite is smaller than that for diamond.
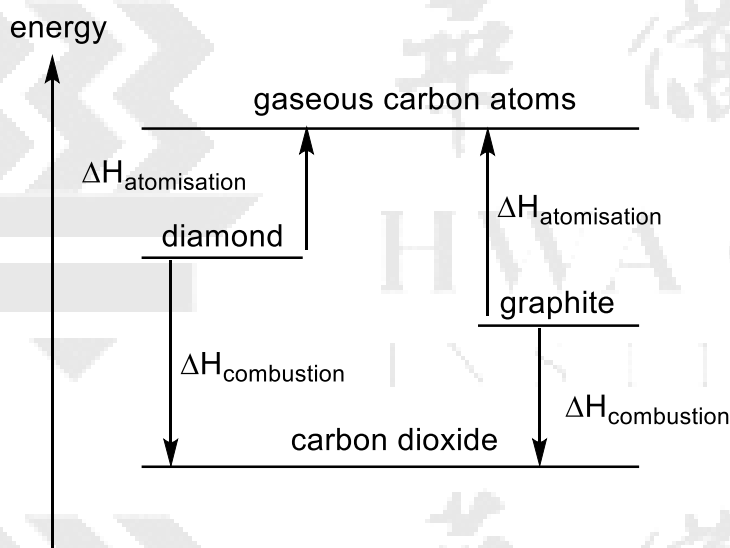
In graphite, each C atom has a 2p orbital containing one electron that is not used in the formation of C–C bonds. The 2p orbitals can overlap with each other to form a two-dimensional delocalised π bonding system spreading throughout the whole sheet of atoms. Thus, the C–C bonds in graphite have partial double bond character. Thus the C–C bonds in graphite are stronger than those in diamond. This is also evident from the larger magnitude of ΔH_{atom} of graphite.

The rearrangement of atoms in a tetrahedral structure of carbon atoms in diamond to the trigonal planar structure of carbon atoms in graphite requires a lot of energy as many strong covalent bonds are broken. This constitutes a very high activation energy such that conversion of diamond to graphite is kinetically unfavorable despite the process having a negative ΔG.

9   C

The number of half-lives that it takes rock sample to decay to a ratio of 2:3 for thorium-234 to protactinium-234 is calculated as follows. Hence fraction of thorium-234 in the rock sample $= \frac{2}{2+3} = \frac{2}{5}$

$$1 \times \left(\frac{1}{2}\right)^n = \frac{2}{5}$$

n = 1.32 half-lives

where 1 = amount of thorium-234 at the start, and $\frac{2}{5}$ is the amount of thorium at the end of the time period of radioactive decay.

Time taken = 1.322 x 24.1 = 31.9 hr

In this question, the strategy is to recognize that more than one half-life, but less than two half-lives, have passed. So the logical answer would lie between 24.1 h and 48.2 h.

10   B

In order to find the correct rate equation based on the suggested reaction mechanisms, the following steps must be taken.

The species found in the rate equation should only include the reactants and not any of the intermediates formed in the mechanism. It is helpful to write down the overall chemical equation so that the reactants are not confused with any of the intermediates.

The stoichiometry of each reactant in the slow step of a mechanism is reflected as the order of reaction of that reactant in the overall rate equation.

1. Overall equation: $2NO + 2H_2 \rightarrow N_2 + 2H_2O$
The reactants in the slow step consist of those found in the overall equation. This means that two NO molecules and one H_2 molecule are involved in the rate determining step. The rate equation should reflect this. Hence the rate equation should be rate = $k[NO]^2[H_2]$.

2. Overall equation: $2NO + O_2 \rightarrow 2NO_2$
The reactants in the slow step contain the intermediate N_2O_2 and reactant O_2. Hence the rate law based on the slow step would look like this.

rate = $k[N_2O_2][O_2]$ --- equation 1

However, N_2O_2 should not appear in the rate equation. We need to substitute $[N_2O_2]$ with the concentration of reactants that produced this intermediate into equation 1, giving rate = $k[NO_2]^2[O_2]$. Although the rate equation seems to indicate a termolecular reaction mechanism, the suggested mechanism shows otherwise.

3. Overall equation $2O_3 \rightarrow 3O_2$
In the slow step, one molecule of O_3 reacts with one atom of Cl. Hence the overall rate equation should be rate = $k[O_3][Cl]$. The species Cl is a homogenous catalyst since it is used up in step one and regenerated in step 2. It should appear in the rate equation as it affects the rate of reaction even if it does not appear in the overall equation.

11   B

	2SO$_3$ (g)	+	O$_2$ (g)	$\rightleftharpoons$	2SO$_3$ (g)
I / mol	0.50		1.00		–
C / mol	– 0.30		– 0.15		+ 0.30
E / mol	0.20		0.85		0.30

The equilibrium constant expression for the formation of SO_3 is written as follows:

$$K=\frac{P^2_{SO_3}}{P^2_{SO_2}P_{O_2}}$$

$$K=\frac{\left(\frac{0.30}{0.5}\right)^2}{\left(\frac{0.20}{0.5}\right)^2\left(\frac{0.85}{0.5}\right)}=\frac{45}{34}$$

The equilibrium constant expression for the equation $SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons SO_3(g)$ is written as follows:

$$K_c = \frac{P_{SO_3}}{P_{SO_2}(P_{O_2})^{1/2}}$$

$$K_c = \sqrt{K} = 1.15$$

12   B

Adding a catalyst to a reversible reaction increases the rate of the forward and backward reactions equally. The equilibrium position is not affected, so the yield of the reaction is not affected by the catalysis. The catalyst merely causes equilibrium to be reached at a faster rate. The catalyst does **not** lower the activation energy of the <u>original</u> reaction pathway, but provides an <u>alternative reaction pathway with a lower activation energy for both the forward and backward reactions</u>.

13   B

See Topic 15, page 14. The graph for α vs V should be similar to that for pH vs V. As the volume of acid increases due to adding more water to dilute the acid, the pH will keep increasing while the extent of dissociation increases to almost 1 (i.e. almost complete dissociation). The pH should not exceed 7, which is the pH of water. K_a only changes with temperature.

14   A

The chemical equation for the oxidation process at the anode is given as follows:

$$2Al(s) + 3H_2O(l) \rightarrow Al_2O_3(s) + 6H^+(aq) + 6e^-$$

$Q = I \times t = n_e \times F$
$n_e = It/F$ ------ (1)
$n_e : n_{Al_2O_3} = 6 : 1$ from the equation. Hence, $n_e = 6 \times n_{Al_2O_3}$ ------ (2)
Therefore, substituting (2) into (1): $n_{Al_2O_3} = It/(6F)$
mass of $Al_2O_3 = It/(6F) \times M_r(Al_2O_3)$

As can be seen, the mass of Al_2O_3 produced is <u>only</u> dependent on the current that passes through the circuit, and the time in which the current has passed through.

15   C

For the molecular formula $C_6H_{14}O$ to be a secondary alcohol with a branched chain, we should start with a five-carbon backbone and the –OH group in the 2nd position first, then in the 3rd position. Then explore a four-carbon backbone and place the –OH group in the 2nd position. Hence, there are a total of 4 constitutional isomers.
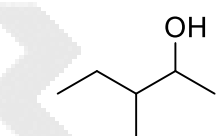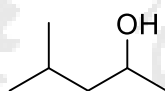
3-methylpentan-2-ol   4-methylpentan-2-ol   2-methylpentan-3-ol
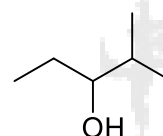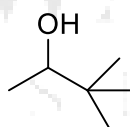
3,3-dimethylbutan-2-ol

16   D

Step 1 involves the attack of the electron-deficient C atom on the C=O group of the phenylethanoic acid (the electrophile) on the benzene ring of phenol. The electrophile substitutes the H atom on the benzene ring of phenol. Hence reaction 1 is an electrophilic substitution.

In **Step 2**, NaH provides the H$^-$ anion, which abstracts a H$^+$ from the carbon next to the C=O group. This is an acid-base reaction with the ketone acting as the acid since it donates a H$^+$ ion, while the H$^-$ acts as the base in receiving the H$^+$.
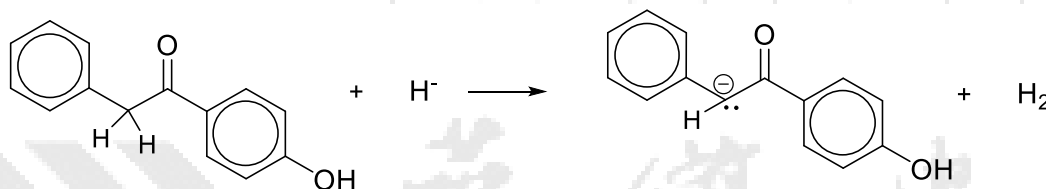
17   A

Identify the alpha-carbons in the backbone of the oligopeptide (in *). You can then easily identify the amide linkages in compound W (circled below). If you are confused as to what is an amide, refer to the table below.

Primary amides	Substituted amides	

* alpha carbon
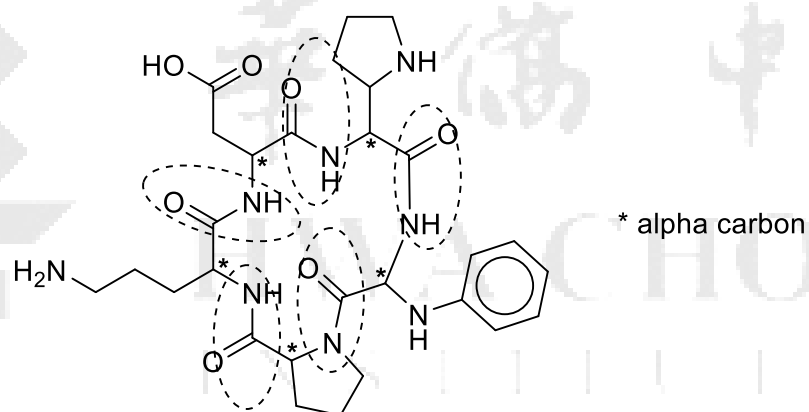
18   B

There are three different types of environments in which the hydrogens in 2,2-dimethylbutane are in, which are circled below.
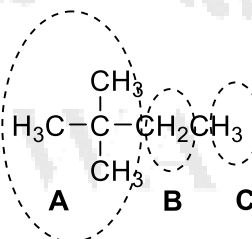
Hence, the 3 different radicals you can obtain from abstracting each type of hydrogen respectively are:
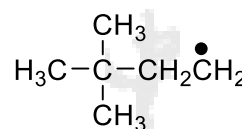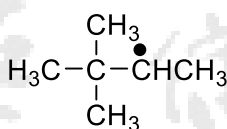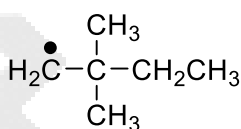
19   C

The C=C in retinol (except that in the cyclic ring) will exhibit cis-trans isomerism, hence 2^4. After mild oxidation to form the diol, all 5 C=C will undergo addition and give 10 chiral carbons, hence 2^{10}.

retinol

Y
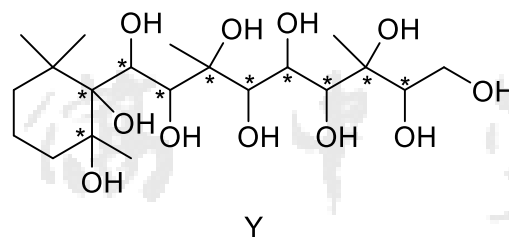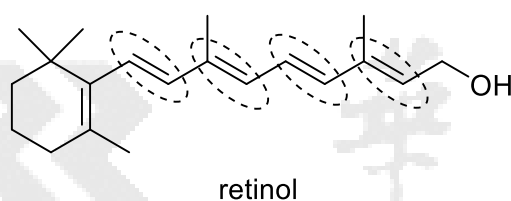
20   C

The bromoalkane undergoes nucleophilic substitution and the ester group undergoes alkaline hydrolysis with hot NaOH(aq).
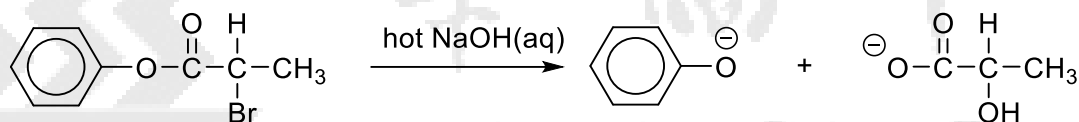
(option 2)

Bromoalkane can undergo elimination with hot ethanolic NaOH.
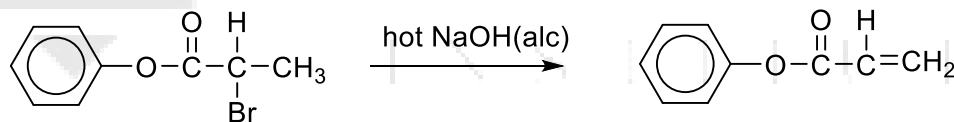
(option 3)

There are other possible products that can form from the reaction above, but they are not in the options provided. Option 1 will not be formed no matter what as no reaction would yield a benzoate ion as a possible product.

21   D

Identify the presence of $CH_3CH(OH)-$ group in the alcohol. The products formed after acidification are the carboxylic acid below and iodine.

2-methylpropanoic acid
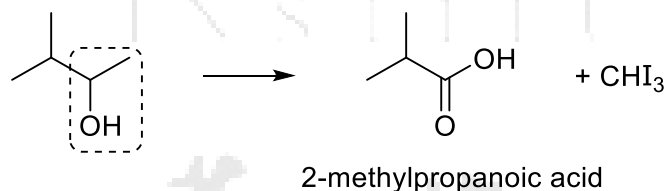
22   D

There must be 2 acidic groups in compound X which undergo acid-base reaction with NaOH(aq) since 2 mol of water is formed. Only phenols and carboxylic acids are strong enough acids to react with NaOH, but alcohols are too weak to donate a proton to NaOH.

23   D

Think of the possible transformations to form a ketone and carboxylic acid.

(3)

nucleophilic substitution with KCN → hydrolysis of nitrile →
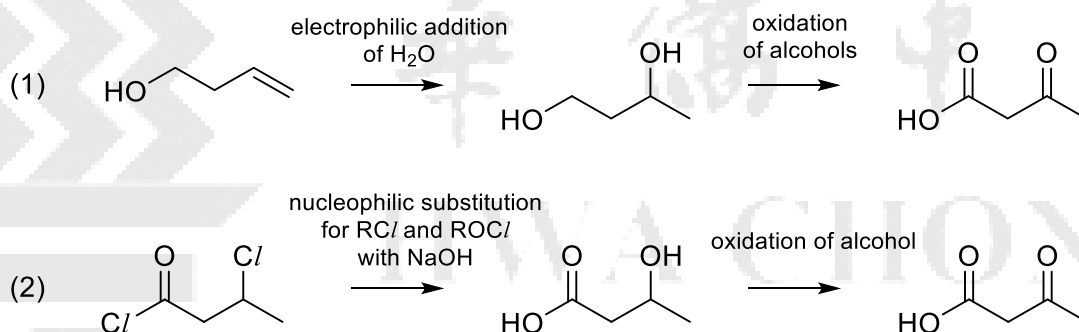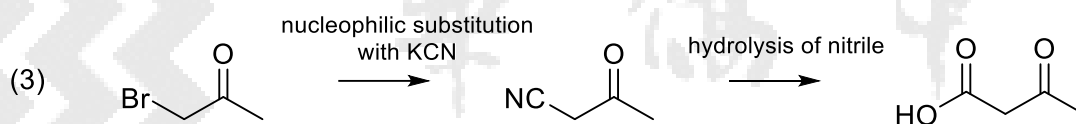
24   A

Ketones and nitriles can be reduced by H_2/Ni but <u>not</u> carboxylic acids. Refer to summary of oxidising and reducing agents on pg 105 of Organic Chemistry (II) lecture notes.

25   C

Apply the same pattern of reduction across the ester bonds to alcohols, bearing in mind that ketones are also reduced to secondary alcohols and amides are reduced to amines. Hence a total of three fragments are produced after the reaction.
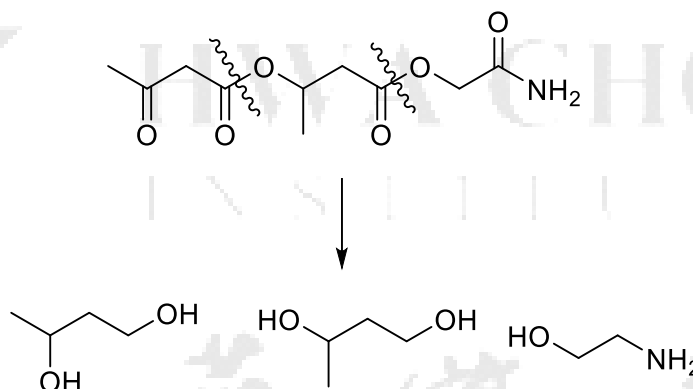
26   B

(1) Asparagine exists in solution as a zwitterion as it undergoes an intramolecular acid-base reaction.

(2) α-amino acids have the amino and carboxyl groups bonded directly to the same α-carbon, differing only in the side chain bonded directly to the α-carbon. The amide functional group in the side chain is neutral.
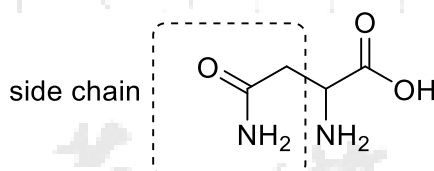
(3) The side chain of asparagine will undergo acidic hydrolysis to give the two products below. No ammonia gas is evolved.
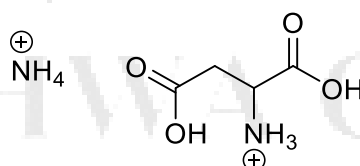
27   A

Ionic oxides tend to be basic in nature, hence higher pH. Covalent oxides tend to be acidic oxides, hence lower pH. SiO_2 is insoluble in water, hence neutral pH. Refer to summary of properties of oxides on pg 15 of Inorganic Chemistry lecture notes.

28   C

Al_2O_3 is an inorganic ionic compound, but is insoluble in water, hence it shouldn't conduct electricity when dissolved in water. When molten, however, its ions are mobile and it will be able to conduct electricity.

$SiCl_4$ exists as simple discrete covalent molecules and cannot conduct electricity. However, it undergoes complete hydrolysis in water to give HCl(aq), which dissociates to give H^+ and Cl^- ions which are mobile charge carriers.

NaF is an inorganic ionic compound, dissolving in water to give Na^+ and F^- ions, which are mobile charge carriers.

29   D

$E^\ominus ([Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}) = +0.36V$
To oxidise $[Fe(CN)_6]^{4-}$, we need to find an oxidising reagent (which can be reduced) and whose $E^\ominus$ is more positive than +0.36V.

In your data booklet, SO_2 and NO_2 are both reducing agents as they can only be oxidized (found on right hand side of half-equations), hence both cannot be used. Cu^{2+} and I_2 are both oxidising agents, and their $E^\ominus$ values are +0.34V and +0.54V respectively, hence I_2 is the only one which can be used.

30   C

A homogeneous catalyst operates in the same phase as the reactants. Iron exhibits variable oxidation states which allows it to perform its role.
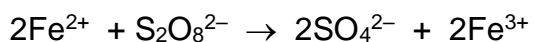
$2Fe^{2+} + S_2O_8^{2-} \rightarrow 2SO_4^{2-} + 2Fe^{3+}$	$E^\ominus_{cell} = 2.01 - 0.77 = +1.24$ V
$2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2$	$E^\ominus_{cell} = 0.77 - 0.54 = +0.23$ V

CANDIDATE NAME		CT GROUP	18S

CENTRE NUMBER		INDEX NUMBER	

CHEMISTRY 9729/02

Paper 2 Structured Questions

18 September 2019

2 hours

Candidates answer on the Question Paper

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your **name**, **CT group, centre number** and **index number** clearly in the spaces above.

Write in dark blue or black pen.

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

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

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

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

A Data Booklet is provided.

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

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

For Examiner's Use	
1	**/ 17**
2	**/ 13**
3	**/ 22**
4	**/ 23**
s.f.	
units	
Total	**/ 75**

Calculator Model:

This document consists of **16** printed pages.

1 (a) Butanone can be converted to compound **C** via the following series of reactions.

butanone → step 1 → **A** (C$_5$H$_9$NO) → LiA/H$_4$ / step 2 → **B** → step 3 → **C** (C$_8$H$_{13}$NO$_3$)
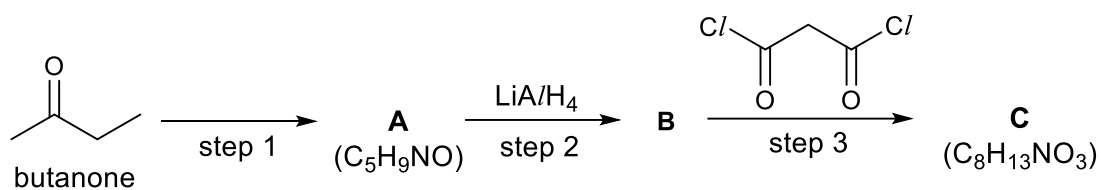
(i) Suggest the reagents and conditions for step 1.

.... [1]

(ii) In the boxes below, draw the structures of compounds **A**, **B** and **C**.

A	**B**
C	

[3]

(b) 2-iodobutane is converted to its corresponding alcohol by heating with aqueous sodium hydroxide.
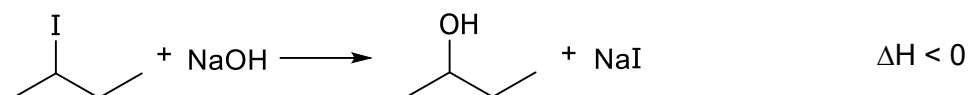
The rate equation is:

$$\text{rate} = k[\text{2-iodobutane}][\text{NaOH}]$$

(i) Describe the mechanism of this reaction. In your answer you should show all charges and lone pairs and show the movement of electrons by curly arrows.

[3]

(ii) Draw a fully labelled reaction pathway diagram for the reaction between 2-iodobutane and sodium hydroxide.

[2]

(c) Describe and explain how the volatilities of the halogens vary from chlorine to iodine.

....

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....

....

.... [2]

(d) Some hydrogen halides are unstable to heat.

(i) Write an equation for the reaction undergone on heating a hydrogen halide.

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

(ii) Describe and explain how the thermal stabilities of the hydrogen halides (HCl, HBr and HI) vary down the group.

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

(e) When sodium thiosulfate, $Na_2S_2O_3$, is reacted with bromine, $NaHSO_4$ is formed. However, when $Na_2S_2O_3$ reacts with iodine, $Na_2S_4O_6$ is formed instead.

Use the following data, and data from the *Data Booklet*, to suggest an explanation for this difference.

$$S_4O_6^{2-} + 2e^- \rightleftharpoons 2S_2O_3^{2-} \qquad E^\oplus = +0.09 \text{ V}$$
$$4SO_2 + 4H^+ + 6e^- \rightleftharpoons S_4O_6^{2-} + 2H_2O \qquad E^\oplus = +0.51 \text{ V}$$
$$SO_4^{2-} + 4H^+ + 2e^- \rightleftharpoons SO_2 + 2H_2O \qquad E^\oplus = +0.17 \text{ V}$$

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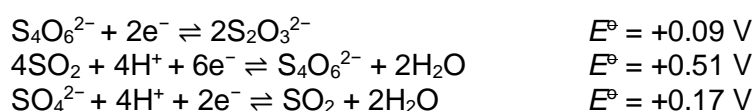
…..……………………………………………………………………………………..………… [3]

[Total: 17]

2 **(a)** 4-Morpholineethanesulfonic acid (MES) is commonly used to prepare buffer solutions. In aqueous solution, MES exists as a dipolar ion which dissociates to give H^+ ions:
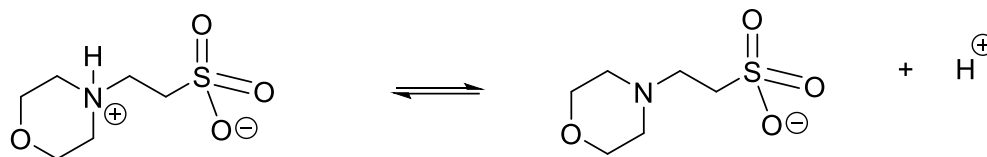
4-Morpholineethanesulfonic acid
(MES)

FA 1 is a buffer solution prepared from MES with a pH of 5.5. The ratio of MES and its conjugate base is 4:1.

(i) Determine the pK_a of MES.

[1]

(ii) State the mole ratio of MES to its conjugate base if the pH = pK_a of MES.

[1]

A student titrated 10.0 cm^3 of **FA 1** with aqueous sodium hydroxide, and found that 20.0 cm^3 of aqueous NaOH was required for complete neutralisation.

(iii) What volume of aqueous NaOH should be added to 10.0 cm^3 of **FA 1** such that the pH of the resulting solution becomes equal to pK_a of MES?

[2]

(iv) Write an equation to show why the pH at equivalence point is more than 7.

[1]

(v) The pH of the solution at equivalence point is 9.4. Suggest a suitable indicator for the titration of **FA 1** with aqueous NaOH, giving a reason for your choice.

Indicators	Working range
Congo red	3.0 – 5.0
Cresolphthalein	8.2 – 9.8
Indigo carmine	11.4 – 13.0

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

(b) Zymase, an enzyme that occurs naturally in yeasts, catalyses the fermentation of sugar into ethanol and carbon dioxide.

$$sugar \rightarrow ethanol + carbon\ dioxide$$
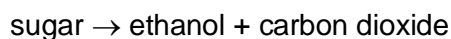
Fig. 2.1 shows the results of an investigation of the initial rate of fermentation of sugar by zymase. In the experiments, the initial concentration of sugar was varied but that of zymase was kept constant.

rate

[sugar]
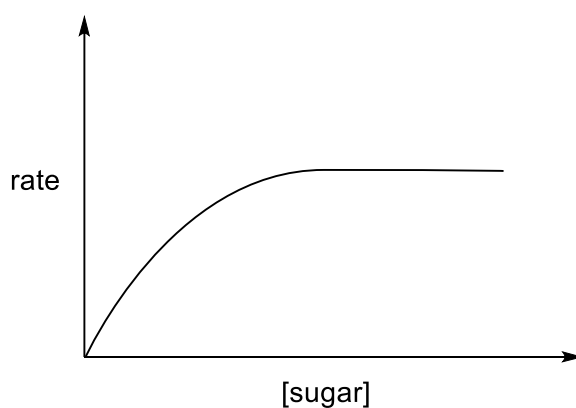
Fig. 2.1

(i) Explain fully the shape of the graph.

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

(ii) Sketch on Fig. 2.1 the shape of the line you would expect when the amount of zymase added was increased.   [1]

(iii) Three other experiments were carried out to measure the initial rates of fermentation at different concentrations of sugar and zymase. The results are shown in Table 2.2.

Table 2.2

Experiment	[sugar] /mol dm^{-3}	[zymase] /mol dm^{-3}	Relative initial rate
1	0.20	0.10	1
2	0.40	0.10	2
3	0.10	0.20	1

Deduce the orders of reaction with respect to sugar and zymase, showing how you arrive at your answers.

[3]

[Total:13]

3 This question is about alkynes, which are hydrocarbons that contain a carbon-carbon triple bond.

(a) In the past, ethyne gas, C_2H_2, was prepared from calcium carbide, CaC_2. Calcium carbide is a crystalline solid with a melting point of approximately 2160 °C.

  (i) Draw the dot-and-cross diagram of CaC_2.

[1]

  (ii) When excess water with a drop of universal indicator is added to some calcium carbide, ethyne is produced and the solution changes from green before the reaction, to blue after the reaction is complete.

Write an equation, with state symbols, for this reaction.

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

(b) **(i)** Draw the structure of ethyne, showing correct geometry, and clearly indicate the bond angle in your drawing. State the type of hybridisation of the carbon atoms in ethyne.

Type of hybridisation of carbon: ……………………………... [2]

  (ii) Ethyne gas approaches ideal behavior at room temperature and pressure. Identify, and explain, **two** characteristics of ethyne that enable it to exhibit ideal gas behaviour.

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

(c) When completely combusted, ethyne reacts with oxygen according to the following equation:

$$C_2H_2(g) + \frac{5}{2}O_2(g) \rightarrow 2CO_2(g) + H_2O(l)$$
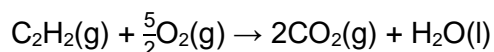
A fixed-volume flask containing a mixture of ethyne and oxygen is connected to a manometer.

The manometer consists of a U-tube containing some liquid mercury, which is exposed to atmospheric pressure at one end. Initially, the mercury levels on both arms are at the same height, as shown in Fig. 3.1 below.
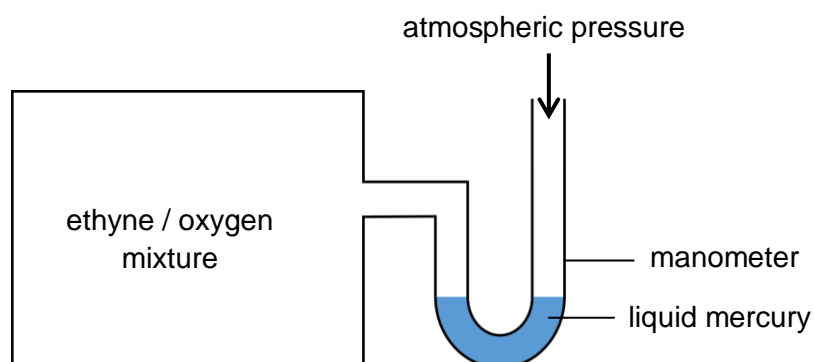
Fig 3.1

When the mixture in the flask was combusted, the final mercury levels in the manometer showed a difference in height of 65 mm. All measurements were made at room temperature and pressure. ["mm Hg" is a unit of pressure, where 760 mm Hg = 1 atm]

The initial partial pressures of ethyne and oxygen are x and y mm Hg respectively. After the combustion, the partial pressure of ethyne changed by p mm Hg.

(i) Express the total initial pressure in the flask in terms of x and y and state its value in mm Hg.

[1]

(ii) Express the total pressure after the combustion in terms of x, y, and p;

[1]

(iii) Hence, show that the difference in height of 65 mm in the mercury levels is due to a **decrease** in pressure inside the flask.

[1]

(iv) Determine the value of p to 1 decimal place.

[1]

(v) Hence, calculate

    (I) the partial pressure, in mm Hg, of carbon dioxide formed after the combustion;

    (II) the values of x and y, assuming all the oxygen was used up during the combustion, and only carbon dioxide and water were produced in the process.

[2]

(d) In more recent years, ethyne has been largely manufactured from methane. One such conversion only employs heat, and produces ethyne according to the following equilibrium:

$$2CH_4(g) \ll C_2H_2(g) + 3H_2(g) \; \text{- - - - - - - - - - - - - - (1)}$$
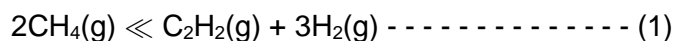
Equilibrium compositions during the conversion of methane to ethyne in a 0.100 m³ vessel may be predicted using the simulated data below.
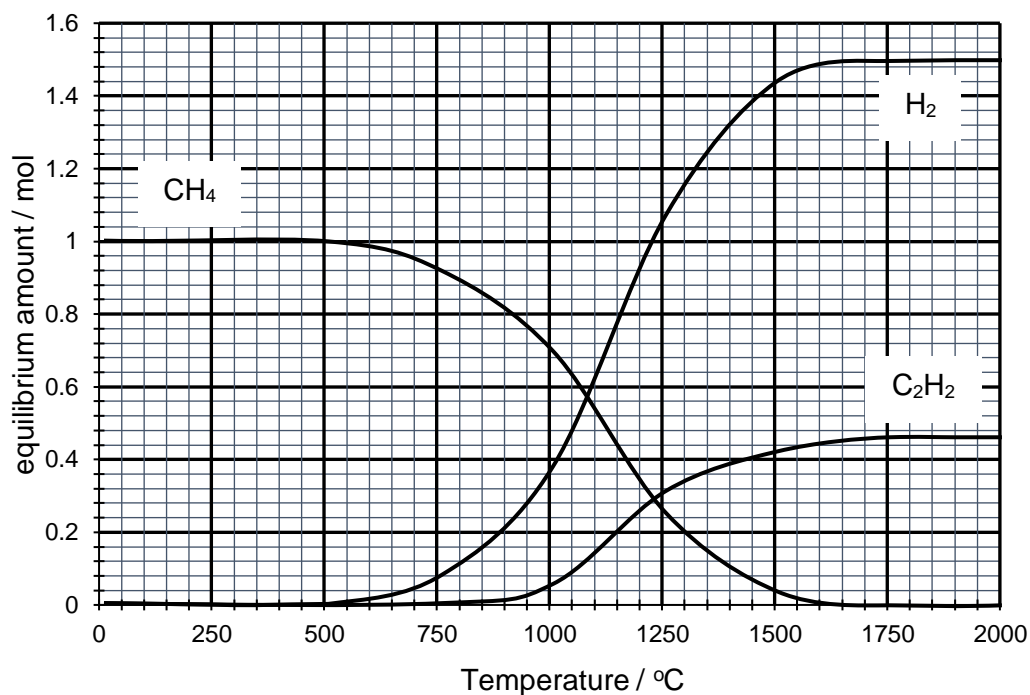
(i) Assuming the gases behave ideally in the range of temperatures shown in the graph, use the simulated data to calculate the pressure of hydrogen gas in the vessel at 1250 °C.

[2]

(ii) Show that, for equilibrium (1) at 1250 °C,

$$K_p = \frac{(n_{H_2})^3(n_{C_2H_2})}{(n_{CH_4})^2} \times \left(\frac{RT}{V}\right)^2$$

where
R is the molar gas constant
T is the temperature in the vessel
V is the volume of the vessel

and hence, calculate K_p, showing its units.

[3]

(iii) State how the value of K_p for equilibrium (1) would change when the temperature is changed from 1250 °C to 1000 °C.

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

(e) Terminal alkynes can undergo hydroboration-oxidation reactions, as shown below.

$$H-C\equiv C-R \longrightarrow H-\underset{\underset{O}{\|}}{C}-CH_2-R \qquad \text{R: alkyl or H}$$
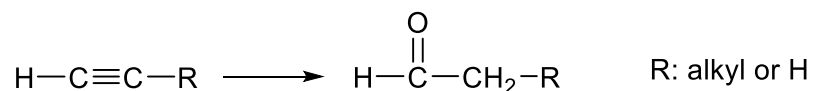
(i) Draw and name the product formed when propyne, C_3H_4, undergoes hydroboration-oxidation.

name of product: ……………………………………………………………..[2]

(ii) Describe a simple chemical test to distinguish propyne from the product you have drawn in **(e)(i)**. You may assume that propyne reacts similarly to propene.

.……………………………………………………………………………….…

.………………………..……………………………………………………….…

.……………………………………………………………………………….…

.……………………………………………………………………….…[2]

[Total: 22]

4 Aromatic compounds like benzene tend to undergo electrophilic substitution reactions.

(a) Explain why aromatic compounds are reactive towards electrophiles but not nucleophiles.

...………………………..…………………………………………………………..…..………....

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

(b) Explain why aromatic compounds tend to undergo substitution reactions instead of addition reactions.

...………………………..…………………………………………………………..…..………....

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

(c) Benzene is a starting material for the synthesis of phenylamine.
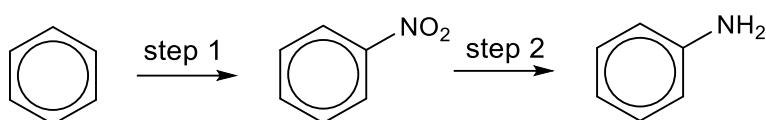
(i) State the reagents and conditions for steps 1 and 2.

step 1: ……………………………………………………………………………………………

step 2: ……………………………………………………………………………………[2]

(ii) Phenylamine reacts readily with excess aqueous bromine to give a white solid **X**. Identify **X** and write a balanced equation for the reaction that occurs.

[2]

(iii) Suggest the order of reactivity of benzene, nitrobenzene and phenylamine with liquid bromine. Explain your answer.

...………………………..…………………………………………………………..…..……

...………………………..…………………………………………………………..…..……

...………………………..…………………………………………………………..…..……

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

(iv) Draw the structure of the monobrominated organic product formed when nitrobenzene reacts with liquid bromine.

[1]

In 1931, the German chemist Erich Hückel formulated a theory to help determine if a species would be considered aromatic. This rule became known as Hückel's rule.

An aromatic species must satisfy all the following criteria:

1. It must be cyclic.
2. Every atom in the ring must have a p orbital.
3. Each p orbital must overlap the p orbitals from either side in a continuous fashion to form a closed loop, which means the structure has to be planar for effective overlap.
4. The cyclic system must contain (4n+2) delocalised π electrons, where n is 0 or a positive integer (1, 2, 3 etc.)

For example, benzene is aromatic because it satisfies all the four criteria, with 6 delocalised π electrons (n = 1).

(d) Consider the following species.

D   E   F
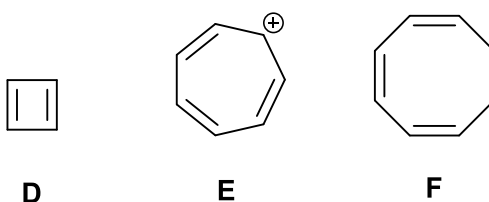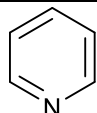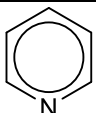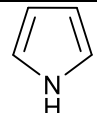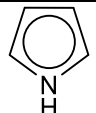
Which species are **not** aromatic? Explain your answer briefly.

……………………..………………………………………………………….…………...

……………………..………………………………………………………….…………...

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

Table 4.1 shows information on three aromatic compounds which obey Hückel's rule.

Table 4.1

compound	hypothetical structure of compound	actual structure of compound	pK_b	resonance energy/ kJ mol^{-1}	boiling point/ °C
pyridine			8.6	134	115
pyrrole			13.6	100	129
furan				80	31

The hypothetical structures of the compounds in Table 4.1 assume that there is no delocalisation of π electrons in the rings. However, in reality, delocalisation of π electrons gives rise to the extra stability of the aromatic compounds. The resonance energy is defined as the energy difference between the actual structure and hypothetical structure of each compound.

(e) (i) All the carbon and nitrogen atoms in pyrrole are sp^2 hybridised.

Draw the arrangement of all the hybridised and unhybridised orbitals of the nitrogen atom in pyrrole. Label the orbitals clearly.

[2]

(ii) Pyrrole has six electrons in the delocalised π electron cloud.

How many electrons does the nitrogen atom in pyrrole contribute to the delocalised π electron cloud? You may find it useful to consider the hypothetical structure of pyrrole.

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

(iii) The nitrogen atom in pyrrole has a lone pair of electrons. Suggest the orbital in which the lone pair resides.

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

(iv) Hence, using your answers in **(e)(ii)** and **(e)(iii)**, suggest why the pK_b of pyrrole is so high.

..……………………………..……………………………………………………….…

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

(f) (i) Furan can behave differently from benzene in its reactions. Under certain conditions, furan undergoes electrophilic addition instead of electrophilic substitution. Based on your answer in **(b)**, explain this phenomenon, using relevant data from Table 4.1.

..……………………………..……………………………………………………….…

..……………………………..……………………………………………………….…

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

(ii) Furan can form hydrogen bonds when added to ethanol. Draw a diagram to show how hydrogen bonding occurs between one molecule of furan and one molecule of ethanol and explain how this interaction arises.

..……………………………..……………………………………………………….…

..……………………………..……………………………………………………….…

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

(g) The enthalpy changes of hydrogenation of pyridine and compound **E** can be represented by the equations below:

(I) + 3H$_2$(g) $\longrightarrow$ (I) $\Delta H_1 = -194$ kJ mol^{-1}

(I) + 2H$_2$(g) $\longrightarrow$ (I) $\Delta H_2 = -240$ kJ mol^{-1}

E
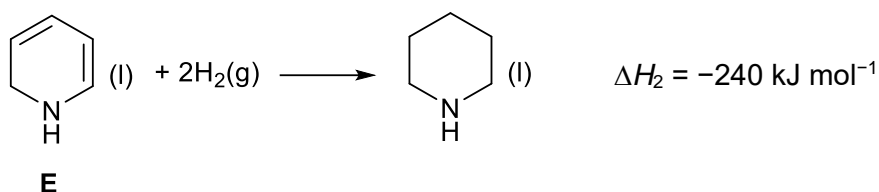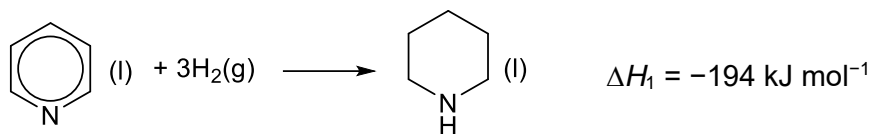
Using the information above and relevant data from Table 4.1, complete the energy diagram below and use it to calculate ΔH_3.
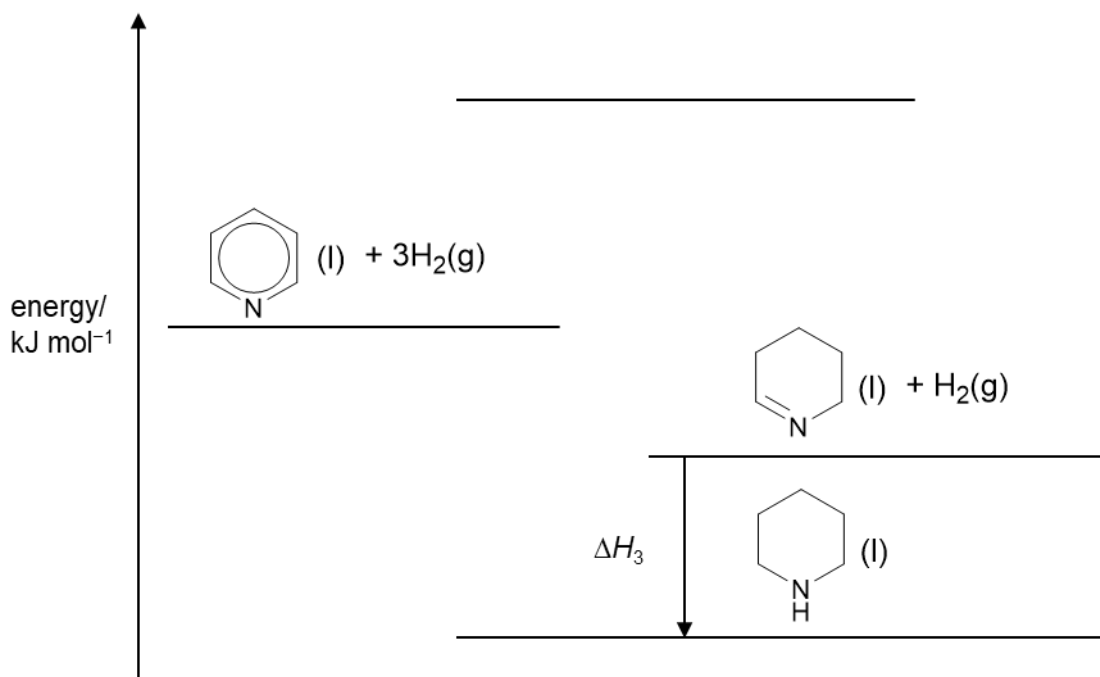
$\Delta H_3 = $ ………………………….. kJ mol^{-1}

[3]

[Total: 23]

END OF PAPER

Paper 2

1 (a) (i) HCN with trace amount of KCN (or NaOH(aq)), cold **[1]**

(ii)
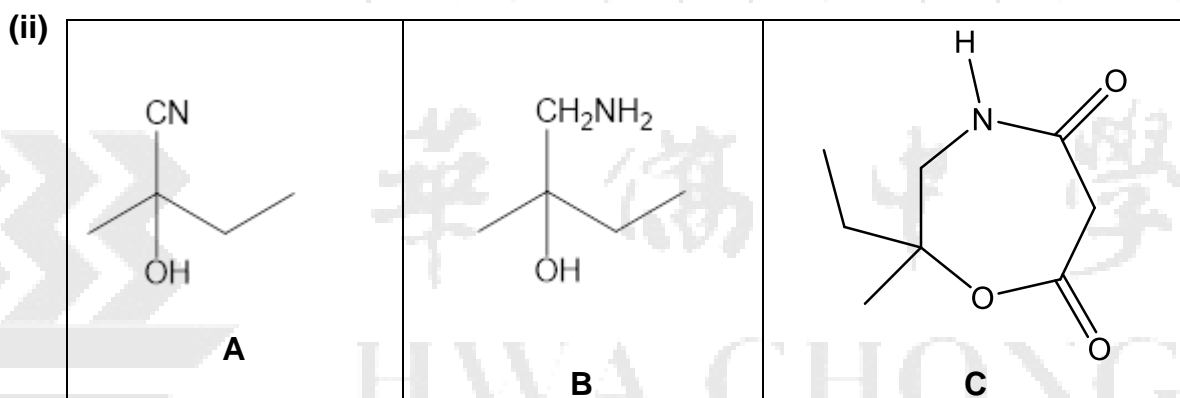
[1] for each correct structure

(b) (i) Mechanism: **Bimolecular** Nucleophilic Substitution (S_N2) **[1]**
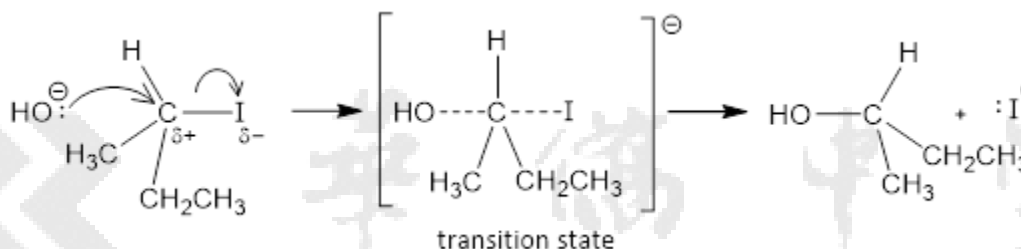
[1] for:
- ✓ OH^- is the nucleophile that attacks $C^{\delta+}$ of C–I (attack from the side that's opposite to the I)
- ✓ partial charges: $C^{\delta+}$–$C^{\delta-}$
- ✓ curly arrow going from <u>lone pair</u> of OH^- to $C^{\delta+}$ of C–I
- ✓ curly arrow going from C–I bond, to I

[1] for:
- ✓ transition state negatively charged (need not label "transition state")
- ✓ I^- is produced at the end of the reaction
- ✓ no slow or fast step

−½m for every mistake

(ii)

Energy vs Progress of reaction diagram. Reactants: $CH_3CHICH_2CH_3$ + NaOH. Products: $CH_3CH(OH)CH_2CH_3$ + NaI. Labelled E_a and $\Delta H < 0$.
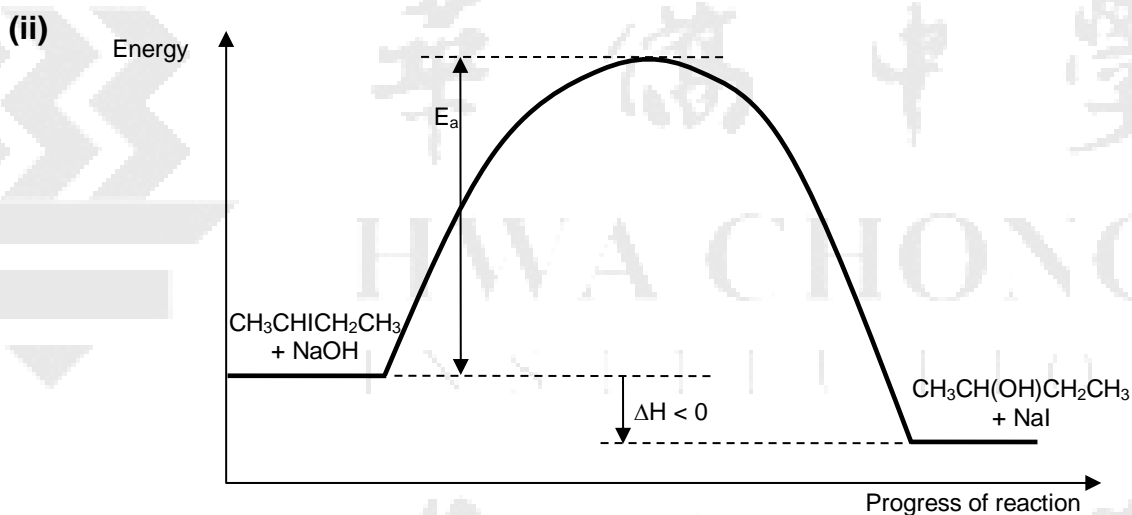
[1] shape of graph	✓ label "reactants" and "products"
[1] labelling graph	✓ label axes
✓ label E_a	−½m for every mistake
✓ label ΔH	

(c) The halogens Cl_2, Br_2 and I_2 exist as simple non-polar covalent molecules. From Cl_2 to Br_2 to I_2, the <u>size of the electron cloud</u> and hence, the polarisability of the halogen molecule <u>increases</u> [1]. More energy is needed to overcome the <u>stronger dispersion forces</u> between the molecules. Hence, the <u>volatility of the halogens decreases</u> [1] from chlorine to iodine.

(d) (i) $2HX \rightarrow H_2 + X_2$ **[1]**

(ii) Down the group, <u>as atomic radius increases</u> from Cl to I, the <u>bond length of the H–X bond increases</u> / <u>bond strength decreases</u> **[1].**
Hence, <u>less energy is needed to break the H–X bond</u>. Thus, the thermal stability of the hydrogen halides <u>decreases</u> down the group **[1].**

Remarks: can also justify by quoting the bond energy data, H–Cl = +431, H–Br = +366, H–I = +299 kJ mol^{-1}. Weaker H–X bond needs less energy to break during thermal decomposition

(e) From *Data Booklet*,

	$E^{\ominus}$/V
$Br_2 + 2e^- \rightleftharpoons 2Br^-$	+1.07
$I_2 + 2e^- \rightleftharpoons 2I^-$	+0.54

Bromine reacts with $S_2O_3^{2-}$ to form $S_4O_6^{2-}$, which will be further oxidised to SO_2 and subsequently SO_4^{2-}.
$E^{\ominus}_{cell}$ = +1.07 − (+0.09) = +0.98 V > 0 (spontaneous)
$E^{\ominus}_{cell}$ = +1.07 − (+0.51) = +0.56 V > 0 (spontaneous)
$E^{\ominus}_{cell}$ = +1.07 − (+0.17) = +0.90 V > 0 (spontaneous)

Iodine reacts with $S_2O_3^{2-}$ to form $S_4O_6^{2-}$ but there is no further oxidation of $S_4O_6^{2-}$ to SO_2.
$E^{\ominus}_{cell}$ = +0.54 − (+0.09) = +0.45 V > 0 (spontaneous)
$E^{\ominus}_{cell}$ = +0.54 − (+0.51) = +0.03 V > 0 (spontaneous but extent of reaction is too small)

[1] $E^{\ominus}_{cell}$ for reaction with bromine or showing that the $E^{\ominus}_{(Br2/Br-)}$ > all the 3 $E^{\ominus}$

[1] $E^{\ominus}_{cell}$ for reaction with iodine or showing that $E^{\ominus}_{(I2/I-)}$ > +0.09 V but only slightly larger than +0.51 V

[½] spontaneous since $E^{\ominus}_{cell}$ > 0

[½] spontaneous but extent of reaction too small

2 (a) (i) $K_a = [H^+][A^-] / [HA]$
$K_a = (10^{-5.5})(1) / 4$
$K_a = 7.91 \times 10^{-7}$ mol dm^{-3}
$pK_a = -\lg(7.91 \times 10^{-7}) = 6.10$ **[1]**

OR

$pH = pKa + \lg[A^-]/[HA]$
$5.5 = pKa + \lg(1/4)$
$pK_a = 6.10$ **[1]**

(ii) 1:1 **[1]**

(iii) Let x be the volume of NaOH required to achieve maximum buffer capacity

For visualization:

0 cm^3		x		20.00 cm^3
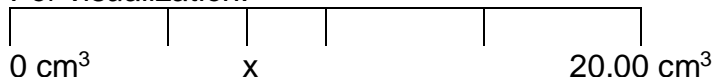
Since the ratio of the [A$^-$]:[HA] in the buffer is 1:4, a titre value of 20.00 cm^3 must correspond to 4 units. Hence, maximum buffer capacity must occur when there are 2.5 units of [A$^-$] and 2.5 units of [HA]. **[1]**

Therefore, the volume of NaOH required, x, corresponds to 1.5 units.

Volume of NaOH required = 20.00/4 × 1.5 = 7.5 cm^3 **[1]**

OR

Let x be the volume of NaOH required to achieve maximum buffer capacity
Since the ratio of the [A$^-$]/[HA] in the buffer is 1:4,
$(20 - 2x) / (20) = 1/4$ **[1]**
$2(10 - x) = 20/4$
$x = 7.5$ cm^3 **[1]**

(iv)

[1]
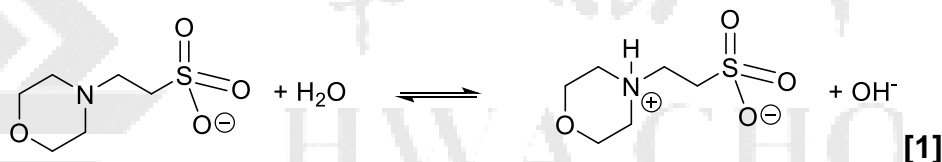
(v) Given that the **region of rapid pH change will be at about pH 9.4,** I would use an indicator with a **working range that coincides with that pH range [1]**, which would be **cresolphthalein**. **[1]**

(b) (i) Initially, the graph is a straight line/increases steadily. This is because the reaction is **first order wrt to [sugar]/ rate is directly proportional to [sugar]/ more enzyme-substrate complex can be formed by increasing [sugar]. [1]** Thus, the rate of reaction increase.

The graph plateaus/becomes horizontal/becomes zero order wrt [sugar] **because the enzyme is now saturated/all active sites are occupied [1],** thus, the rate of reaction cannot be increased by increasing [sugar].

(ii)
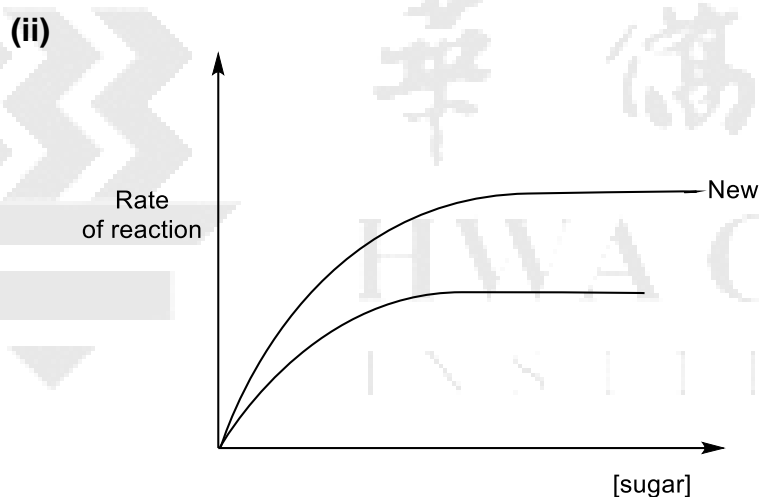
Fig. 2.1

[1]
Key points
- Initial rate increases more quickly
- Plateau occurs at a higher concentration of sugar
- Plateau occurs at a higher rate

(iii) Order wrt to [sugar]:
Comparing experiment 1 and 2,
When [sugar] is doubled from 0.20 mol dm^{-3} to 0.40 mol dm^{-3}, the relative rate of reaction doubled.
Thus, [sugar] is directly proportional to the rate of reaction, and is first order.
[1] for explanation

Order wrt to [zymase]:
Comparing experiment 1 and 3,
When [sugar] is halved from 0.20 mol dm^{-3} to 0.10 mol dm^{-3}, the relative rate of reaction is expected to halve.
When [zymase] is doubled from 0.010 mol dm^{-3} to 0.020 mol dm^{-3}, the relative rate is doubled from ½ to 1
Thus, [zymase] is directly proportional to the rate of reaction, and is first order.
[1] for explanation
[½] x 2 for each correctly identified order

3 (a) (i)

$$\left[\text{Ca} \right]^{2+} \left[:C \overset{\times}{\underset{\times}{:}} C \overset{\times}{\underset{\times}{}} \right]^{2-}$$
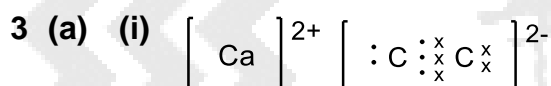
Anion:
additional electrons of opposite symbol were accepted
additional electrons of third symbol were accepted
dative bonds were rejected
[½] for each ion
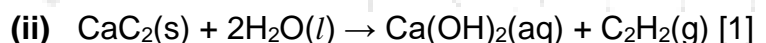
(ii) $CaC_2(s) + 2H_2O(l) \rightarrow Ca(OH)_2(aq) + C_2H_2(g)$ [1]
[1] balanced equation with correct state symbols

(b) (i)

$$\overset{\frown}{\text{180}°}$$
$$H - C \equiv C - H$$
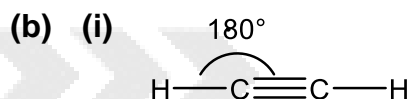
[1] for correct bond angle (only one needs to be labelled on the diagram itself), and correct Lewis structure which must show linear shape.

Type of hybridisation: sp **[1]**

(ii) Two characteristics of ethyne, and explanation:
1. Ethyne has a <u>small molecular size</u>, which means the <u>volume of the particles of ethyne is small compared to the volume of the container</u>, and so can be considered negligible just as for ideal gases; and
2. Ethyne is a <u>non-polar molecule</u>, so it has relatively <u>weak intermolecular dispersion forces</u>, which could therefore be considered negligible, just as for ideal gases.

[1] x 2 for each characteristic

(c) (i) Total initial pressure $= x + y$
$= 760$ mm Hg **[1]**
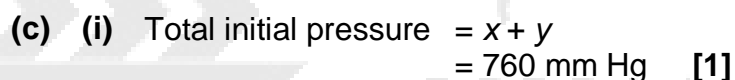
(ii) Since p mm Hg is the change in partial pressure of ethyne during the combustion:

	$C_2H_2(g)$	+	$5/2\ O_2(g)$	→	$2CO_2(g)$	+	$H_2O(l)$
Initial partial pressure / mm Hg	x		y		0		-
Change / mm Hg	$-p$		$-5/2p$		$+2p$		-
Final partial pressure / mm Hg	$x - p$		$y - 5/2p$		$2p$		-

Total pressure after combustion $= (x - p) + (y - \frac{5}{2}p) + 2p$
$= [(x + y) - \frac{3}{2}p]$ mm Hg

[1] Correct expression of total pressure after combustion in terms of x, y and p

(iii) Total initial pressure = $(x + y)$ mm Hg

Total pressure after combustion = $(x + y) - \frac{3}{2}p$ mm Hg

Since a reaction occurs, p must be > 0

$$\text{so } (x + y) - \frac{3}{2}p < (x + y),$$

i.e. (final pressure) < (initial pressure)

and $\therefore$ the term "$-\frac{3}{2}p$" represents a fall in pressure from the original $(x + y)$ mm Hg (shown)

[1] Convincing argument in which there is a comparison of initial and final pressures in terms of x, y and p.

(iv) From **(ii)** and **(iii)**, we know that the fall in pressure inside the flask corresponds to difference in height (atmospheric pressure remains unchanged):

$\frac{3}{2}p = 65$

$p = 65 \div (3/2)$

$\quad = \underline{43.3}$ (to 1 d.p.) (in mm Hg)

[1] Answer must be to 1 d.p. to get the full credit.

(v) (I) Since final partial pressure of CO_2 is $2p$

$\therefore P_{CO2} = 2p = \underline{86.7 \text{ mm Hg}}$ **[1]** (to 3 s.f.)

(II) If all oxygen was used up, then $y - 5/2p = 0$

$\therefore y = 5/2p$

$\quad y = 5/2 (65 \div 3/2) = 108.3$ mm Hg (1 d.p.)

$\qquad\qquad\qquad\qquad = \underline{108}$ mm Hg (3 s.f.) **[½]**

And $x = 760 - 108.3 = 651.7$ mm Hg (1 d.p.)

$\qquad\qquad\qquad\qquad = \underline{652}$ mm Hg (3 s.f.) **[½]**

(d) (i) $pV = nRT$

From graph, $\eta_{H2} = \underline{1.06}$ mol (accepted 1.04 – 1.06)

[1] for correct reading of no. of moles of H_2 from graph

$P_{H2} = nRT/V = (1.06)(8.31)(1250 + 273) / (0.100)$

$\qquad\qquad = 134,155$ Pa

$\qquad\qquad = \underline{1.34 \times 10^5 \text{ Pa}}$

$\qquad\qquad = \underline{134 \text{ kPa}}$ (to 3 s.f.)

[1] for correct use of ideal gas equation, and answer

ALTERNATIVE:

From graph, $\eta_{(total)} = (1.06 + 0.30 + 0.26)$

$\qquad\qquad\qquad = 1.62$ mol

$$P_{(total)} = n_{(total)}RT/V = (1.62)(8.31)(1250 + 273) / (0.100)$$
$$= 205{,}029 \text{ Pa}$$

$$P_{H2} = (\text{mole fraction of } H_2) \times P_{(total)}$$
$$= (1.06/1.62) \times 205{,}029$$
$$= 134{,}155 \text{ Pa} = \underline{1.34 \times 10^5 \text{ Pa}} = \underline{134 \text{ kPa}} \text{ (to 3 s.f.)}$$

(ii) $K_p = \dfrac{(P_{H_2})^3 (P_{C_2H_2})}{(P_{CH_4})^2}$

$\left. \begin{array}{l} = \dfrac{(\frac{n_{H2}RT}{V})^3 (\frac{n_{C2H2}RT}{V})}{(\frac{n_{CH4}RT}{V})^2} \\[2em] = \dfrac{(n_{H2})^3 (n_{C2H2})}{(n_{CH4})^2} \times \left(\dfrac{RT}{V}\right)^{4-2} \\[2em] = \dfrac{(n_{H2})^3 (n_{C2H2})}{(n_{CH4})^2} \times \left(\dfrac{RT}{V}\right)^{2} \end{array} \right\}$ **[1]** for <u>convincing</u> proof and use of pV = nRT

$= \dfrac{1.06^3 \times 0.30}{0.26^2} \times \left(\dfrac{8.31 \times 1523}{0.100}\right)^2$ **[1]** for substitution of correct terms from graph

$= \underline{8.47 \times 10^{10} \text{ Pa}^2}$ (3 s.f.)   **[1]** for correct answer and units

Other accepted units of K_p: $(J^2 \text{ m}^{-6})$

$\equiv Pa^2$

(iii) When the temperature is changed from 1250 °C to 1000 °C, the value of K_p would <u>decrease / be smaller</u> **[1]**.

(e) **(i)**

H—C(=O)—CH$_2$—CH$_3$ **[1]**
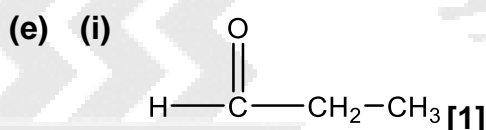
Propanal **[1]** (must be spelt clearly and correctly, no benefit of doubt)

(ii) To each separate samples of propyne and propanal, (any of the following):

	Chemical test	Observations	
		propyne	**propanal**
1	Add 2,4-DNPH	No orange ppt	Orange ppt formed
2	warm with Tollen's reagent	No silver mirror	Silver mirror produced
3	warm with Fehling's solution	No brick-red ppt	Brick-red ppt formed
4	add aqueous bromine	Yellow-orange aqueous bromine decolourised	Yellow-orange colour remains
5	Add Br$_2$(l) (at r.t., no UV) or Br$_2$ in CCl_4 (at r.t., no UV)	Reddish-brown liquid bromine decolourised Orange-red Br$_2$ in CCl_4 decolourised	Reddish-brown colour remains Orange-red colour remains

| 6 | Heat with acidified potassium dichromate | Orange colour remains | Orange solution turns green |

Careful! hot acidified or alkaline $KMnO_4$ is not ideal here as both propyne and propanal can undergo oxidation (propyne undergoes oxidative cleavage, while propanal will be oxidsed to propanoic acid). However, students who added hot *acidifed* $KMnO_4$ to both compounds and used the effervescence of CO_2 to identify propyne (effervescence not seen for propanal) were awarded the mark.

Careful! Cold $KMnO_4$ to form the diol for propyne is a dubious choice, as propanal may still get oxidized in cold conditions, so decolourisation might happen for both compounds.

[1] correct choice of test
[1] correct distinguishing observation (incorrect colours of ppts or solutions were penalized)

Ecf was only awarded if product drawn in (e)(i) was an aldehyde or ketone

4 (a) The π cloud has <u>high electron density/ is electron-rich</u> that will <u>attract</u> electron-deficient electrophiles but will repel electron-rich nucleophiles. **[1]**

(b) Electrophilic addition <u>destroys the delocalisation</u> in the π electron cloud/<u>disrupts aromaticity</u> which requires a significant amount of energy, whereas electrophilic substitution retains aromaticity. **[1]**

(c) (i) Step 1: Conc. HNO_3, conc. H_2SO_4, maintained at 55 °C **[1]**
Step 2: 1. Sn, (excess) conc. HC*l*, heat 2. NaOH(aq) **[1]**

(ii)
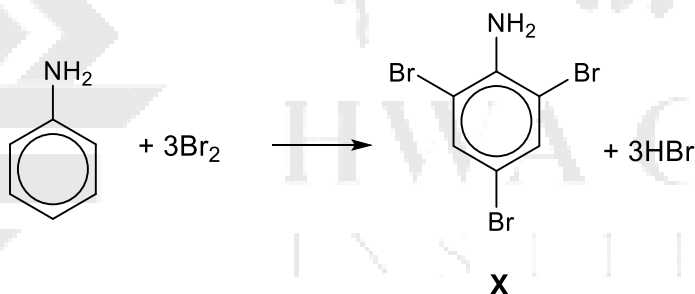
[1] for X
[1] for equation (ecf for equation if X is monosubstituted)

(iii) <u>Nitrobenzene < benzene < phenylamine.</u>**[½]**

The <u>nitro group is electron withdrawing and withdraws electron density from the</u> π electron cloud on the benzene ring **[½]**, reducing the <u>susceptibility of the benzene ring towards electrophiles/deactivating the ring towards electrophiles</u> **[½]**. The NH_2 group on phenylamine is electron-donating as it can <u>donate its lone pair of electrons to the ring</u> and <u>increases electron density</u> of the π electron cloud in the benzene ring. **[½]**
(only need to mention susceptibility towards electrophiles/activating or deactivating towards electrophiles once)

(iv)

 [1]
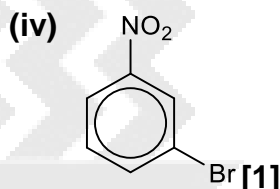
(d) **D** has only 4 π electrons in the ring, so it doesn't satisfy criteria 4. **[1]**

F has two carbon atoms in the ring that are sp^3 hybridised, so those carbons do not have available p orbitals, so it doesn't satisfy criteria 2

OR

F does not satisfy criteria 3, since the p orbitals are not overlapped in a continuous fashion/ since the structure is not planar at the carbons that are sp^3. **[1]**

(e) **(i)**
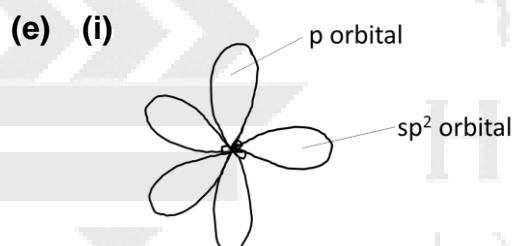
[1] for correct shape, arrangement and label for p orbital
[1] for correct shapes, arrangement and label for sp^2 orbitals

(ii) <u>2</u> **[1]**

(iii) p orbital. **[1]**

(iv) The <u>lone pair</u> on N of pyrrole is <u>delocalised</u> into the π cloud and is <u>less/not available</u> for donation to a H$^+$. **[1]**

(f) **(i)** Furan has very low resonance energy of <u>80 kJ mol^{-1}</u> **[1]**, so disrupting its aromaticity requires very little energy OR formation of strong σ bonds in an addition can compensate for the loss in its small resonance energy **[1]**.

(ii)
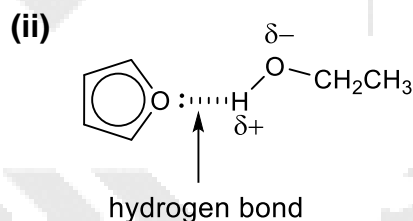
[1] (correct bond, lone pair, partial charges and label) (-1/2 per mistake)

The <u>hydrogen</u> atom <u>bonded to the</u> highly <u>electronegative O</u> on ethanol has a very significant <u>$\delta+$ charge</u> and the electron density in the covalent bond is highly polarised towards the oxygen atom. As a result, the H can form a very strong <u>attraction to the lone pair of electrons</u> on the highly electronegative <u>oxygen atom on furan</u>. This is a hydrogen bond. **[1]**

(g)

(l) + 3H$_2$(g)

(l) + 3H$_2$(g)

+134

−240

energy/
kJ mol^{-1}

(l) + H$_2$(g)

−194

ΔH_3

(l)
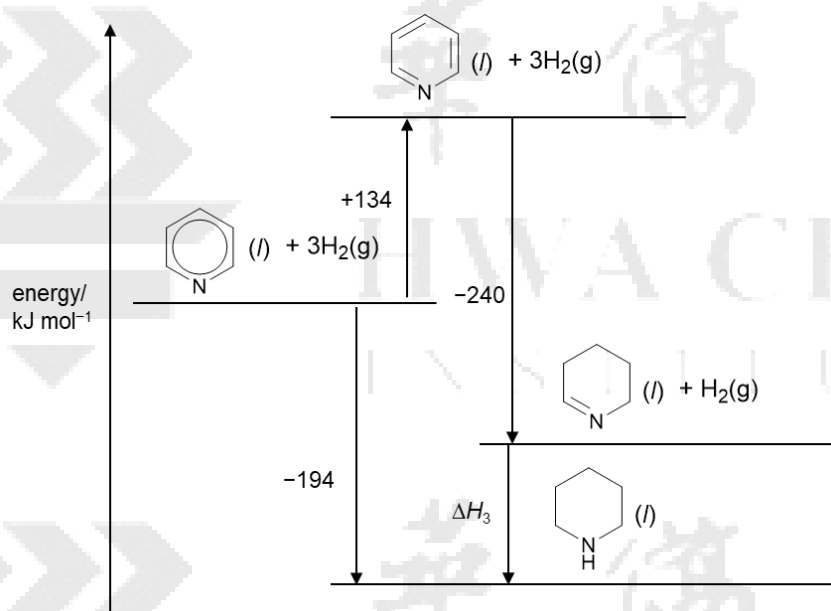
Cycle: **[2]**
−[½]m per mistake (max ½ m for cycle if students put the diene on the highest energy level, the ½ m can only be awarded if they put in -194 at the correct position)

By Hess' Law,

$\Delta H_3 = -(-120 - 120) - 134 + (-194) = -88$ kJ mol^{-1} **[1] ecf for correct use of Hess' Law.**

CANDIDATE NAME		CT GROUP	18S
CENTRE NUMBER		INDEX NUMBER	

CHEMISTRY   **9729/03**

Paper 3 Free Response   **20 September 2019**

2 hours

Candidates answer on separate answer booklet.

Additional Materials: 12-Page Answer Booklet

Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your **name**, **CT group, centre number** and **index number** on all the work you hand in.

Write in dark blue or black pen.

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

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

Section A

Answer **all** questions.

Section B

Answer **one** question.

Begin each question on a **new page of writing paper**.

A Data Booklet is provided.

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

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

At the end of the paper, submit only the 12-Page Answer Booklet and any additional booklets you have used.

This document consists of **11** printed pages.

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

1 (a) (i) Write an equation for the thermal decomposition of $MgCO_3$. [1]

(ii) Explain how the magnitude of the lattice energy of $MgCO_3$ differs from that of the solid product formed in **(a)(i)**. [2]

(iii) The thermal decomposition of $MgCO_3$ is an endothermic process. Explain whether the decomposition of $MgCO_3$ is spontaneous at high or low temperature. [2]

(iv) State whether $MgCO_3$ or $BaCO_3$ has the lower decomposition temperature. Explain your answer. [3]

(b) The Strecker synthesis is a method used to prepare amino acids. Alanine, 2-aminopropanoic acid, can be prepared from ethanal via Strecker synthesis as shown below.
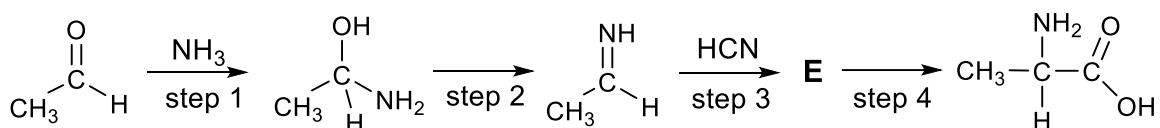
(i) Suggest the type of reaction occurring in steps 1 and 2. [2]

(ii) Draw the fully displayed structure of compound **E**. [1]

(iii) Suggest why step 3 produces an equimolar mixture of two stereoisomers. [2]

(iv) Another amino acid, isoleucine, can be prepared from aldehyde **F** via Strecker synthesis.

isoleucine
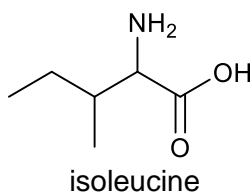
Draw the structure of aldehyde **F**. [1]

(c) In the Petasis reaction, carbonyl compounds, amines and suitable boronic acids can react to form substituted amines.

The general structure of a boronic acid is $B(OH)_2R$ where R is an alkyl or aryl group.

An example of the Petasis reaction is given below.
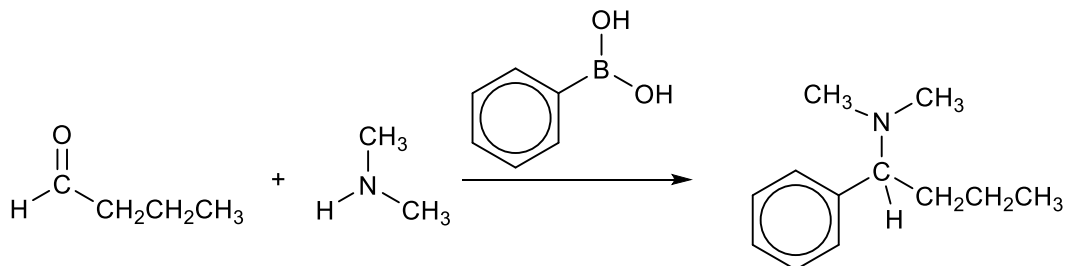
Consider the following Petasis reaction:
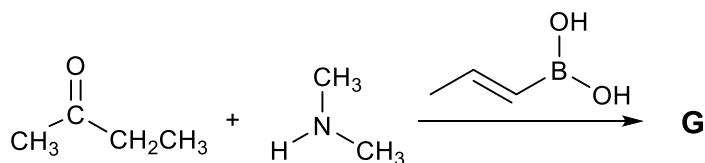
(i) Draw the structure of compound **G**. [1]

(ii) The Petasis reaction can be used in step 4 of the following synthesis of compound **K** from butanal.
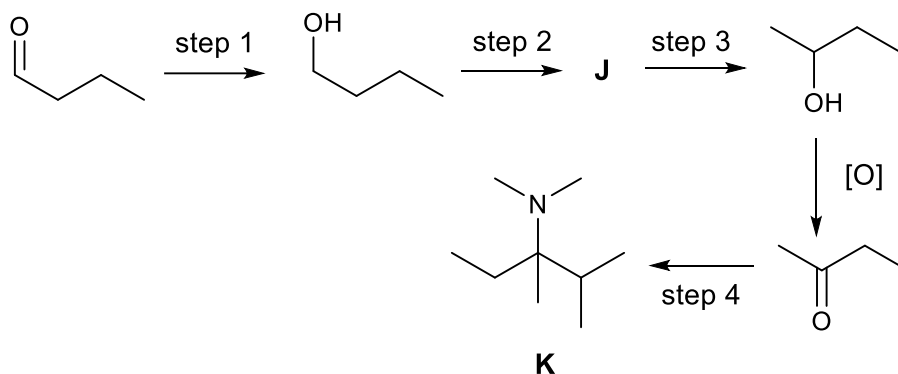
Suggest reagents and conditions for steps 1 to 4, and the structure of compound **J**.

[5]

[Total: 20]

2 When an onion is cut, the damaged tissues release the lachrymatory factor molecule, **LF**, that makes eyes water. The diagram below shows how **LF** is produced in the cut onion, starting from compound **P**.
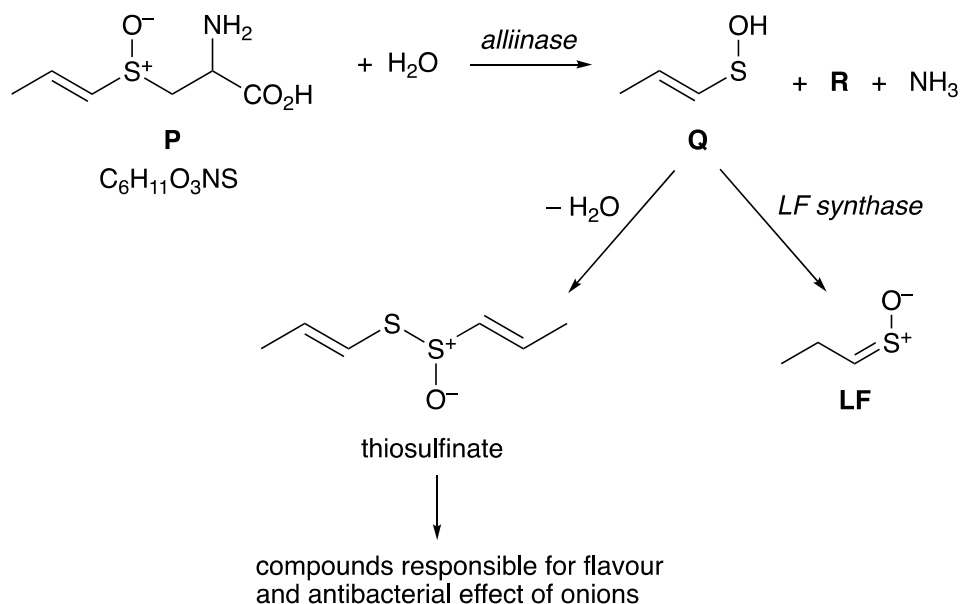
(a) In the first step, **P** reacts with a water molecule, in the presence of the enzyme *alliinase*, to give **Q**, **R** and ammonia.

   (i) Find the molecular formula of compound **R**. [1]

   (ii) Compound **R** reacts in a 1:1 ratio with PCl_5 and gives a yellow precipitate with alkaline aqueous iodine. Draw the structure of compound **R**. [1]

(b) State the isomeric relationship between **Q** and **LF**. [1]

(c) **LF** is very soluble in water. Explain why **LF** dissolves well in water. [1]

(d) **LF** is also volatile. For years, the conversion of **Q** to **LF** was thought to be direct, but in 2002, scientists discovered the pathway requires an enzyme *LF synthase*.

   Two methods, found on the internet, claim to prevent eyes from watering while cutting onions. Suggest how **each** of these methods could work, considering the volatility of **LF**, and the pathway that produces **LF**.

   (i) "Cool the onion before cutting it." [1]

   (ii) "Heat the onion before cutting it." [1]

(e) In 2016, scientists developed "tearless" onions by irradiating seeds with heavy-ion beams to reduce *LF synthase* levels. This mutation causes increased thiosulfinate production from **Q** via the alternate pathway above.

   (i) In this alternate pathway, two molecules of **Q** react to form thiosulfinate, losing a water molecule. Name the type of reaction that occurs. [1]

Increased thiosulfinate means higher amounts of compounds which give onions flavor and antibacterial properties. One of these compounds is cepaene.
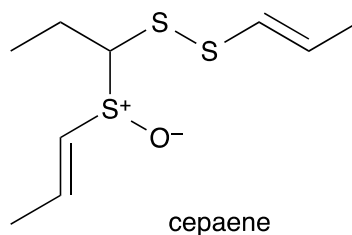
cepaene

The percentage of sulfur in an organic compound, such as cepaene, can be determined via the elemental analysis set-up in Fig. 2.1:
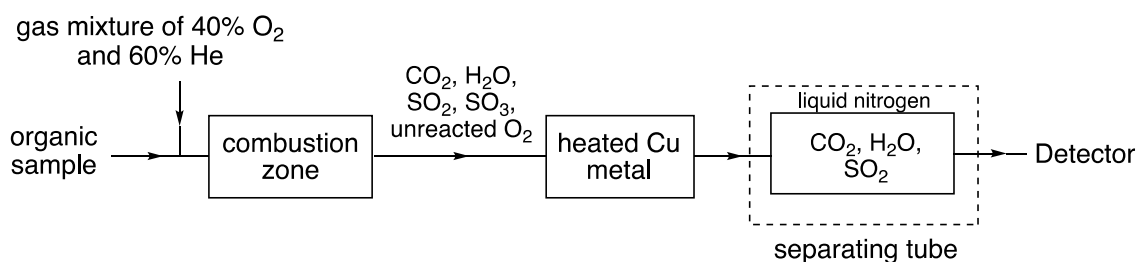
Fig. 2.1

The organic sample is first combusted in a gas mixture of 40% O_2 and 60% He, to form CO_2, H_2O and oxides of sulfur: SO_2 and SO_3.

The resultant gases then flow over a vessel containing heated copper metal to convert any SO_3 into SO_2. The heated copper also removes any unreacted O_2.

CO_2, H_2O and SO_2 gases are cooled in a separating tube immersed in liquid nitrogen at $-196\ ^\circ C$, and then released one by one, by increasing the temperature, to the detector.

In one analysis, 5.0 mg of cepaene ($C_9H_{16}OS_3$, $M_r = 236.3$) is introduced into the combustion zone.

(ii) Write an equation for the combustion of cepaene in the combustion zone to form CO_2, H_2O and SO_3 only. [1]

(iii) Hence, calculate the minimum volume of the O_2/He gas mixture at r.t.p. (in cm^3) required for the combustion of 5.0 mg of cepaene. [2]

(iv) State the role of the heated copper metal, and hence write an equation to show how the unreacted O_2 is removed by the heated copper. [2]

(v) If the temperature of the heated copper metal is not high enough or insufficient copper is used, a sulfur-containing compound could be formed in the vessel as blue crystals. Identify the blue crystals and suggest how they may be formed. [1]

(vi) Predict the sequence in which the three compounds in the separating tube are released to the detector. Explain your answer fully. [3]

[Total: 16]

3 Cobalt is a *transition element* that can be found in the blue pigments used for jewellery and paints.

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

(b) A cobalt-chrome alloy is a metal alloy of cobalt and chromium.

A sample of this alloy was dissolved in dilute HCl to form a solution containing 1.23×10^{-2} mol dm^{-3} of Cr^{3+}(aq) and 5.77×10^{-3} mol dm^{-3} of Co^{2+}(aq).

Aqueous NaOH was then added slowly to 1 cm^3 of the solution.

(i) Using the K_{sp} information below, show that the addition of NaOH will **not** allow for the separation of the Cr^{3+} and Co^{2+} metal cation ions in the above solution.

compound	K_{sp}
$Cr(OH)_3$	1.60×10^{-20}
$Co(OH)_2$	5.92×10^{-15}

[3]

(ii) A better way to separate the two aqueous ions is to add excess NaOH into the solution as $Cr(OH)_3$ dissolves.

With the aid of equations, explain why the precipitate of $Cr(OH)_3$ dissolves in excess NaOH using *Le Chatelier's Principle*. [3]

(c) When cobalt(II) chloride is dissolved in water, it forms a pink solution. Upon addition of excess aqueous potassium thiocyanate, KSCN, the solution turns blue.

(i) Draw a fully labelled diagram to account for the splitting of the degenerate d orbitals into two energy levels in an octahedral ligand field.

Explain how you arrived at your answer, taking into account the shape and the orientation of the d orbitals. [2]

(ii) Using your diagram in **(c)(i)**, account for the pink colour of the solution when cobalt(II) chloride is dissolved in water. [2]

(iii) Identify the type of reaction responsible for the colour change from pink to blue. [1]

(iv) Different proportions of 0.1 mol dm^{-3} Co^{2+}(aq) and 0.2 mol dm^{-3} SCN$^-$(aq) were mixed. The intensity of the blue colour of the resultant solution was measured using a colorimeter. The maximum colour intensity was observed when 2 cm^3 of SCN$^-$(aq) was added to 1 cm^3 of Co^{2+}(aq). Deduce the identity of the species responsible for the blue solution. [2]

(d) When cobalt(II) chloride is dissolved in aqueous ammonia, it forms $[Co(NH_3)_6]^{2+}$ which is oxidised by air to the +3 oxidation state.

    (i) Explain why cobalt shows variable oxidation states as compared to a main group element like calcium. [2]

    (ii) With the aid of the *Data Booklet* and the information below, calculate the $E^{\ominus}_{cell}$ for the oxidation of $[Co(NH_3)_6]^{2+}$ by atmospheric oxygen.

$$[Co(NH_3)_6]^{3+} + e^- \ll [Co(NH_3)_6]^{2+} \qquad E = +0.17 \text{ V}$$

[1]
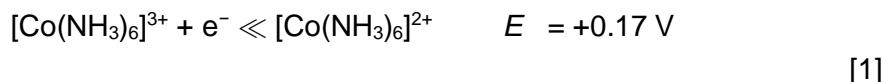
(e) **S** and **T** are ionic compounds which contain six-coordinate cobalt(III) complex ions, whose ligands are either NH_3 or Cl^-.

When excess aqueous $AgNO_3$ is added to 1 mole of **S** and 1 mole of **T** separately, 2 moles of a white precipitate is formed from **S** while 1 mole of the same white precipitate is formed from **T**.

    (i) Identify the white precipitate and explain why different amounts of the white precipitate are formed from **S** and **T**. [2]

    (ii) Draw the cobalt(III) complex ion in **S**, showing clearly how the ligands are bonded to the central metal ion. [1]

    (iii) The cobalt(III) complex ion in **T** exhibits *cis-trans* isomerism. Suggest the structure of the *trans* isomer. [1]

(f) Cobalt is used as a heterogeneous catalyst in the synthesis of aldehydes from carbon monoxide and water.

Describe the mode of action of the cobalt catalyst in the reaction. [3]

[Total: 24]

Section B
Answer **one** question from this section.

4 (a) The world's first implantable cardiac pacemaker is powered by zinc and platinum electrodes which are placed directly within the body tissues.

These electrodes in the body fluid at a pH of 7.4 form a 'biogalvanic' cell in which zinc is oxidised to zinc hydroxide and oxygen is reduced.

(i) State the polarities of the zinc and platinum electrodes and write a half-equation for the reaction that occurs at **each** electrode. [3]

(ii) Given that the value of $\Delta G^\ominus$ at 298 K for the reaction in the biogalvanic cell is –637 kJ per mole of oxygen reduced, calculate a value for $E^\ominus_{cell}$.

Hence, determine the value of the standard reduction potential of zinc hydroxide. [2]

(iii) A pacemaker operates at an average current of 8.0×10^{-4} A. Calculate how long the pacemaker will last when 5.0 g of zinc electrode is used before it needs to be replaced. Give your answer to the nearest day. [3]

(b) Zinc and silver are often present as impurities in crude copper obtained from minerals.

Explain, in terms of electrode reactions, how zinc and silver are removed in the industrial process of the purification of copper, using relevant data from the *Data Booklet*. Illustrate your answer with a labelled diagram. [4]

(c) Zinc oxide is used as a catalyst in the condensation of ethylene glycol and urea. One of the products formed is ethylene urea ($M_r = 87.0$),

urea   ethylene glycol   ethylene urea
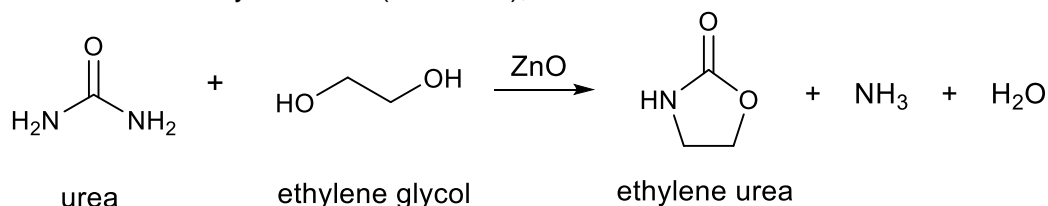
(i) The reaction between ethylene glycol and urea also produces two other molecules, **X** ($M_r = 86.0$) and **Y** ($M_r = 88.0$). Suggest the structures of **X** and **Y**. [2]

(ii) Suggest the products formed when ethylene urea is heated with aqueous sodium hydroxide. [2]

(d) Zinc chloride may be used in the free radical substitution of but-1-ene as shown below. N-bromosuccinimide (NBS) is the source of molecular bromine, Br_2.
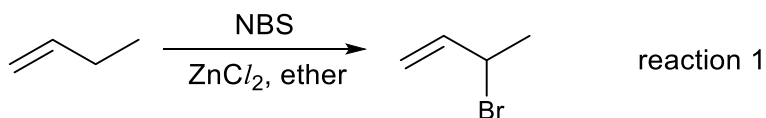
In the initiation step below, $ZnCl_2$ (initiator•) reacts with Br_2 to form Br• radicals:

$$initiator• + Br–Br \rightarrow initiator–Br + Br•$$
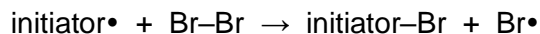
(i) Draw curly arrows to show the movement of electrons in the initiation step shown above. [1]

(ii) Write equations for the propagation steps in the mechanism for reaction 1, starting from the Br• radical. The use of curly arrows is **not** required. [2]

(iii) NBS is a preferred source of Br_2 as it maintains a low concentration of Br_2 in this reaction. Suggest why liquid bromine is not directly added to but-1-ene instead. [1]

[Total: 20]

5 (a) Describe and explain the trend and variations in first ionisation energies of the Period 3 elements from sodium to chlorine. [3]

(b) The halogens can form many interhalogen compounds. Most interhalogen compounds contain two halogens and have the general formula XY_n where n = 1, 3, 5 or 7.

ClF_3 is an interhalogen compound which exists as a colourless gas.

(i) ClF_3 and Cl_2 react to form another interhalogen compound. No other product is formed in the reaction.

State the oxidation numbers of chlorine in ClF_3 and Cl_2 and write an equation for the reaction between ClF_3 and Cl_2. [2]

The standard enthalpy change of formation, $\Delta H^{\ominus}_f$, of $ClF_3(g)$ is -163 kJ mol^{-1}.

(ii) What can you infer about the stability of ClF_3 from its standard enthalpy change of formation? [1]

(iii) Use the standard enthalpy change of formation, $\Delta H^{\ominus}_f$, of $ClF_3(g)$ and data from the *Data Booklet* to determine a value for the bond energy of the Cl–F bond. [2]

Another interhalogen compound is ICl_3. In the solid state, ICl_3 exists as a dimer, I_2Cl_6, which consists of two bridging Cl atoms. The shape around each iodine atom is square planar.

(iv) Draw the structure of the I_2Cl_6 dimer including its co-ordinate (dative covalent) bonds. [2]

Cyclic esters are called lactones. One of the most effective ways to synthesise lactones is iodolactonisation, which involves the addition of an oxygen and iodine across a carbon-carbon double bond. An example using 4-pentenoic acid is shown below.

4-pentenoic acid → 1. NaHCO$_3$, 2. I$_2$ → **A**
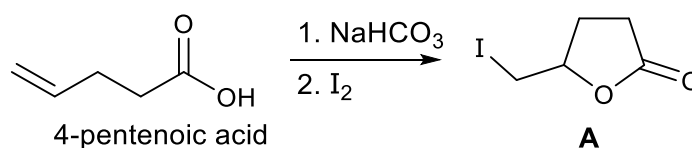
(c) (i) Draw the structure of the organic product formed when 4-pentenoic acid reacts with NaHCO$_3$. [1]

(ii) Hence, suggest a mechanism for the formation of compound **A** from your product in **(c)(i)**.

Show all charges and relevant lone pairs and show the movement of electron pairs by using curly arrows. [2]

(d) Compound **B** contains only carbon, hydrogen and oxygen and exhibits stereoisomerism. 1 mole of **B** produces 4 moles of carbon dioxide gas when heated with acidified potassium manganate(VII). No other carbon-containing product is formed in the reaction with potassium manganate(VII).1 mole of **B** also reacts with 2 moles of aqueous NaOH.

Deduce the structure of **B**, giving your reasoning. [3]

(e) Both non-cyclic esters and lactones undergo hydrolysis reactions.
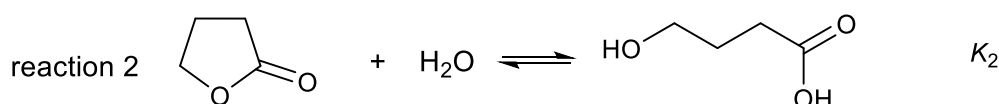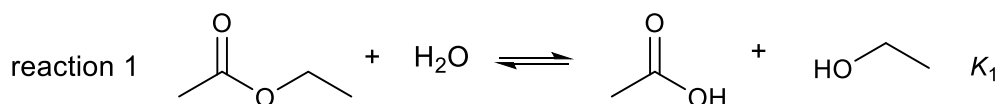
(i) State the reagents and conditions needed to carry out the hydrolysis. [1]

(ii) State and explain whether the ΔH for the two reactions would be similar or different. [1]

(iii) The ΔS for reaction 1 is more positive than the ΔS for reaction 2. Use this information, and your answer to **(e)(ii)**, to compare the ΔG for both reactions and hence the magnitudes of the equilibrium constants, K_1 and K_2. [2]

[Total: 20]

END OF PAPER

Paper 3

1 **(a)** **(i)** $MgCO_3(s) \rightarrow MgO(s) + CO_2(g)$ **[1]**
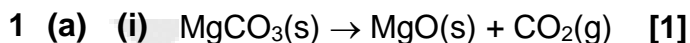
(ii) $\text{L.E} \propto \dfrac{q_+ q_-}{r_+ + r_-}$ **[1]**

Both $MgCO_3$ and MgO have the <u>same charges and cationic radius</u> **[0.5]**
<u>Anionic radius for CO_3^{2-} is bigger than O^{2-}</u> **[0.5]**
Magnitude of L.E. of $MgCO_3$ is smaller than that of MgO.

(iii) **ΔS is positive** as **gaseous CO_2 is evolved [1]**. Hence, $-T\Delta S$ term is negative.
$\Delta G = \Delta H - T\Delta S$
Since the decomposition of $MgCO_3$ is endothermic, ΔH is positive.
So for the decomposition to be spontaneous, **for ΔG to be negative**, the decomposition should take place at **high temperature [1]**.

(iv) **$MgCO_3$** has the lower decomposition temperature. **[0.5]**

Both Mg^{2+} and Ba^{2+} have the same charge. The **ionic radius of Mg^{2+} is smaller than Ba^{2+} (0.5)**. So Mg^{2+} has a **higher charge density (0.5)** and a **greater polarizing power** and it can **distort the electron cloud of the CO_3^{2-} to a greater extent (0.5 for either point)**, **weakening** the C−O **covalent bonds** in CO_3^{2-} to a **greater extent (0.5)**, hence **less energy is needed for decomposition (0.5).**

(b) **(i)** Type of reaction (reaction 1): Nucleophilic Addition **[1]**

Type of reaction (reaction 2): Elimination/Dehydration **[1]**

(ii)

[1]
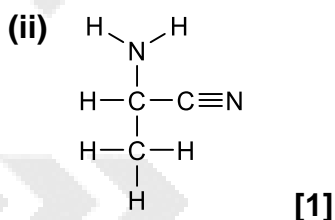
(iii) The geometry about the center C is **trigonal planar [1]**. Hence, there is **equal probability for the CN⁻ ion to attack from either side of the plane [1]**, giving rise to an equimolar mixture of two stereoisomers.

(iv)

[1]

(c) **(i)**
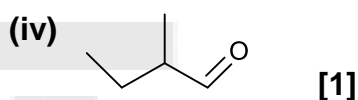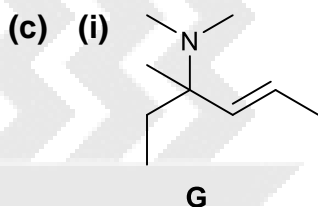
G **[1]**

(ii) Reagents and Conditions:
Step 1: LiAlH$_4$ in dry ether **[1]**
Step 2: excess concentrated H$_2$SO$_4$, heat **[1]**
Step 3: steam, concentrated H$_3$PO$_4$, high T high P **[1]**

Step 4:

, **[1]**

J:

[1]

2 (a) **(i)** C$_3$H$_4$O$_3$ **[1]**

(ii)
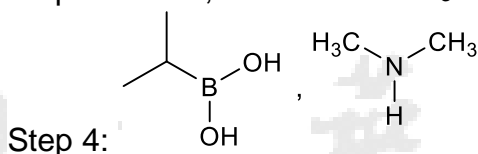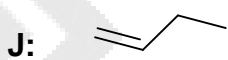
[1]
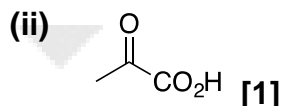
(b) constitutional/structural/functional group isomerism **[1]**

(c) The **LF** molecule is polar and can form strong/favourable permanent-dipole permanent-dipole interactions/hydrogen bonding/ion-dipole interactions with water molecules. **[1]**

(d) **(i)** When the onion is cooled, <u>less **LF** will vaporise and come into contact with the eyes</u>. **[1]**

(ii) Heating the onion can <u>denature the enzyme *LF synthase*</u> so that **LF** <u>will not be formed</u>. **[1]**

(e) **(i)** condensation **[1]**
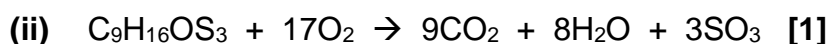
(ii) C$_9$H$_{16}$OS$_3$ + 17O$_2$ → 9CO$_2$ + 8H$_2$O + 3SO$_3$ **[1]**

(iii) n(cepaene) = 5 x 10^{-3} / 236.3 = 2.116 x 10^{-5} mol **[½]**
n(O$_2$) = 2.116 x 10^{-5} x 17 = 3.597 x 10^{-4} = 3.60 x 10^{-4} mol **[½] ecf from ii**
volume of O$_2$ mixture at r.t.p. = 3.597 x 10^{-4} x 24000 = 8.63 cm^3 **[½]**
volume of mixture = 8.63 x 100/40 = 21.6 cm^3 **[1]**

(iv) Role of copper: reducing agent **[1]**
Cu + ½O$_2$ → CuO **[1]**
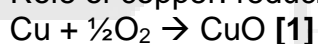
(v) The blue crystals are CuSO$_4$ **[1]**, which can be formed from the reaction of CuO with SO$_3$. **[1]**

$$CuO + SO_3 \rightarrow CuSO_4$$
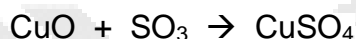
(vi) Order of gases released: CO_2, then SO_2, then water. **[1]**

CO_2 is a non-polar molecule, hence intermolecular forces are the weakest – only dispersion forces, so it is released first at a lower temperature. followed by SO_2.

SO_2 is a polar molecule with *both* intermolecular permanent-dipole permanent-dipole interactions, which are stronger than dispersion forces, *and* dispersion forces, which are also stronger than those of CO_2 due to SO_2 having more electrons and the larger electron cloud size than CO_2.

Water has intermolecular hydrogen bonding, which are the strongest intermolecular forces, and most energy required to vapourise it, and hence it is released last.

[1] correct types of intermolecular forces for all 3 molecules
[1] correct comparison of the strength of the 3 different intermolecular forces and relate to energy required to overcome the intermolecular forces for the gas to escape to the detector.

3 (a) Transition elements are **d-block elements** that **form one or more stable ions** with **partially filled d-subshell**. **[1]**

(b) (i) Precipitation occurs when I.P. = Ksp

For Cr^{3+}:
$Ksp = [Cr^{3+}][OH^-]^3$

$1.6 \times 10^{-20} = 1.23 \times 10^{-2}[OH^-]^3$
$[OH^-] = 1.09 \times 10^{-6}$ mol dm^{-3} **[1]**

For Co^{2+}:
$Ksp = [Co^{2+}][OH^-]^2$

$5.92 \times 10^{-15} = 5.77 \times 10^{-3}[OH^-]^2$
$[OH^-] = 1.01 \times 10^{-6}$ mol dm^{-3} **[1]**

Since the $[OH^-]$ required for IP = Ksp is similar for both precipitates to form, it does not allow for the separation of the two metal ions. **[1]**

(ii) **either**

$Cr(OH)_3$ is sparingly soluble and dissolves to give small concentrations of Cr^{3+} and OH^-.

$Cr(OH)_3 \ll Cr^{3+}$ (aq) $+ 3OH^-$ (aq)   (1)   **[1]**
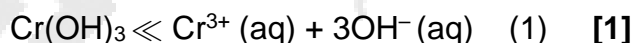
When excess OH^- is added, complex formation takes place.
Cr^{3+} (aq) $+ 6OH^-$ (aq) $\ll [Cr(OH)_6]^{3-}$ **[1] (accept if $[Cr(OH)_4^-]$)**

The [Cr^{3+}] falls shifting the position of equilibrium of (1) to the right, causing the precipitate to dissolve. **[1]**

or

$[Cr(H_2O)_3(OH)_3]$ (s) + $3OH^-$ (aq) $\ll$ $[Cr(OH)_6]^{3-}$ + $3H_2O$ (l) **[2]**
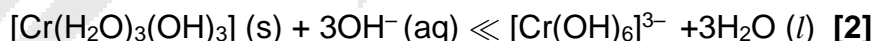
(**[1] for [$Cr(H_2O)_3(OH)_3$] and [$Cr(OH)_6]^{3-}$, [1] for balancing equation)**

When the [OH^-] increases, position of equilibrium shifts forward to offset the increase in the [OH^-] concentration. This causes the solid to dissolve. **[1]**

(c) (i)
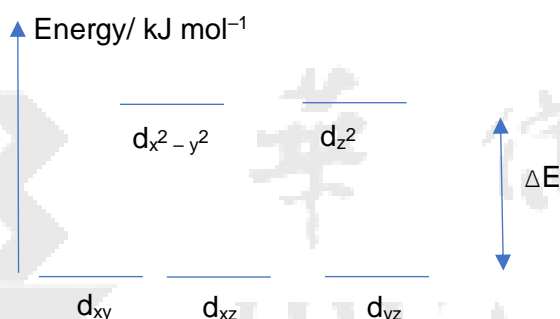
[1] (no need to show axes and ΔE)

The 5 *d* orbitals can be classified into two groups. The $d_{x^2-y^2}$ and d_{z^2} have their lobes along the axis, while the d_{xz}, d_{xy} and d_{yz} have lobes in between the axis. Since the ligands approach the central metal ion along the axis, **the repulsion felt by the d_{xz}, d_{xy} and d_{yz} orbitals is less than for the $d_{x^2-y^2}$ and d_{z^2} orbitals**. **[1]** As such the d_{xz}, d_{xy} and d_{yz} orbitals are at the lower energy.

(ii) When an electron is promoted from the lower energy d-orbitals, **energy is absorbed corresponding to a wavelength in the visible spectrum**. **[1]**

The colour observed is the **complement** of the colours absorbed. **[1]**

(iii) Ligand exchange reaction. **[1]**

(iv) Identify the 1:4 ratio for Co^{2+}: SCN^- **[1]**

$[Co(SCN)_4]^{2-}$ **[1]**

(d) (i) The **energy levels of 3d and 4s electrons in cobalt are similar**, hence once the 4s electrons are removed, some or all of the 3d electrons may also be removed without requiring much more energy. **[1]**

However in calcium, once the 4s electrons are removed, the subsequent removal of electrons must come **from an inner quantum shell which requires too much energy**. **[1]**

(ii) $[Co(NH_3)_6]^{3+}$ + e $\ll$ $[Co(NH_3)_6]^{2+}$ E = +0.17 V

O_2 + $2H_2O$ + 4e $\ll$ $4OH^-$ E = +0.40 V
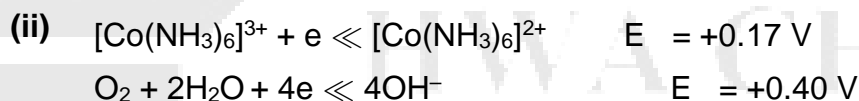
$E_{cell} = +0.40 - (+0.17) = +0.23V$ **[1]**

(e) (i) AgCl **[1]**

The number of moles of **free** Cl^- ions/ Cl^- **counter ions** are different in both the complexes. **[1]**

S has one Cl^- ion datively bonded to the Co^{3+} while **T** has two Cl^- ion datively bonded to the Co^{3+} central metal ion.

(ii) **complex from S**
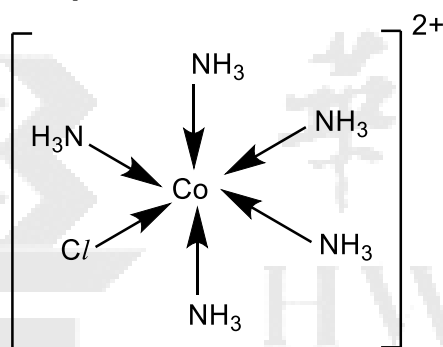
[1] (mark for dative bonds and positive charge)

(iii) **complex from T**
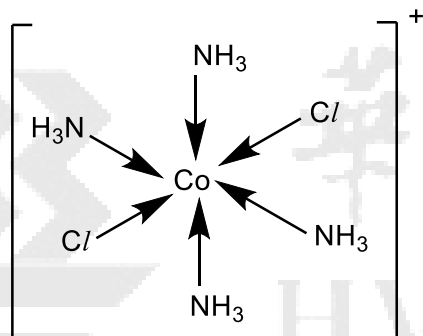
[1] (as long as *trans* structure is shown, ignore dative bonds/charges etc.)

(f) Reactant molecules, CO and H$_2$O are **adsorbed onto the active sites** of the catalyst surface by formation of weak attractive forces.

This brings the **molecules closer together, weakens the C˜O and O–H bond**, **orientating them in the right position for reaction**, hence lowering the activation energy. (**[2]** for all 3 points, **[1]** for any 2 points)

Once the reaction has taken place, the aldehyde formed **desorbs and diffuses away** from the catalyst surface so that the **active sites are exposed** for further reaction.

[1] adsorb and desorb + active sites

4 (a) (i) Zn($-$): $Zn + 2OH^- \rightarrow Zn(OH)_2 + 2e^-$ **[1]**
Pt(+): $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ **[1]**
[1] on polarity

(ii) $\Delta G = -nFE^{\ominus}_{cell}$

$-637 \times 1000 = -(4)(96500)E_{cell}$

$E^{\ominus}_{cell} = 1.65$ V **[1]**

$E_{cell} = E_{O2/OH^-} - E_{Zn(OH)2/Zn}$

$+1.65 = 0.40 - E_{Zn(OH)2/Zn}$

$E_{Zn(OH)2/Zn} = -1.25$ V **[1] ecf**

(iii) Amount of Zn = $\dfrac{5}{65.4}$ = 0.0765 mol   **[0.5]**

Amount of electrons = 2 × 0.0765 = 0.153 mol **[0.5]**
Since charge on 1 mol of electron = 96500 C
∴ charge = 0.153 × 96500 = 14755 C

$t = \dfrac{Q}{I} = \dfrac{14755}{0.8 \times 10^{-3}}$ **[1] substitution, ecf**

$= 1.84 \times 10^7$ s
= 213 days   **[1] ecf; conversion to exact days**

(b)
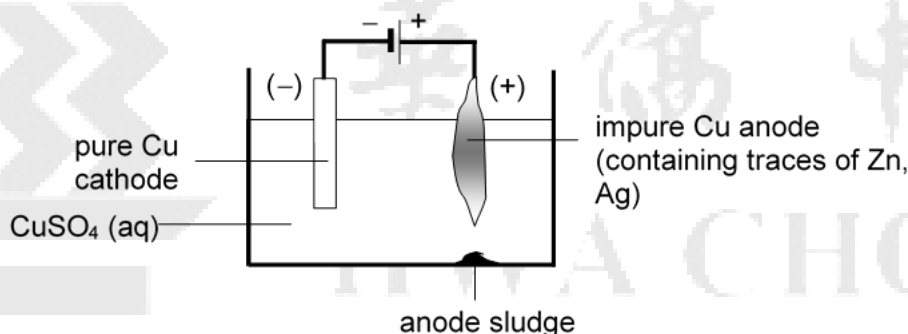
[1] deduct 0.5 for every mistake

$E^{\ominus}_{Zn2+/Zn} = -0.76$ V
$E^{\ominus}_{Cu2+/Cu} = +0.34$ V
$E^{\ominus}_{Ag+/Ag} = +0.80$ V **(0.5 for these 3 values correctly quoted)**

At the <u>anode</u>, Zn is oxidised to Zn^{2+} (can be described in equation form) as $E^{\ominus}_{Zn2+/Zn}$ <u>is more negative</u> than $E^{\ominus}_{Cu2+/Cu}$ and dissolves into the <u>electrolyte</u>. **[0.5]**

Ag will not be oxidised as $E^{\ominus}_{Ag+/Ag}$ <u>is more positive</u> than $E^{\ominus}_{Cu2+/Cu}$, **[0.5]** hence Ag drops off as <u>anode sludge</u>. **[0.5] can be drawn in diagram**

At the <u>cathode</u>, only Cu^{2+} is reduced as $E^{\ominus}_{Cu2+/Cu}$ <u>is more positive than</u> $E^{\ominus}_{Zn2+/Zn}$. **[0.5]** Hence Cu is collected, whereas <u>Zn^{2+} is not reduced/remains in solution</u>. **[0.5]**

(c) (i)

X: Y:
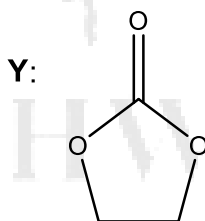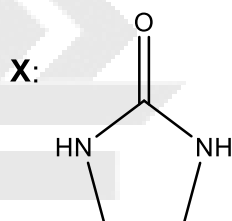
[1] each; deduct 1m if X and Y are swapped

(ii) CO_3^{2-} or HCO_3^- **[1]**
$HOCH_2CH_2NH_2$ **[1]**

(d) (i)

initiator• ⌒ Br—Br ⟶ initiator-Br + Br•   **[1]**

[1/2] if only the arrows of the homolytic fission is shown

(ii)

 + Br• ⟶ + HBr

 + Br_2 ⟶ + Br•
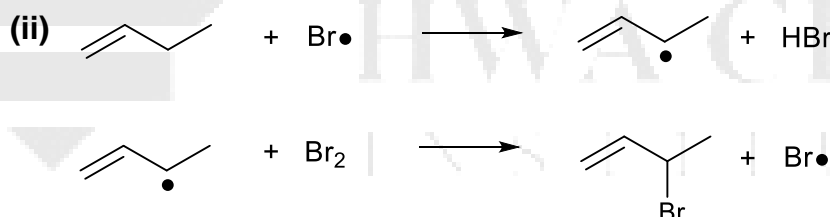
[1] per step

(iii) If liquid bromine were added, the high concentration of Br_2 will result in <u>electrophilic addition</u> across the <u>C=C bond</u>. **[1]**

5 (a) First ionisation energy (I.E.) <u>generally increase</u> across Period 3. **[½]**
Across the period, <u>nuclear charge</u> (or number of protons) <u>increases but shielding effect remains relatively constant</u> so effective nuclear charge increase and the outermost electrons are more strongly attracted to the nucleus. **[½]**

The <u>1st I.E. of A*l*</u>, $[Ne]3s^23p^1$, <u>is lower than that of Mg</u>, $[Ne]3s^2$. **[½]**
The electron is removed from the <u>3p subshell in A*l*</u>, which is <u>further away</u> from the nucleus compared to the 3s subshell in Mg. **[½]**

The <u>1st I.E. of S</u>, $[Ne]3s^23p^4$, <u>is lower than that of P</u>, $[Ne]3s^23p^3$. **[½]**
The <u>inter-electronic repulsion between the paired 3p electrons</u> in S is absent in P as the 3p electrons are unpaired. **[½]**

(b) (i) Oxidation number of chlorine in C*l*F_3 is +3; in C*l*$_2$ is 0 **[½, ½]**
C*l*F_3 + C*l*$_2$ → 3C*l*F **[1]** no ecf

(ii) C*l*F_3 is (energetically) <u>more stable than</u> its constituent <u>elements</u> (C*l*$_2$ and F_2).**[1]**

Accept:
The decomposition of C*l*F_3 into its elements is not feasible.
The formation of C*l*F_3 from its elements is feasible.

(iii)

$$\text{1/2 } Cl\text{---}Cl \ + \ \text{3/2 } F\text{---}F \longrightarrow ClF_3$$
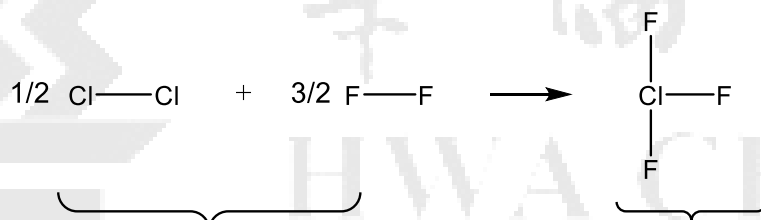
bonds broken = 1/2 × 244 + 3/2 × 158   bonds formed = 3 × BE(Cl–F)

−163 = 1/2 × 244 + 3/2 × 158 − **3** × BE(Cl–F)

BE(Cl–F) = 522 ÷ 3 = **174 kJ mol⁻¹**

Correct BE(Cl–Cl), BE(F–F) and three Cl–F bonds in one ClF₃ molecule **[1]**
Correct BE(Cl–F) with units (no negative sign) **[1]**

(iv)
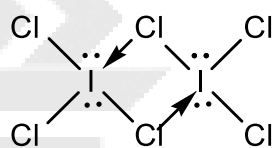
correct shape and lone pairs **[1]**
correct dative bonds (from Cl to I) **[1]**

(c) (i)
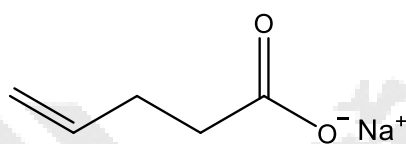
[1]

(ii)
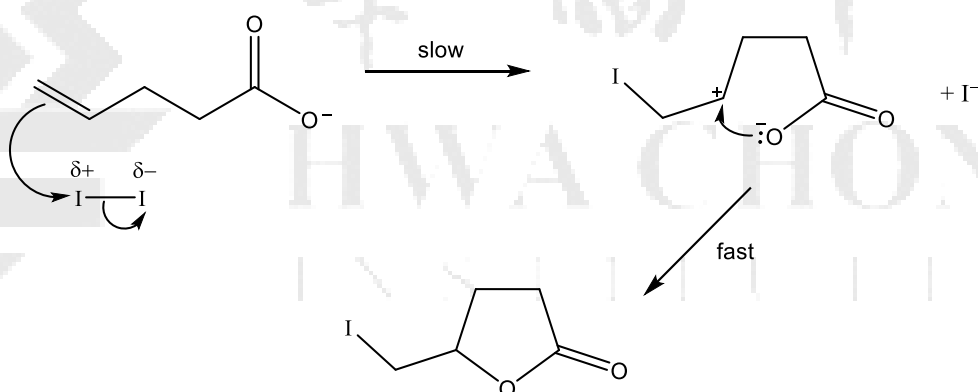
Partial charges on I–I, positive charge on carbocation, lone pair on O atom, 3 curly arrows, first step is slow step **[2]**
−½ mark for each mistake

(d)

1 mol **B** undergoes <u>oxidative cleavage</u> to give only 4 mol CO₂	⇒	**B** contains <u>4 C atoms</u> and one <u>C=C bond</u>
1 mol **B** undergoes <u>neutralisation</u> with 2 mol NaOH	⇒	**B** contains <u>two –CO₂H</u>
B exhibits stereoisomerism	⇒	**B** exhibits <u>cis-trans isomerism</u>
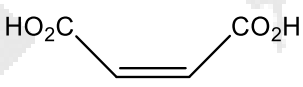
5-6 correct **[2]**
any 4 **[1.5]**

B is   HO₂C⎯⎯⎯CO₂H   (not required to show cis or trans arrangement)   **[1]**

(e) **(i)** dilute HC*l*, heat
(accept NaOH(aq), heat followed by dilute aqueous acid e.g. HC*l*)   **[1]**

(ii) ΔH would be <u>similar</u> (or the same) as the <u>same bonds are broken and formed</u>.
   [1]

(iii) Reaction 1 has a <u>more negative / less positive ΔG</u> (from $\Delta G = \Delta H - T\Delta S$).   **[1]**
ecf from **(e)(ii)**

Hence, <u>K_1 is larger</u> than K_2 (from $\Delta G = -RT\ln K$).   **[1]**
ecf from ΔG

	HWA CHONG INSTITUTION
	C2 Preliminary Examination
	Higher 2

NAME		CT GROUP	18S

CHEMISTRY 9729/04

Paper 4 Practical

28 August 2019

2 hours 30 minutes

Candidates answer on the Question Paper

READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work you hand in.
Give details of the practical shift and laboratory where appropriate, in the boxes provided.
Write in dark blue or black pen.
You may use 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.
You may lose marks if you do not show your working or if you do not use appropriate units.
Qualitative Analysis Notes are printed on pages 17 and 18.

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

Shift
Laboratory

For Examiner's Use	
1	
2	
3	
4	
Total	

This document consists of **18** printed pages.

Answer **all** the questions in the spaces provided.

1 **Determination of the enthalpy change of neutralisation, ΔH_{neut}, of a strong acid by a strong base**

The enthalpy change of neutralisation, ΔH_{neut}, is the enthalpy change when one mole of water is formed during a neutralisation reaction as shown in equation 1.

equation 1 $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$

FA 1   is a solution of sulfuric acid, H_2SO_4
FA 2   is 1.50 mol dm^{-3} sodium hydroxide, NaOH

You will perform a series of experiments using different volumes of **FA 1** and **FA 2** which together give a total volume of 50 cm^3. The change in temperature, ΔT, for each experiment will be determined and used to plot a graph of ΔT against volume of **FA 1** used.

You will then use data from the graph to determine the concentration of sulfuric acid in **FA 1**, and a value for the enthalpy change of neutralisation, ΔH_{neut}.

(a)   (i)   Determining the change in temperature for a series of reactions between FA 1 and FA 2

1. Place the Styrofoam cup in a 250 cm^3 beaker to prevent it from tipping over. Use a measuring cylinder to transfer 10.0 cm^3 of **FA 1** into the cup.

2 Use a measuring cylinder to measure 40.0 cm^3 of **FA 2.**

3. Measure the temperature of the **FA 1** solution using the thermometer. Record the initial temperature of **FA 1** as T_{FA1}.

4. Add **FA 2** to **FA 1** in the Styrofoam cup. Stir the mixture using the thermometer and record the maximum temperature, T_{max}, reached.

5. Wash and dry the Styrofoam cup.

6. Repeat steps 1 to 5 using 20.0 cm^3, 25.0 cm^3, 30.0 cm^3, 35.0 cm^3 and 40.0 cm^3 of **FA 1** and appropriate volumes of **FA 2** each time such that the total volume of the reacting mixture is 50.0 cm^3.

Keep the remaining FA 1 and FA 2 solutions for use in questions 2 and 4.

In an appropriate format in the space provided on **page 3**, record:

- all measurements of volumes used,
- all temperatures measured and the change in temperature, ΔT.

Results

[4]

(ii) On the grid provided, plot a graph of ΔT (y-axis) against volume of **FA 1** (x-axis) using the data you obtained in **1(a)(i)**.
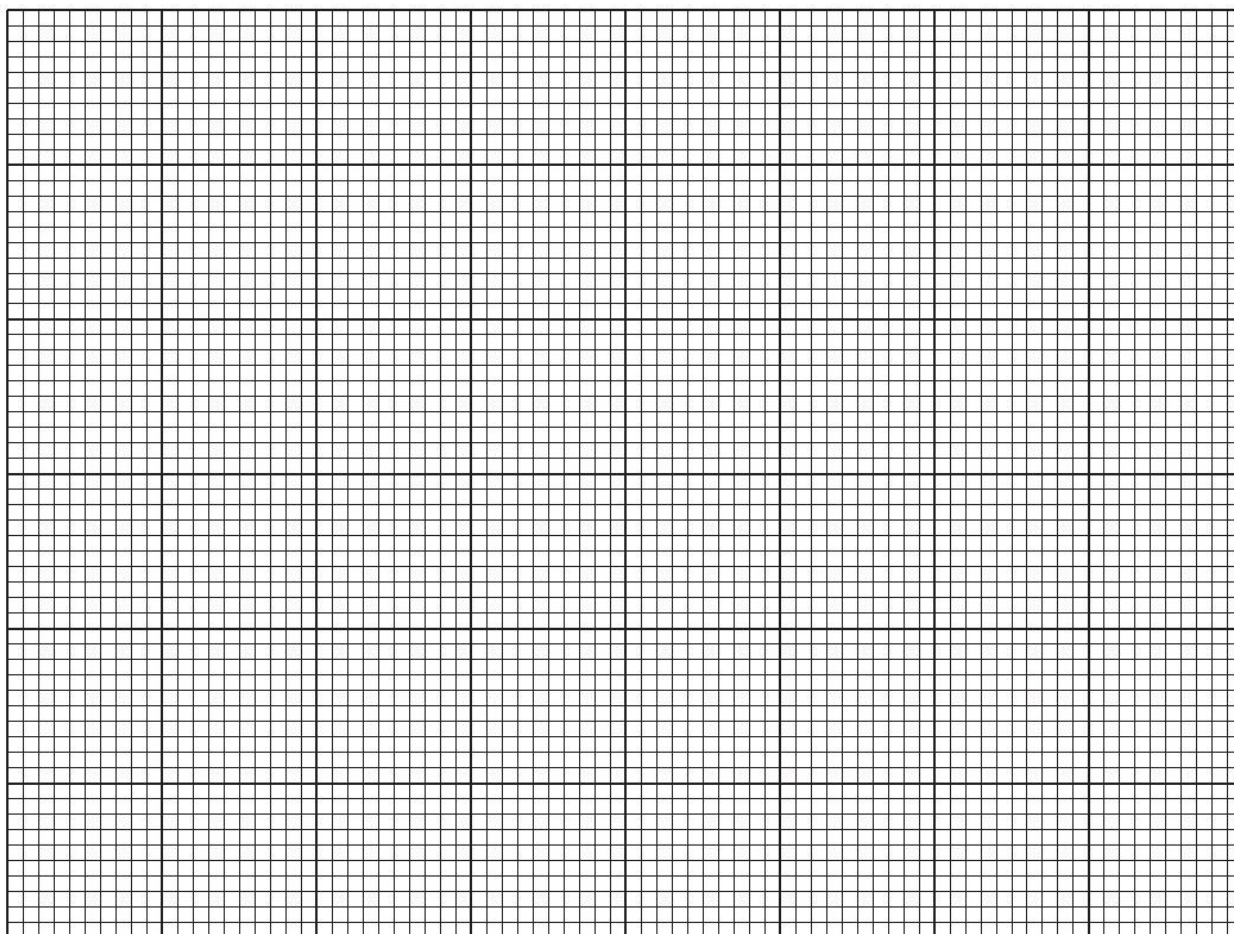
Draw two lines of best fit.

- The first best-fit line should be drawn using the plotted points before the maximum change in temperature.
- The second best-fit line should be drawn using the plotted points after the maximum change in temperature.

Extrapolate these lines until they cross.

[3]

(iii) Determine from your graph, the maximum change in temperature, ΔT_{max}, and the volume, V_{max}, of **FA 1** required to obtain this value.

$\Delta T_{max} = $ …………………………… $V_{max} = $ ……………………………
[1]

(b) Using your answers in **1(a)(iii),** calculate

(i) the concentration, in mol dm^{-3}, of H$_2$SO$_4$ in **FA 1**.

concentration of H$_2$SO$_4$ in **FA 1** = ...[1]

(ii) the heat change for the neutralisation reaction at ΔT_{max}.

You should assume that the specific heat capacity of the final solution is 4.18 J g^{-1}K^{-1}, and the density of the final solution is 1.00 g cm^{-3}.

heat change = ...[1]

(c) Using your answers from **1(b)(i)** and **1(b)(ii),** calculate a value for the enthalpy change of neutralisation, ΔH_{neut}.

ΔH_{neut} =..[1]

(d) Predict the effect on ΔH_{neut} if the experiment was repeated with malonic acid, $HO_2CCH_2CO_2H$, of the same concentration instead of sulfuric acid. Explain your answer.

……………………………………………………….………………………………………………

……………………………………………………….………………………………………………

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

(e) State one significant source of error in the experiment and suggest an improvement that can be made to reduce this error.

……………………………………………………….………………………………………………

……………………………………………………….………………………………………………

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

[Total: 13]

2 **Determination of water of crystallisation in a hydrated iron(III) salt**

FA 3 is hydrated iron(III) sulfate with formula $Fe_2(SO_4)_3 \cdot nH_2O$. The addition of excess zinc to a solution of **FA 3** reduces the Fe^{3+} ions to Fe^{2+} ions.

The amount of Fe^{2+} ions can be determined quantitatively by titration against a standard solution of potassium manganate(VII), $KMnO_4$. The reaction is shown in equation 2.

equation 2 $\qquad 5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$

In this experiment, you will prepare a standard solution using **FA 3** and perform titrations to determine the value of n, the water of crystallisation in **FA 3**.

You are also provided with
  FA 4, 0.0200 mol dm^{-3} potassium manganate(VII), $KMnO_4$,
  zinc powder.

You will also need access to the **FA 1** solution you used earlier.

(a) **Preparation of standard solution of hydrated iron(III) salt**

1. Weigh accurately the sample of **FA 3** provided with the weighing bottle. Transfer all the solid into a 250 cm^3 beaker. Determine the mass of solid **FA 3** used and record all your weighings, to an appropriate level of precision, in the space below.

[1]

2. Use a measuring cylinder to add about 100 cm^3 of **FA 1** to the beaker. Stir the mixture with a glass rod for 3 minutes. Ignore any cloudiness that remains.

3. Transfer the solution into a 250 cm^3 volumetric flask. Rinse the beaker with deionised water and pour the washings into the volumetric flask.

4. Make up to the 250 cm^3 mark with deionised water, stopper and mix thoroughly by inverting the flask a number of times.

5. Label this solution **FA 5**.

(b) **Preparation of Fe^{2+} solution from FA 5**

6.   Use a measuring cylinder to transfer 100 cm^3 of **FA 5** into a **dry** 250 cm^3 beaker.

7.   Add all the zinc powder provided in the bottle into the beaker. Cover the beaker with a watch glass.

8.   Allow the reaction to take place for about 5 minutes, stirring the reaction mixture from time to time. Record your observations in the space below.

Observations in step 8

[1]

9.   Filter the mixture into the **dry** conical flask provided using **dry** filter paper and filter funnel. Ignore any reaction that may still be taking place.

10.   Label the filtrate as **FA 6**. Proceed to **2(c)** once you have collected sufficient filtrate.

(c) **(i)** Titration of **FA 6** against **FA 4**

11.   Fill a burette with **FA 4**.

12.   Use a pipette to transfer 10.0 cm^3 of **FA 6** into a 250 cm^3 conical flask.

13.   Use a measuring cylinder to add about 10 cm^3 of **FA 1** to this flask.

14.   Run **FA 4** from the burette into this flask until the appearance of the first permanent pale-pink colour.

15.   Record your titration results, to an appropriate level of precision, in the space below.

16.   Repeat steps 12 to 15 until consistent results are obtained.

Keep the remaining FA 1 and FA 4 solutions for use in question 4.

Titration results

[3]

(ii) From your titrations, obtain a suitable volume of **FA 4**, $V_{FA\ 4}$, to be used in your calculations. Show clearly how you obtained this volume.

$V_{FA\ 4}$ = ………………………………………………[3]

(d) **(i)** Calculate the amount of Fe^{2+} in 10.0 cm^3 of **FA 6**.

amount of Fe^{2+} in 10.0 cm^3 of **FA 6** = ………………………………………… [1]

(ii) In step 7, an excess of zinc was added to convert the Fe^{3+} to Fe^{2+}.

Calculate the amount of Fe^{3+} in 250 cm^3 of **FA 5**.

amount of Fe^{3+} in 250 cm^3 of **FA 5** = ………………………………………. [1]

(iii) Use your answer from **2(d)(ii)** to calculate the M_r of the hydrated iron(III) sulfate, $Fe_2(SO_4)_3.nH_2O$, in **FA 3**.

M_r of the hydrated iron(III) sulfate = ………………………………….

Hence, deduce the value of n, the water of crystallisation in the hydrated iron(III) sulfate.

[A_r: Fe, 55.8; S, 32.1; O, 16.0; H, 1.0]

n = ………………………….…..

[5]

(e) Explain all the observations in step 8 in terms of the chemical processes involved.

....

....

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

(f) In step 9, excess zinc was filtered off before titration of **FA 6** against **FA 4** to avoid any possible reaction between zinc and **FA 4**.

Suggest another reason why it was necessary to filter off the excess zinc metal, and what effect failing to do it would have on the titre values.

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

[Total: 17]

3 Planning

Iron(III) ion, Fe^{3+}(aq), and thiocyanate ion, SCN^-(aq), react to give the thiocyanatoiron(III) complex ion, $FeSCN^{2+}$(aq), as shown in equation 3.

equation 3 $\qquad\qquad\qquad Fe^{3+}$(aq) + SCN^-(aq) $\rightleftharpoons$ $FeSCN^{2+}$(aq)
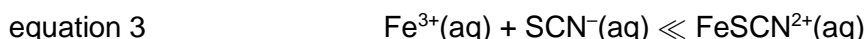
(a) Write an expression for the equilibrium constant, K_c, of the reaction between Fe^{3+}(aq) and SCN^-(aq).

[1]

The colour of $FeSCN^{2+}$(aq) varies from deep red to orange depending on its concentration. It is possible to determine the concentration of a solution of $FeSCN^{2+}$(aq) by placing 3 cm^3 of the solution inside a glass sample holder, known as a *cuvette*, into the spectrophotometer. The machine measures the amount of light absorbed when blue light is shone through the solution. The amount of light absorbed is expressed as an *absorbance value*. The more concentrated the solution, the higher the absorbance value.

(b) A plot of absorbance against concentration is known as a *calibration line*. Fig. 3.1 shows the calibration line obtained when the absorbance values of a series of standard solutions containing $FeSCN^{2+}$(aq) were measured.

absorbance

0
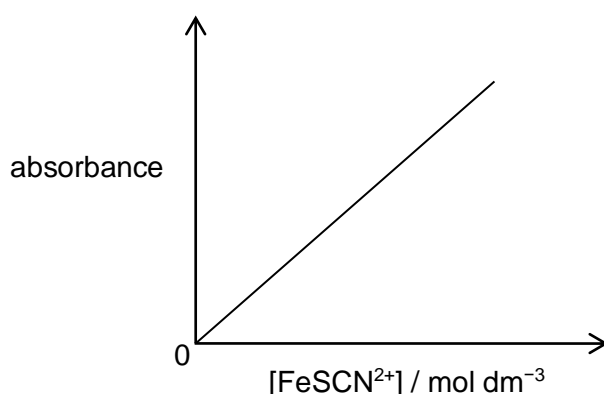
$[FeSCN^{2+}]$ / mol dm^{-3}

Fig. 3.1

One of the standard solutions was prepared by mixing 5.00 cm^3 of 0.200 mol dm^{-3} aqueous iron(III) nitrate, $Fe(NO_3)_3$, and 5.00 cm^3 of 2.00 x 10^{-3} mol dm^{-3} potassium thiocyanate, KSCN.

Show that the concentration of $FeSCN^{2+}$(aq) is 1.00 x 10^{-3} mol dm^{-3} in this standard solution, and explain why the amount of aqueous iron(III) nitrate used must be in large excess in the standard solutions used to obtain the calibration line.

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

To determine a value for K_c, known amounts of $Fe^{3+}(aq)$ and $SCN^-(aq)$ are mixed to produce a solution of $FeSCN^{2+}(aq)$. The absorbance of this solution is then measured. Using the calibration line in Fig 3.1, the concentration of $FeSCN^{2+}(aq)$ can be determined. This can be used to calculate the concentrations of $Fe^{3+}(aq)$ and $SCN^-(aq)$ in the equilibrium mixture and hence K_c.

The following equation represents the relationship between K_c and temperature in kelvin, T:

$$\ln K_c = -\frac{\Delta H^\ominus}{R}\left(\frac{1}{T}\right) + \frac{\Delta S^\ominus}{R}$$

R is the molar gas constant with a value of 8.31 J K^{-1} mol^{-1}.
$\Delta H^\ominus$ is the standard enthalpy change of reaction.
$\Delta S^\ominus$ is the standard entropy change of reaction.

A plot of $\ln K_c$ against $1/T$ can then be used to graphically determine $\Delta H^\ominus$ and $\Delta S^\ominus$.

(c) Plan an investigation to determine the effect of temperature, T, on the equilibrium constant, K_c of the reaction between $Fe^{3+}(aq)$ and $SCN^-(aq)$.

You may assume that you are provided with:
- 2.00×10^{-3} mol dm^{-3} iron(III) nitrate,
- 2.00×10^{-3} mol dm^{-3} potassium thiocyanate,
- a cuvette,
- access to a spectrophotometer and instructions for its use,
- the equipment normally found in a school or college laboratory.

In your plan you should include:
- an outline of how you would prepare a solution of $FeSCN^{2+}(aq)$,
- an outline of how you would determine the concentration of $FeSCN^{2+}(aq)$ in the solution at different temperatures,
- brief, but specific, details of how the concentrations, in mol dm^{-3}, of $Fe^{3+}(aq)$ and $SCN^-(aq)$ in the equilibrium mixture can be determined, and how you would use these concentrations to determine K_c for one of your chosen temperatures.

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(d) **(i)** Given that the reaction between $Fe^{3+}(aq)$ and $SCN^-(aq)$ is exothermic, sketch a graph you would expect to obtain using data obtained from **3(c)** on the axes in Fig 3.2.

Explain your answer.
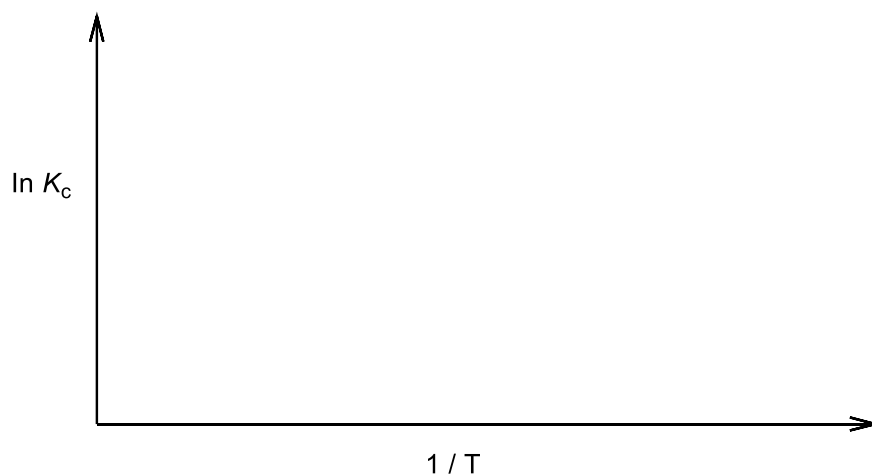
Fig. 3.2

Explanation …………………………………………………..…………………………….…...

………………………………………………………………………………………………......

[2]

(ii) Describe how would you use your graph in **3(d)(i)** to determine values for $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$.

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…………………………………………………………………………………………….…......

[2]

[Total: 13]

4 Investigation of some reactions involving manganese compounds

FA 7 is solid manganese dioxide, MnO_2.
FA 8 is an aqueous solution of hydrogen peroxide, H_2O_2.

In addition to access to the usual bench reagents, you are also provided with the following.
- aqueous sodium thiosulfate, $Na_2S_2O_3(aq)$

You will also need access to the **FA 1**, **FA 2** and **FA 4** solutions you used earlier.

Perform the tests described in Tables 4.1, 4.2 and 4.3 and record your observations. Test any gases produced.

Table 4.1

	test	observations
(a)	Place 1 cm depth of **FA 1** in a test-tube. Add a spatula of **FA 7** to this test-tube, followed by another 2 cm depth of aqueous potassium iodide. Filter the mixture into a clean test-tube and collect the filtrate. To the filtrate, add aqueous sodium thiosulfate dropwise, with shaking, until the solution first becomes colourless. Divide the filtrate into two portions.	
	To the first portion, add **FA 2** slowly until no further change is seen.	
	To the second portion, add aqueous ammonia slowly until no further change is seen.	

[3]

(b) Suggest the role of **FA 7** in the reaction occurring in **4(a)**. Explain your answer with **two** observations from your experiment.

Role of **FA 7** ………………………………………………………………

Explanation

…..………………………………………………………………………………………......................

…..………………………………………………………………………………………......................

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

Table 4.2

	test	observations
(c)	Place 3 cm depth of **FA 8** into a test-tube. Add a spatula of **FA 7** to this test-tube.	[1]

(d) The mixture in **4(c)** was filtered and the filtrate divided into two portions. When **FA 2** and $NH_3(aq)$ were added to the two portions respectively, no precipitate was formed.

Explain why this observation shows that **FA 7** plays a different role in the reaction taking place in **4(c)** as compared to **4(a)**.

…..………………………………………………………………………………….......................

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

(e) Hence, suggest the role of **FA 7** in the reaction in **4(c)** and justify your answer with an observation from your experiment.

Role of **FA 7**…………………………………………………………….……

Explanation

…..………………………………………………………………………………….......................

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

Question 4 continues on the next page.

Table 4.3

	test	observations
(f)	Place 1 cm depth of **FA 2** into a test-tube. Add 5 drops of aqueous potassium iodide and shake. Add **FA 4** to the mixture dropwise, with shaking, until 10 drops have been added. Then add 1 cm depth of aqueous barium nitrate slowly, with shaking, into the same test-tube. Filter the mixture into a boiling tube. Wash the residue thoroughly with deionised water. Discard the washings. Retain the residue for use in **4(g)**.	
(g)	Place the filter funnel with the residue from **4(f)** over a clean test-tube. Carefully add **FA 1** slowly until it covers the residue. Observe until no further changes are seen.	[2]

(h) When aqueous barium nitrate was added to the mixture in **4(f)**, a Mn-containing species was precipitated and collected as residue on filtration. When **FA 1** was then added to this residue in **4(g)**, two Mn-containing species, **X** and **Y**, were produced which could be found in the final residue and filtrate respectively.

Suggest the identities of **X** and **Y**.

Identity of **X** in the residue ……………………

Identity of **Y** in the filtrate ………………….....   [1]

(i) A white precipitate is also formed after adding **FA 1** in **4(g)** but it is unlikely that you will have noticed it. Suggest the identity of this white precipitate.

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

[Total: 12]

Qualitative Analysis Notes

[ppt. = precipitate]

(a)   Reactions of aqueous cations

cation	reaction with	
	NaOH(aq)	NH$_3$(aq)
aluminium, Al^{3+}(aq)	white ppt. soluble in excess	white ppt. insoluble in excess
ammonium, NH$_4^+$(aq)	ammonia produced on heating	-
barium, Ba^{2+}(aq)	no ppt. (if reagents are pure)	no ppt.
calcium, Ca^{2+}(aq)	white ppt. with high [Ca^{2+}(aq)]	no ppt.
chromium(III), Cr^{3+}(aq)	grey-green ppt. soluble in excess giving dark green solution	grey-green ppt. insoluble in excess
copper(II), Cu^{2+}(aq)	pale blue ppt. insoluble in excess	blue ppt. soluble in excess giving dark blue solution
iron(II), Fe^{2+}(aq)	green ppt., turning brown on contact with air insoluble in excess	green ppt., turning brown on contact with air insoluble in excess
iron(III), Fe^{3+}(aq)	red-brown ppt. insoluble in excess	red-brown ppt. insoluble in excess
magnesium, Mg^{2+}(aq)	white ppt. insoluble in excess	white ppt. insoluble in excess
manganese(II), Mn^{2+}(aq)	off-white ppt., rapidly turning brown on contact with air insoluble in excess	off-white ppt., rapidly turning brown on contact with air insoluble in excess
zinc, Zn^{2+}(aq)	white ppt. soluble in excess	white ppt. soluble in excess

(b) Reactions of aqueous anions

ion	reaction
carbonate, CO_3^{2-}	CO_2 liberated by dilute acids
chloride, Cl^-(aq)	gives white ppt. with Ag^+(aq) (soluble in NH_3(aq))
bromide, Br^-(aq)	gives pale cream ppt. with Ag^+(aq) (partially soluble in NH_3(aq))
iodide, I^-(aq)	gives yellow ppt. with Ag^+(aq) (insoluble in NH_3(aq))
nitrate, NO_3^-(aq)	NH_3 liberated on heating with OH^-(aq) and Al foil
nitrite, NO_2^-(aq)	NH_3 liberated on heating with OH^-(aq) and Al foil; NO liberated by dilute acids (colourless NO → (pale) brown NO_2 in air)
sulfate, SO_4^{2-}(aq)	gives white ppt. with Ba^{2+}(aq) (insoluble in excess dilute strong acids)
sulfite, SO_3^{2-}(aq)	SO_2 liberated on warming with dilute acids; gives white ppt. with Ba^{2+}(aq) (soluble in dilute strong acids)

(c) Tests for gases

gas	test and test result
ammonia, NH_3	turns damp red litmus paper blue
carbon dioxide, CO_2	gives a white ppt. with limewater (ppt. dissolves with excess CO_2)
chlorine, Cl_2	bleaches damp litmus paper
hydrogen, H_2	"pops" with a lighted splint
oxygen, O_2	relights a glowing splint
sulfur dioxide, SO_2	turns aqueous acidified potassium manganate(VII) from purple to colourless

(d) Colour of halogens

halogen	colour of element	colour in aqueous solution	colour in hexane
chlorine, Cl_2	greenish yellow gas	pale yellow	pale yellow
bromine, Br_2	reddish brown gas / liquid	orange	orange-red
iodine, I_2	black solid / purple gas	brown	purple

Paper 4

1 (a) (i)
- Tabulates volumes and temperature data in **(a)(i)**
  Table should contain correct headers and units. Data headers to include
  volume of **FA 1,** volume of **FA 2**, T_{FA1}, T_{max} and ΔT.   **[1]**

Volume of **FA 1** / cm³	Volume of **FA 2** / cm³	$T_{FA\,1}$ / °C	T_{max} / °C	ΔT / °C
10.0	40.0	32.0	36.0	4.0
20.0	30.0	32.0	39.5	7.5
25.0	25.0	32.0	41.5	9.5
30.0	20.0	32.0	41.0	9.0
35.0	15.0	32.0	38.5	6.5
40.0	10.0	32.0	36.0	4.0

- Complete 6 sets of volume/temperature readings in **(a)(i)**
  Required volumes: Volume of **FA 1** = 10.0 cm³, 20.0 cm³, 25.0 cm³,
  30.0 cm³, 35.0 cm³ and 40.0 cm³
  and
  use appropriate volume of **FA 2** such that the total volume of reacting
  mixture in each set of data is 50 cm³   **[1]**

- Records all temperature data in **(a)(i)** to 0.5°C,
  all volumes for **FA 1** and **FA 2** in **(a)(i)** to 1 d.p.   **[1]**

- Correctly calculates all ΔT values to 1 d.p. in **(a)(i)**   **[1]**

(a) (ii)
- Axes correct way round **and** correct labels **and** units **and** scale   **[1]**
  Note: Scale chosen must allow for the lines to be extrapolated to cross *each other. The plotted points should occupy at least half the grid in both directions.*

- All points are correctly plotted to within ± ½ small square.   **[1]**
- All drawn graph lines are <u>straight</u> best-fit lines and are extrapolated to cross each other.
  and
  there are at least three points on each side of the graphically determined ΔT_{max} **[1]**

(a) (iii) ΔT_{max} and V_{max} are read correctly to ± ½ small square from graph

From the sample graph, $\Delta T_{max} = 10.4\ °C$ $V_{max} = V(H_2SO_4) = 27.25\ cm^3$

[1]

(b) (i) $H_2SO_4 + 2\ NaOH \rightarrow Na_2SO_4 + 2\ H_2O$

$V(NaOH) = 50.0 – 27.25 = 22.75\ cm^3$
$n(NaOH) = 1.50 × (22.75/1000) = 0.03413\ mol$

$n(H_2SO_4) = 0.03413 / 2 = 0.01706\ mol$
$[H_2SO_4] = 0.01706 / (27.25/1000) = 0.626\ mol\ dm^{-3}$ **[1]**

(ii) Heat change $= m_{solution}c\Delta T_{max} = 50.0 × 4.18 × 10.4 = 2174\ J$ **[1]**

(c) $n(H_2O) = n(NaOH) = 0.03413\ mol$
$\Delta H_{neut} = - 2174 / 0.03413 = - 6.37 × 10^4\ J\ mol^{-1} = - 63.7\ kJ\ mol^{-1}$ (Sign must be negative)   **[1]**

(d) ΔH_{neut} would be <u>less exothermic</u> as malonic acid is a <u>weak acid</u>. <u>Energy is absorbed</u> to <u>ionise</u> the un-ionised weak acid.   **[1]**

(e) Suggested sources of errors **and** its appropriate improvements: **[1]**

heat loss to the surrounding **and** use a cup lid to minimise heat exchange with the surrounding air

$V_{FA\,1}$ and $V_{FA\,2}$ is to 1 d.p. as measured using less precise measuring cylinders **and** can be measured using more precise burettes to give 2 d.p.

initial temperature of **FA 2** was not accounted for **and** weighted initial temperature should be calculated where

$T_{weighted\ initial} = \dfrac{(\text{Volume of }\textbf{FA 1} \times T_{FA1}) + (\text{Volume of }\textbf{FA 2} \times T_{FA2})}{\text{Volume of }\textbf{FA 1} + \text{Volume of }\textbf{FA 2}}$

heat capacity of the calorimeter (Styrofoam cup) was not accounted for **and** heat absorbed by the styrofoam cup can be included in the calculation of heat change

2 (a)

Mass of weighing bottle and **FA 3** / g	
Mass of weighing bottle and residual **FA 3** / g	
Mass of **FA 3** used / g	

Tables have correct **headers and units** (*included in the header or with <u>each entry</u> in the table*)   **[1]**

(b) <u>Effervescence</u> observed. **[0.5]**
and
<u>Yellow</u> / <u>greenish yellow</u> / <u>yellow green</u> solution <u>turned colourless</u> / very <u>pale green</u>. **[0.5]**

(c) (i)

Final burette reading / cm^3	
Initial burette reading / cm^3	
Volume of **FA 4** used / cm^3	

- Tables have correct headers and units (included in the header or with each entry in the table) **[1]**
  Note: Mark is lost if any final and initial burette readings are inverted or 50 is used as the initial burette reading.

- All mass reading in **(a)** are recorded to the nearest **0.01 g** and burette readings & volume used for all accurate titres in the titration table are recorded to the nearest **0.05 cm^3**. **[1]**

- At least two uncorrected titres for end-point within ±0.10 cm^3. **[1]**

(c) (ii) • Student obtains average titre, to **2 d.p.**, from any experiments with <u>end-point titre values within 0.10 cm^3</u> **[1]**

Mark is lost if there are arithmetic errors in the table.
Mark is lost if the titres used are not identified either in the table (by, for example, a tick) or in a calculation.

- Accuracy

  Supervisor's $V_{FA\,4}$ / $m_{FA\,3}$ = 1.530
  Difference between student's and supervisor's $V_{FA\,4}$ / $m_{FA\,3}$
  If difference is ≤ **0.045 cm^3 g^{-1}** **[2]**
  If difference is > **0.045** but ≤ **0.075 cm^3 g^{-1}** **[1]**
  For a difference > **0.075** **[0]**

(d) (i) If $V_{FA\,4}$ = 10.10 cm^3

$\eta(Fe^{2+})$ = 10.10 × 10^{-3} × 0.020 × 5 = 1.01 × 10^{-3} mol (3 s.f) **[1]**

(d) (ii) $\eta(Fe^{3+})$ = 1.01 × 10^{-3} × 250 / 10.0 = 0.0253 mol (3 s.f) **[1]**

(d) (iii) $m_{FA\,3}$ = 6.60 g

Mole ratio of $Fe_2(SO_4)_3.nH_2O$: Fe^{3+} = 1 : 2

Number of moles of $Fe_2(SO_4)_3.nH_2O$ = 0.0253 ÷ 2 = 0.01265 mol

M_r of $Fe_2(SO_4)_3.nH_2O$ = 6.60 / 0.01265 = 521.7 **[1]**

n = {521.7 − [2(55.8) + 3(32.1) + 12(16.0)]} ÷ 18.0
  = 7 (nearest whole number) **[1]**

- Shows working in **1(b)(i)**, **1(b)(ii)**, **1(c)**, **2(d)(i)**, **2(d)(ii)** and **2(d)(iii)**. All calculations must be relevant although they may not be complete or correct. *Any calculation not attempted loses this mark.* **[1]**

- Shows appropriate significant figures (3 or 4 sf) in all final answers (in the blank) in **1(b)(i)**, **1(b)(ii)**, **1(c)**, **2(d)(i)** and **2(d)(ii)**. For **2(d)(iii)**, M_r can be given to 1 d.p. or 3 s.f. but n should be given as a whole number. *Any calculation not attempted loses this mark.* **[1]**

- Shows appropriate units in all final answers (in the blank) in **1(a)(iii)** ($^\circ$C, cm^3), **1(b)(i)** (mol dm^{-3}), **1(b)(ii)** (J or kJ), **1(c)** (J mol^{-1} or kJ mol^{-1}), **2(c)(ii)** (cm^3), **2(d)(i)** (mol), **2(d)(ii)** (mol). Units should not be given for M_r or n in **2(d)(iii)**. *Any calculation not attempted loses this mark.* **[1]**

(e) Effervescence was observed as <u>zinc reacted with acid to form H_2 gas.</u> **[0.5]**

Yellow solution turned colourless / very pale green as <u>Fe^{3+} was reduced to Fe^{2+}</u>. **[0.5]**

(f) Zinc metal that is not removed will <u>continue to reduce Fe^{3+} formed during the titration to Fe^{2+}</u>, resulting in a <u>higher than expected titre</u>. **[1]**

3 (a)
$$K_c = \frac{[FeSCN^{2+}]}{[Fe^{3+}][SCN^-]}$$
[1]

(b) no. of moles of $FeSCN^{2+}$ formed $\approx$ no. of moles of SCN^- added
$$= 2.00 \times 10^{-3} \times (5/1000) = 1.00 \times 10^{-5} \text{ mol}$$
$[FeSCN^{2+}] = (1.00 \times 10^{-5})/(10/1000) = 1.00 \times 10^{-3}$ mol dm^{-3} **[1]**

Large excess of Fe^{3+} is used to <u>drive the equilibrium **almost completely** to the right</u>. **[1]**
Hence, the amount of $FeSCN^{2+}$ produced will be essentially equal to the amount of SCN^- added.

(c) <u>**Procedure**</u> (sample answer)

1. Using separate <u>burettes</u>, transfer 5.00 cm^3 of $Fe(NO_3)_3$ and 5.00 cm^3 of KSCN into a <u>boiling tube</u>. Stopper and <u>shake</u> to ensure a homogeneous solution.
2. Rinse and fill a cuvette with 3 cm^3 of the mixture.
3. Place the cuvette in a <u>thermostatically controlled water bath</u> maintained at <u>50 $^\circ$C</u> for <u>about 5 min</u>.
4. Measure and record the <u>temperature</u> of the solution using a <u>thermometer</u>.

5. Remove the cuvette from the water bath, and <u>immediately</u> measure and record the <u>absorbance</u> (at wavelength of blue light 447 nm) using a spectrophotometer.
6. Repeat steps 3 – 5 at <u>40 °C, 30 °C, 20 °C and 10 °C</u>.

or

Repeat steps 2 – 5 (total volume must then be at least 5×3=15 cm^3) at <u>40 °C, 30 °C, 20 °C and 10 °C</u>.

M1 – Logical sequence [1] (minus ½ mark for each missing point)
- <u>Mixing known volumes</u> of $Fe(NO_3)_3$ and KSCN, amount of Fe^{3+} not more than <u>10 times</u> of SCN^-, <u>total volume > 3 cm^3</u>
- Measure (and record) the <u>temperature</u> of the mixture
- Measure (and record) the <u>absorbance</u> of the mixture

M2 – Apparatus [1] (½ mark for each point)
- <u>separate burettes</u> for $Fe(NO_3)_3$ and KSCN (or other <u>precise apparatus</u> e.g. micropipette or pipette)
- <u>thermostatically controlled water bath</u>

M3 – Essential details [1] (½ mark for each point)
- <u>Shake boiling tube</u> / test-tube/ swirl conical flask (with stopper) or stir beaker (with glass rod)
- Allow <u>time</u> for the mixture to <u>equilibrate</u> in the water bath (e.g. 5 - 10 min) **and** measure absorbance <u>immediately</u>

M4 – Choice of temperatures [1] (½ mark for each point)
- at least <u>5 different temperatures</u>
- with at least <u>5 °C difference, 0 ºC < T < 100 ºC</u>

M5 and M6 – Treatment of results [2] (½ mark for each point)
- use calibration line to determine [$FeSCN^{2+}$] (accept if show how on calibration line)
- correct [Fe^{3+}]$_{initial}$ and [SCN^-]$_{initial}$
- correct [Fe^{3+}]$_{eqm}$ and [SCN^-]$_{eqm}$; ecf from initial conc
- correct expression for K_c in terms of [$FeSCN^{2+}$]$_{eqm}$; ecf from eqm conc

Sample answer:

For each absorbance obtained, read off the <u>calibration line</u> to determine the corresponding [$FeSCN^{2+}$] at each temperature.

	Fe^{3+}	+ SCN$^-$	⇌ FeSCN^{2+}
initial / mol dm^{-3}	$\frac{2\times10^{-3}\times5}{10}$ = 1.00×10^{-3}	$\frac{2\times10^{-3}\times5}{10}$ = 1.00×10^{-3}	0
change / mol dm^{-3}	– x	– x	+ x
eqm / mol dm^{-3}	0.001 – x	0.001 – x	[$FeSCN^{2+}$] = x

$$K_c = \frac{x}{(0.001-x)^2}$$

(d) **(i)**

In K_c (y-axis), $1/T$ (x-axis)
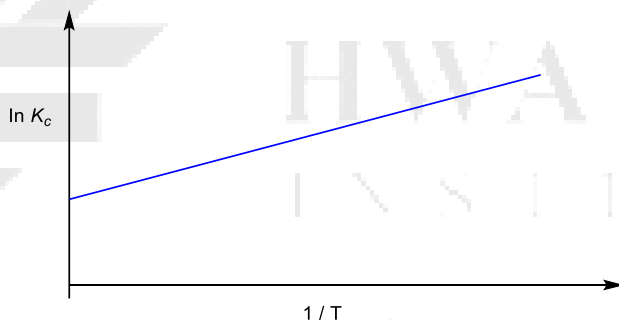
Fig. 3.1

[1]

Compare the equation given to y = mx + c, <u>gradient = $-\Delta H / R$</u>.
As <u>$\Delta H < 0$</u> and $R > 0$, <u>gradient is positive</u>

[1]

Accept correct explanation using LCP.
Mark for explanation may be lost if graph is incorrect.

(d) **(ii)** gradient = $\Delta y / \Delta x = -\Delta H / R$
Hence, <u>$\Delta H = -$ gradient $\times R$</u> = $-$ gradient $\times$ 8.31 **[1]**

y-intercept = $\Delta S / R$
Hence, <u>$\Delta S =$ y-intercept $\times R$</u> = y-intercept $\times$ 8.31 **[1]**

Correct expressions for ΔH and ΔS (i.e. both must be the subject). Accept correct descriptions instead of expressions.

4 (a) 1. <u>Black/dark brown/grey</u> residue obtained.
2. <u>Brown/orange/yellow</u> filtrate obtained.
3. <u>Off-white/light brown/yellow/orange ppt</u> formed <u>insoluble</u> in excess NaOH(aq). (REJECT: brown ppt).
4. Off-white ppt <u>which turned</u> <u>brown/darkened</u> on standing (must appear at least once either with NaOH(aq) or NH$_3$(aq)).
5. <u>Off-white/light brown/yellow/orange ppt</u> formed <u>insoluble</u> in excess NH$_3$(aq) (insoluble must appear at least once in point 3 or 5).

(c) 6. <u>Effervescence</u> observed (REJECT: gas evolved).
7. Gas <u>relit glowing splint</u>.

(f) 8. Solution turned <u>green</u>
9. Then <u>darker green</u>.
10. Dark <u>blue</u>/dark <u>green</u>/<u>blue-green</u> residue obtained.
11. <u>Colourless</u> filtrate.

(g) 12. <u>Purple/Pink</u> filtrate obtained.
13. Residue turned <u>brown/black/grey</u> (must show a change in colour from point 10)

Observation points
11 – 13 = 6 marks
9 – 10 = 5 marks
7 – 8 = 4 marks
5 – 6 = 3 marks
3 – 4 = 2 marks
1 – 2 = 1 mark
0 = 0 mark   **[6]**

(b)   Oxidising agent **[1]**
Evidence 1: Since a <u>brown/orange/yellow solution</u> is formed that decolourises
with $S_2O_3^{2-}$, <u>I⁻ was oxidised to I_2</u>. **[½]**
Evidence 2: <u>MnO_2 was reduced</u> to Mn^{2+}, as seen by the <u>off-white/light brown
ppt</u> formed with NaOH(aq) that darkened on standing. **[½]**

(d)   Since there was no ppt with NaOH(aq), MnO_2 was not reduced to Mn^{2+} or an
off-white ppt will be formed, hence it is not acting as an oxidising agent. **[1]**

(e)   Heterogeneous <u>catalyst</u> **[½]**
Since there was brisk <u>effervescence</u>, it indicates that rate of decomposition of
H_2O_2 is <u>faster</u>. **[½]**

(h)   **X**: MnO_2 **[½]**
Y: MnO_4^- **[½]** (no credit if colour of filtrate is not correct)

(i) $BaSO_4$. **[1]**