INNOVA JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
in preparation for General Certificate of Education Advanced Level
Higher 2

CANDIDATE NAME			
CLASS		INDEX NUMBER	

CHEMISTRY 9729/01

Paper 1 Multiple Choice **14 Sep 2018**

1 hour

Additional Materials: *Data Booklet*
Multiple Choice Answer Sheet

READ THESE INSTRUCTIONS FIRST

Write your index number, name and class on all the work you hand in.
Write in soft pencil.
Do not use staples, paper clips, highlighters, glue or correction fluid.

There are **thirty** questions on this paper. Answer **all** questions. For each question there are four possible answers **A**, **B**, **C** and **D**.
Choose the **one** you consider correct and record your choice in **soft pencil** on the separate Answer Sheet.

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.

This document consists of **16** printed pages and **1** blank page.

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

1 In an experiment, 0.002 mol acidified iron (II) sulfate is quantitatively oxidised by 0.001 mol of an oxidising agent, $\mathbf{Z}O_3^-$. Given that Fe^{2+} is oxidised to Fe^{3+}, what is the final oxidation state of **Z**?

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

2 Gaseous particle **X** has a proton number n and a charge of +1.

Gaseous particle **Y** has a proton number of (n + 1) and is isoelectronic with **X**.

Which of the following statements correctly describe **X** and **Y**?

1 **Y** has a smaller radius than **X**.

2 **Y** requires less energy than **X** when a further electron is removed from each particle.

3 **Y** releases less energy than **X** when an electron is added to each particle.

A 1 only

B 2 only

C 1 and 2 only

D 2 and 3 only

3 What is the electronic configuration of an element with a **second** ionisation energy higher than that of each of the elements either side of it in the Periodic Table?

A $1s^22s^22p^63s^2$

B $1s^22s^22p^63s^23p^1$

C $1s^22s^22p^63s^23p^2$

D $1s^22s^22p^63s^23p^3$

4 The table shows the charge and radius of each of six ions.

ion	J^+	L^+	M^{2+}	X^-	Y^-	Z^{2-}
radius / nm	0.14	0.18	0.15	0.14	0.18	0.15

The ionic solids JX, LY and MZ are of the same lattice type. What is the correct order of their lattice energies, placing the most exothermic first?

A JX, MZ, LY

B LY, MZ, JX

C MZ, JX, LY

D MZ, LY, JX

5 In certain microwave ovens, the wave energy produced is absorbed by certain polar molecules.

Which of the following would absorb microwave energy?

1 CH_3CH_2OH
2 $AlCl_3$
3 CO_2
4 CH_3F

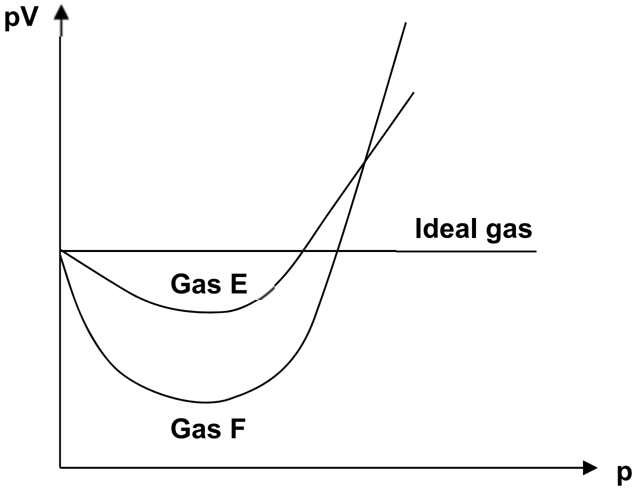
A 1 and 2 only

B 1 and 4 only

C 2 and 3 only

D 3 and 4 only

6



Which one of the following statements is true for the observation?

A Gas **E** could be He while gas **F** could be CO_2.

B Gas **E** could be NH_3 while gas **F** could be H_2.

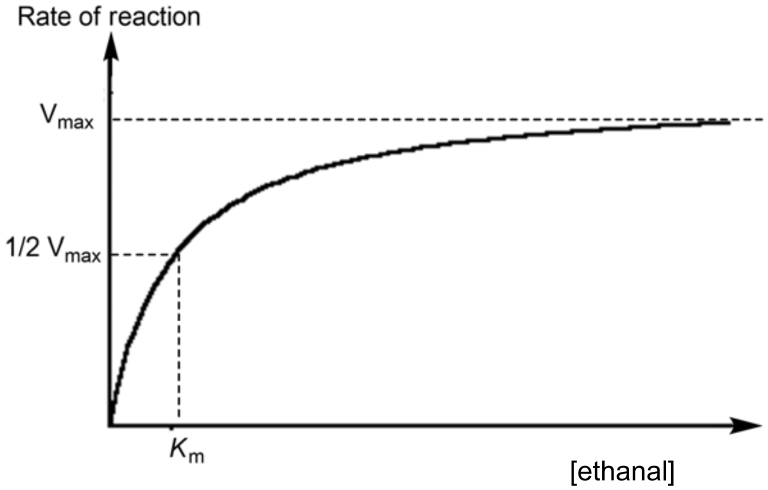
C Gas **E** could form intermolecular hydrogen bonds while gas **F** could form intermolecular permanent dipole-permanent dipole.

D Gas **E** could form stronger intermolecular instantaneous dipole-induced dipole than gas **F**.

7 The enzyme alcohol dehydrogenase catalyses an important step in the production of ethanol by fermentation.

$$CH_3CHO + 2[H] \rightarrow CH_3CH_2OH$$

The graph shows how the rate of this enzyme-catalysed reaction varies with the concentration of ethanal.



Which statement best explains the reason for the flattening off of the curve?

A All the ethanal has been used up and the reaction has finished.

B As the ethanol product builds up the reaction slows down.

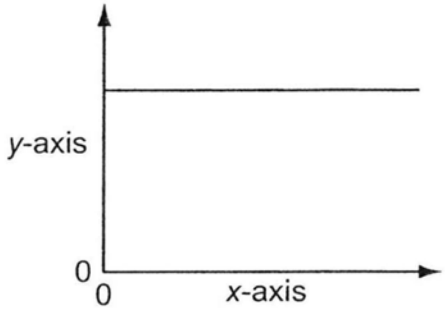
C At high ethanal concentrations all the active sites in the enzyme molecules are occupied by ethanal molecules.

D At high ethanal concentrations the ethanal inhibits the action of enzyme.

8 The kinetics of the zero order reaction P → Q were investigated under different conditions.

The table shows pairs of quantities that were plotted as graphs.

Which pairs gave the following graph?



	y-axis	*x*-axis
1	rate	time
2	rate constant	time
3	rate constant	temperature
4	rate	concentration

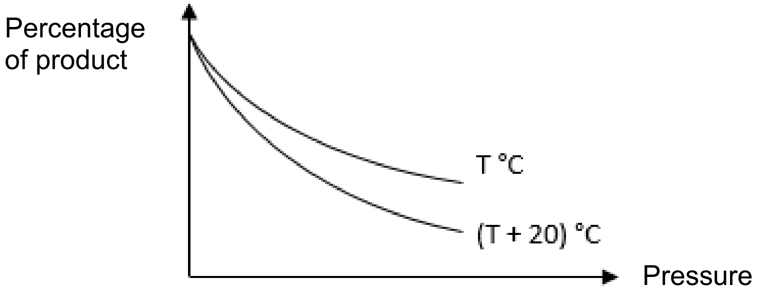
A 1 and 4 only

B 2 and 3 only

C 1, 2 and 3 only

D 1, 2 and 4 only

9 The graph below shows how the percentage of product present at equilibrium varies with temperature and pressure for a reaction.



Which reaction could the graph represent?

A $4Fe(s) + 3O_2(g) \rightleftharpoons 2Fe_2O_3(s)$ $\Delta H = -1644$ kJ mol^{-1}

B $2C(s) + O_2(g) \rightleftharpoons 2CO(g)$ $\Delta H = -222$ kJ mol^{-1}

C $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ $\Delta H = +57.2$ kJ mol^{-1}

D $CO(g) + Cl_2(g) \rightleftharpoons COCl_2(s)$ $\Delta H = +86$ kJ mol^{-1}

10 The standard enthalpy change of the following reaction is −896.4 kJ mol^{-1}.

$$2HN_3(l) + 2NO(g) \rightarrow H_2O_2(l) + 4N_2(g)$$

	NO(g)	$H_2O_2(l)$
ΔH^{θ}_{f}/kJ mol^{-1}	+ 90.3	− 187.8

Using the standard enthalpy change of formation in the above table, what is the standard enthalpy change of formation, in kJ mol^{-1}, of $HN_3(l)$?

A +264

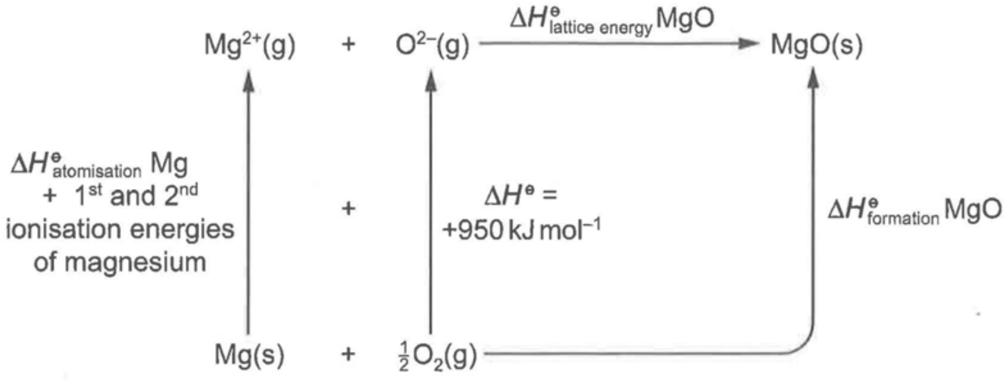
B +528

C +618

D +632

11 A student calculated the lattice energy for magnesium oxide using the cycle shown.

The enthalpy change of atomisation of magnesium, $\Delta H^{\theta}_{atomisation}$ Mg, is the energy needed when 1 mol of gaseous magnesium atoms is formed from 1 mol of solid magnesium under standard conditions.



However, the value calculated by the student for the lattice energy was **less** exothermic than the correct value.

Which errors could have been made in the calculation?

1 omitting the enthalpy change of atomisation of magnesium

2 omitting the first ionisation energy of magnesium

3 using the standard enthalpy change of combustion of magnesium rather than the standard enthalpy change of formation of magnesium oxide

A 1 and 2 only

B 1 and 3 only

C 2 and 3 only

D 1, 2 and 3

12 Which changes are accompanied by an increase in entropy of the system?

1 freezing of water
2 sublimation of iodine
3 vaporisation of ethanol
4 conversion of O_2(g) to O_3(g)

A 1 and 2 only

B 2 and 3 only

C 3 and 4 only

D 1 and 4 only

13 The value of the ionic product of water, K_w, varies with temperature.

Temperature / °C	K_w / mol^2 dm^{-6}
25	1.0×10^{-14}
62	1.0×10^{-13}

What can be deduced from this information?

A The ionic dissociation of water is an exothermic process.

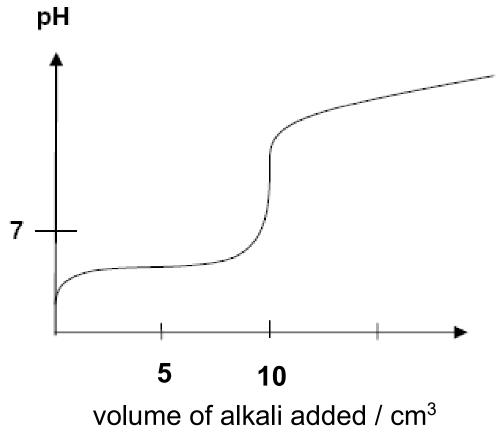
B The association of water molecules by hydrogen bonding increases as temperature increases.

C The pH of pure water increases with temperature.

D At 62 °C, water with a pH of 6.5 is neutral.

14 The following graph shows the changes in pH of 20.0 cm^3 of 1.0 mol dm^{-3} acid solution when excess 1.0 mol dm^{-3} alkali solution is added gradually.

Which one of the following pairs of solution with a suitable indicator could have resulted in the graph below?



	alkali	acid	indicator
A	NaOH	H_2SO_4	Methyl orange
B	NH_3	HNO_3	Phenolphthalein
C	KOH	CH_3CO_2H	Methyl orange
D	$Ba(OH)_2$	$CH_3CH_2CO_2H$	Phenolphthalein

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

The AgC*l* / Ag reference electrode is based on the following reaction:

$$AgCl + e^- \rightleftharpoons Ag + Cl^-$$

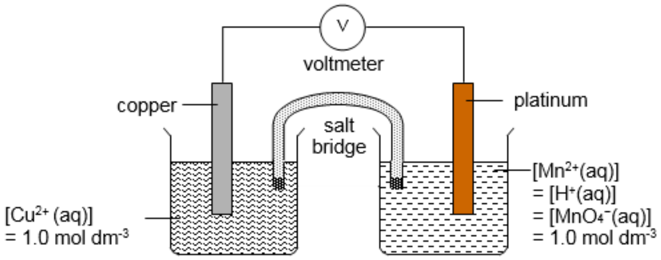
The reduction potential of the Fe^{2+} / Fe half−cell was found to be −0.64 V when measured using the AgC*l* / Ag reference electrode.

What is the reduction potential of the AgC*l* / Ag electrode with respect to the standard hydrogen electrode?

A −1.10 V **B** −0.20 V **C** +0.20 V **D** +1.10 V

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

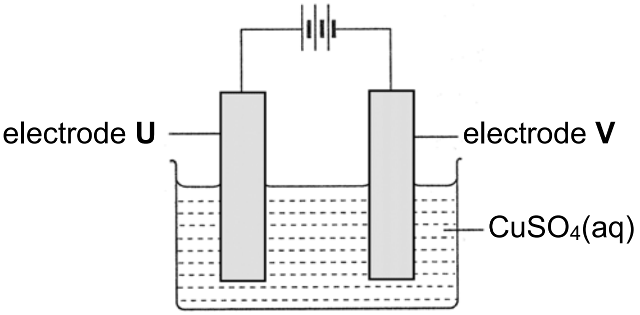
A cell is set up by connecting a Cu^{2+}/Cu half-cell and an acidified MnO_4^-/Mn^{2+} half-cell.



Which change in the set up will cause the corresponding effect on the e.m.f (potential difference) of the cell?

	change	effect on e.m.f of cell
A	addition of excess NH_3 (aq) into oxidation half-cell	increases
B	addition of concentrated H_2SO_4 into reduction half-cell	decreases
C	increase the size of the copper electrode	increases
D	replace copper with an alloy of copper and zinc	remains the same

17 In an experiment, a cell was set up to obtain pure copper from a copper-silver alloy as shown below. Electrode **V** is pure copper and electrode **U** is the copper-silver alloy.



When a current of 40.0 A flows through the electrolyte for 26.8 minutes, the mass of the anode changes by 26.47 g.

What is the percentage of silver by mass in the electrode **U**?

A 20%

B 40%

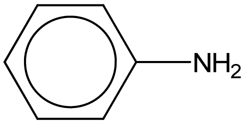
C 60%

D 80%

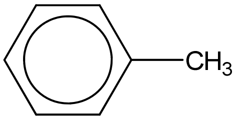
18 Which of the following is a planar molecule?

A $H-C\equiv C-CH_2CH_3$

B



C

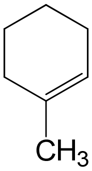


D $H_2C=CH-CHO$

19 A hydrocarbon, on heating with an excess of hot concentrated acidic $KMnO_4$ produces $HO_2CCH_2CH_2CH_2COCH_3$.

What could the hydrocarbon be?

1



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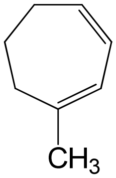

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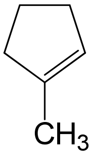


A 1 and 2 only

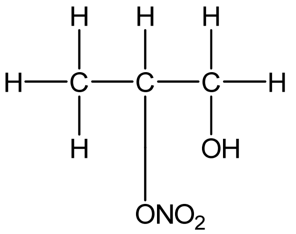
B 1 and 3 only

C 2 and 3 only

D 1, 2 and 3

20 When propene reacts with Br_2 in the presence of excess aqueous KNO_3, what are the two major products formed?

A



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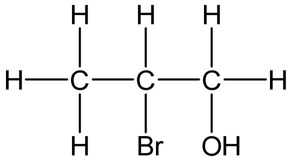
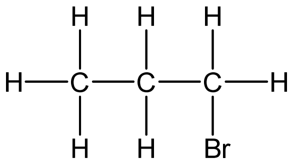


B



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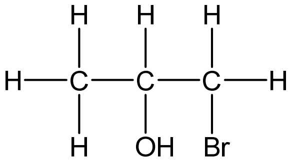
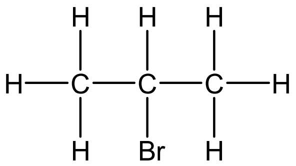


C



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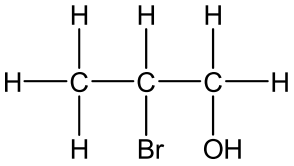

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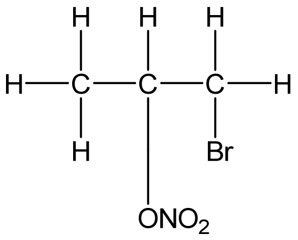

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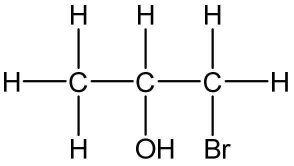


21 The molecule of benzene, C_6H_6 is a regular hexagon in which the π electrons are described as delocalised.

Which of the following statements are true for benzene?

1 It prevents benzene from undergoing addition reactions.

2 All C–C bonds lengths in benzene are intermediate between C–C bond in an alkane and C=C bond in an alkene.

3 The enthalpy change of hydrogenation of benzene is less exothermic than that predicted for cyclohexatriene.

4 The presence of π electrons enables benzene to be a good electrical conductor.

A 1 and 2 only

B 2 and 3 only

C 1, 2 and 3 only

D 1, 2 and 4 only

22 Some chlorobutanes were separately treated with hot ethanolic sodium hydroxide. Two of these gave the same hydrocarbon, C_4H_6.

From which pair of chlorobutanes was this hydrocarbon obtained?

A $CH_3CH_2CH_2CH_2Cl$ and $CH_3CH_2CH_2CHCl_2$

B $CH_3CH_2CH_2CH_2Cl$ and $ClCH_2CH_2CH_2CH_2Cl$

C $CH_3CH_2CCl_2CH_3$ and $ClCH_2CH_2CH_2CHCl_2$

D $CH_3CHClCHClCH_3$ and $ClCH_2CH_2CH_2CH_2Cl$

23 Deuterium, D, is the ${}^{2}_{1}H$ isotope of hydrogen.

Which of the following reactions yield a carbon compound containing deuterium?

1 $CH_3CH_2CN \xrightarrow[\text{heat}]{D_2\text{, Ni catalyst}}$

2 $CH_3CO_2CH_2CH_3 \xrightarrow[\text{heat}]{D_2SO_4\text{, }D_2O}$

3 $CH_3COCI_3 \xrightarrow[D_2O]{\text{NaOD}}$

4 $(CH_3)_3OH \xrightarrow[\text{heat}]{\text{conc }D_2SO_4}$

A 1 and 2 only

B 1 and 4 only

C 1, 2 and 3 only

D 2, 3 and 4 only

24 Which of the following synthetic routes **does not** produce ethanoic acid?

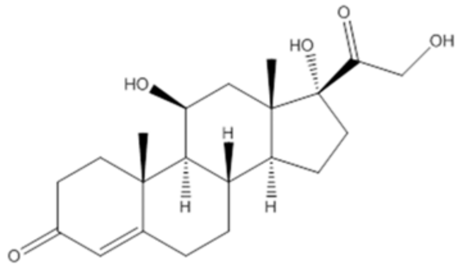
A $CH_3Br \xrightarrow[\text{heat}]{\text{alcoholic KCN}} \xrightarrow[\text{heat}]{\text{dil HC}l}$

B $CH_3CHO \xrightarrow[\text{warm}]{[Ag(NH_3)_2]^+} \xrightarrow[\text{r.t.p.}]{H^+}$

C $CH_3CH(OH)CH_3 \xrightarrow[\text{warm}]{\text{aqueous alkaline iodine}} \xrightarrow[\text{r.t.p.}]{H^+}$

D $CH_3CH(OH)CH_2CH_3 \xrightarrow[180\ ^{o}C]{\text{excess conc }H_2SO_4} \xrightarrow[\text{heat}]{\text{acidic }K_2Cr_2O_7}$

25 Hydrocortisone is a steroid hormone produced by the adrenal gland and is released in response to stress. It is commonly used as an active ingredient in anti-inflammatory creams.



Hydrocortisone

Which of the following statements about Hydrocortisone is true?

A When treated with $NaBH_4$ in the presence of methanol, it forms a compound containing 5 hydroxy groups.

B When warmed with aqueous alkaline iodine, a yellow precipitate is observed.

C When treated with cold dilute $KMnO_4$, it forms a compound containing 2 hydroxy groups.

D When treated with an excess of hot concentrated acidified $KMnO_4$, it forms a compound containing 7 chiral centres.

26 Equal amounts of compounds **P**, **Q**, **R** and **S** are separately shaken with 100 cm^3 of water. The pH of each resultant solution is then measured.

$CH_3CH_2CO_2H$	CH_3CH_2COCl	$ClCH_2CH_2CO_2H$	$BrCH_2CH_2CO_2H$
P	**Q**	**R**	**S**

Which of the following shows the correct order of increasing order of acidity of the solutions formed?

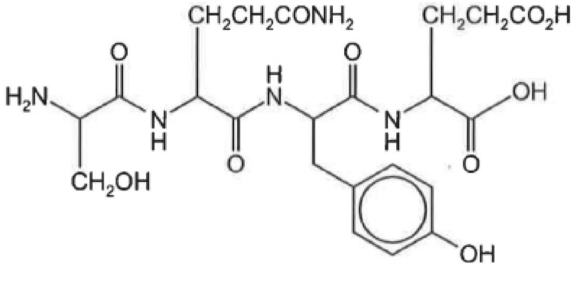
A P, R, S, Q

B P, S, R, Q

C Q, P, S, R

D Q, S, R, P

27 The diagram shows the structure of the tetrapeptide **T**.

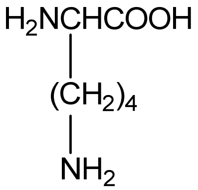


T

When 0.1 mole of **T** is heated under reflux with NaOH(aq) until no further reaction occurs, how many moles of NaOH will react?

A	0.4	**B**	0.5
C	0.6	**D**	0.7

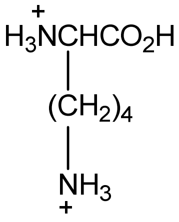
28 Lysine is an α-amino acid.



$$\begin{array}{l} H_2NCHCOOH \\ \quad\;\; | \\ \quad (CH_2)_4 \\ \quad\;\; | \\ \quad NH_2 \end{array}$$

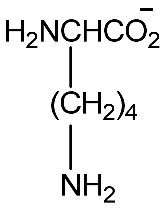
Which structure is predominant when lysine is in an aqueous solution of pH 9.5, given that lysine has three pK_a values of 2.2, 8.9 and 10.5?

A



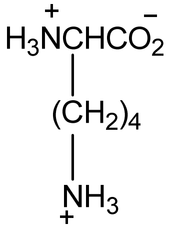
$$\begin{array}{l} H_3\overset{+}{N}CHCO_2H \\ \quad\;\; | \\ \quad (CH_2)_4 \\ \quad\;\; | \\ \quad \underset{+}{N}H_3 \end{array}$$

B



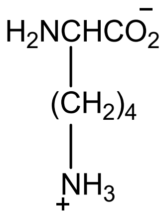
$$\begin{array}{l} H_2NCHCO_2^- \\ \quad\;\; | \\ \quad (CH_2)_4 \\ \quad\;\; | \\ \quad NH_2 \end{array}$$

C



$$\begin{array}{l} H_3\overset{+}{N}CHCO_2^- \\ \quad\;\; | \\ \quad (CH_2)_4 \\ \quad\;\; | \\ \quad \underset{+}{N}H_3 \end{array}$$

D



$$\begin{array}{l} H_2NCHCO_2^- \\ \quad\;\; | \\ \quad (CH_2)_4 \\ \quad\;\; | \\ \quad \underset{+}{N}H_3 \end{array}$$

29 Element **J** is in Period 3 of the Periodic Table. The following three statements are the properties of element **J** or its compounds.

- Adding NaOH(aq) to the solution resulting from the reaction of a chloride of **J** with water produces a white precipitate which is soluble in an excess of NaOH(aq).
- Element **J** is a solid at room temperature.
- The oxide of element **J** is soluble in hydrochloric acid.

What is the identity of element **J**?

A	magnesium	**C**	silicon
B	aluminium	**D**	phosphorus

30 *The use of the Data Booklet is relevant to this question.*

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

Oxidation state	V	IV	III	II
Ion	VO_2^+	VO^{2+}	V^{3+}	V^{2+}
Colour	yellow	blue	green	violet

What is the final colour of the solution when excess zinc powder is added to an acidified solution containing VO_2^+ ions?

A	yellow	**C**	green
B	blue	**D**	violet

End of Paper

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H

INNOVA JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
in preparation for General Certificate of Education Advanced Level
Higher 2

CANDIDATE NAME	**MARK SCHEME**
CLASS	
INDEX NUMBER	

CHEMISTRY

9729/01

Paper 1 Multiple Choice

XX XXX 2018

1 hour

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

A: 7 B: 6 C:7 D: 10

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

Innova Junior College **[Turn over**

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

1 In an experiment, 0.002 mol acidified iron (II) sulfate is quantitatively oxidised by 0.001 mol of an oxidising agent, **Z**O_3^-. Given that Fe^{2+} is oxidised to Fe^{3+}, what is the final oxidation state of **Z**?

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

Answer: C

Amount of electrons released by Fe^{2+} = 0.002 mol

= amount of electrons accepted by YO_3^-

Amount of YO_3^- ; amount of e = 1 : 2

Oxidation number of Y in YO_3^- = +5

New oxidation number of Y = +5 – 2 = +3

2 Gaseous particle **X** has a proton number n and a charge of +1.

Gaseous particle **Y** has a proton number of (n + 1) and is isoelectronic with **X**.

Which of the following statements correctly describe **X** and **Y**?

1 **Y** has a smaller radius than **X**.

2 **Y** requires less energy than **X** when a further electron is removed from each particle.

3 **Y** releases less energy than **X** when an electron is added to each particle.

A 1 only

B 2 only

C 1 and 2 only

D 2 and 3 only

Answer: A

particle	proton number	electron number	charge
X	n	n-1	+1
Y	n+1	n-1	+2

Since **Y** has higher nuclear charge than **X**, and both **X** and **Y** have same shielding effect (same electron number), **Y** has higher effective nuclear charge and valence electrons are more strongly attracted to the nucleus.

Thus, **Y** has smaller radius than **X**. (Option 1 is correct)

Y requires more energy than **X** when a further electron is removed from each particle. (Option 2 is wrong)

Y releases more energy than **X** when an electron is added to each particle. (Option 3 is wrong)

3 What is the electronic configuration of an element with a **second** ionisation energy higher than that of each of the elements either side of it in the Periodic Table?

A $1s^22s^22p^63s^2$

B $1s^22s^22p^63s^23p^1$

C $1s^22s^22p^63s^23p^2$

D $1s^22s^22p^63s^23p^3$

Answer: B

The electronic configuration for second ionisation energy of the above species:

A: $1s^22s^22p^63s^1$

B: $1s^22s^22p^63s^2$

C: $1s^22s^22p^63s^23p^1$

D: $1s^22s^22p^63s^23p^2$

As there is a decrease in ionisation energy between the species between ns^2 and ns^2np^1, species that have electronic configuration of ns^2 will have second ionisation energy higher than that of each of the elements either side of it (ns^1 and ns^2np^1) in the Periodic Table.

4 The table shows the charge and radius of each of six ions.

ion	J^+	L^+	M^{2+}	X^-	Y^-	Z^{2-}
radius / nm	0.14	0.18	0.15	0.14	0.18	0.15

The ionic solids JX, LY and MZ are of the same lattice type. What is the correct order of their lattice energies, placing the most exothermic first?

A JX, MZ, LY

B LY, MZ, JX

C MZ, JX, LY

D MZ, LY, JX

Answer: C

Since $\left|\text{Lattice energy, } \Delta H_{\text{latt}}^{\theta}\right| \alpha \left|\dfrac{q_+q_-}{r_+ + r_-}\right|$, compound MZ has the most exothermic lattice energy as M^{2+} and Z^{2-} has higher charge than that of J^+, L^+, X^- and Y^-. Compound LY has the least exothermic lattice energy as L^+ and Y^- has larger ionic radius than that of J^+ and Y^-.

5 In certain microwave ovens, the wave energy produced is absorbed by certain polar molecules.

Which of the following would absorb microwave energy?

1 CH_3CH_2OH

2 $AlCl_3$

3 CO_2

4 CH_3F

A 1 and 2 only

B 1 and 4 only

C 2 and 3 only

D 3 and 4 only

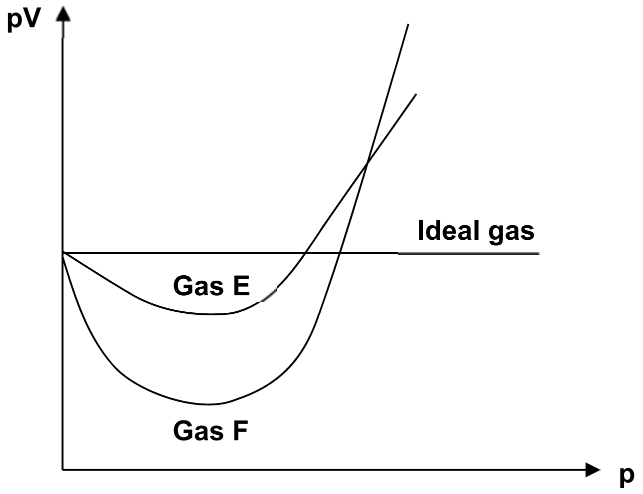
Answer: B

Option 2 is non polar molecule. $AlCl_3$ is trigonal planar in shape and there is no net dipole moment in the molecule as all the dipole moments cancel out each other.

Option 3 is non polar molecule. CO_2 is linear in shape and there is no net dipole moment in the molecule as all the dipole moments cancel out each other.

Option 1 and 4 are polar as there is net dipole moment in the molecule.

6



Which one of the following statements is true for the observation?

A Gas **E** could be He while gas **F** could be CO_2.

B Gas **E** could be NH_3 while gas **F** could be H_2.

C Gas **E** could form intermolecular hydrogen bonds while gas **F** could form intermolecular permanent dipole-permanent dipole.

D Gas **E** could form stronger intermolecular instantaneous dipole-induced dipole than gas **F**.

Answer: A

$pV = nRT$
$1.5 \times 101325 \times V = 1 \times 8.31 \times (273+27)$
$V = 0.0164\ m^3$
$V = 16.4\ dm^3$
From the above calculation, it can be deduced that gas **E** behave more ideally than gas **F**.

Option A is correct. He behaves more like an ideal gas as it has smaller electron cloud size and weaker i.d.-i.d. than that of CO_2. Intermolecular forces of attraction between He is negligible.

Option B is wrong. NH_3 can form hydrogen bonds between molecules and there is significant intermolecular forces of attraction. NH_3 deviates more from ideal gas.

Option C is wrong. Gas **E** should form weaker i.d.-i.d. between molecules than that of **F** as gas **E** behave more ideally than gas **F**.

Option D is wrong. Gas **E** should form weaker i.d.-i.d. than gas **F** as gas **E** behave more ideally than gas **F**.

7 The enzyme alcohol dehydrogenase catalyses an important step in the production of ethanol by fermentation.

$$CH_3CHO + 2[H] \rightarrow CH_3CH_2OH$$

The graph shows how the rate of this enzyme-catalysed reaction varies with the concentration of ethanal.

[ethanal]

Which statement best explains the reason for the flattening off of the curve?

A All the ethanal has been used up and the reaction has finished.

B As the ethanol product builds up the reaction slows down.

C At high ethanal concentrations all the active sites in the enzyme molecules are occupied by ethanal molecules.

D At high ethanal concentrations the ethanal inhibits the action of enzyme.

Answer: C

Option A is wrong as there is an increase in the concentration of ethanal. The ethanal has not been used up and the reaction has not finished.

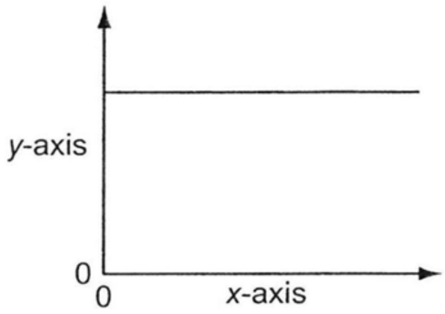
Option B is wrong as the concentration of the ethanol product builds up the reaction will not slow down the rate of reaction.

Option D is wrong as ethanal is not an inhibitor but substrate (reactant) of this reaction.

8 The kinetics of the zero order reaction P → Q were investigated under different conditions.

The table shows pairs of quantities that were plotted as graphs.

Which pairs gave the following graph?



	y-axis	*x*-axis
1	rate	time
2	rate constant	time
3	rate constant	temperature
4	rate	concentration

A 1 and 4 only

B 2 and 3 only

C 1, 2 and 3 only

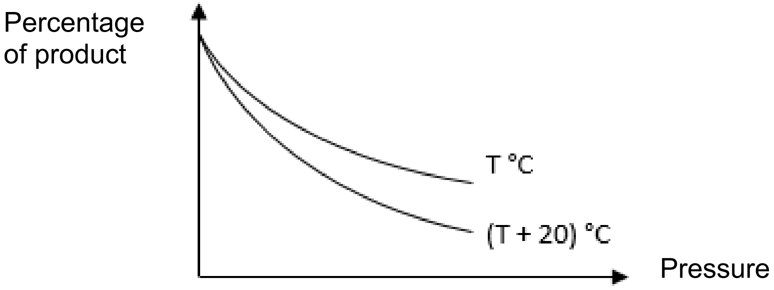
D 1, 2 and 4 only

Answer: D

For a zero order reaction, rate of the reaction is independent of time and concentration.

Also, rate constant is dependent on temperature and activation energy (from Arrhenius equation.)

9 The graph below shows how the percentage of product present at equilibrium varies with temperature and pressure for a reaction.



Which reaction could the graph represent?

A $4Fe\,(s) + 3O_2\,(g) \rightleftharpoons 2Fe_2O_3\,(s)$ $\Delta H = -1644$ kJ mol^{-1}

B $2C\,(s) + O_2\,(g) \rightleftharpoons 2CO\,(g)$ $\Delta H = -222$ kJ mol^{-1}

C $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ $\Delta H = +57.2$ kJ mol^{-1}

D $CO(g) + Cl_2(g) \rightleftharpoons COCl_2(s)$ $\Delta H = +86$ kJ mol^{-1}

Answer: B

From the graph, when the pressure increases, the proportion of product molecules decrease. This indicates that when pressure increases, the equilibrium position shifts to left (which have fewer gaseous molecules to decrease the pressure). Option A and option D is wrong.

From the graph, when the temperature increases, the proportion of product molecules decrease too. This indicates that when temperature increases, the equilibrium position shifts to left (which is endothermic to reduce the temperature. Since option B is exothermic in the forward reaction, it would be endothermic in the backward reaction.

Only Option B shows the correct trend when temperature and pressure increase.

10 The standard enthalpy change of the following reaction is −896.4 kJ mol^{-1}.

$$2HN_3(l) + 2NO(g) \rightarrow H_2O_2(l) + 4N_2(g)$$

	NO(g)	H_2O_2(l)
ΔH^{θ}_{f}/kJ mol^{-1}	+ 90.3	− 187.8

Using the standard enthalpy change of formation in the above table, what is the standard enthalpy change of formation, in kJ mol^{-1}, of HN_3(l)?

A +264

B +528

C +618

D +632

Answer: A

Using $\Delta H_r^{\theta} = \sum n\Delta H_f^{\theta}$ (products) $-$ $\sum m\Delta H_f^{\theta}$ (reactants)

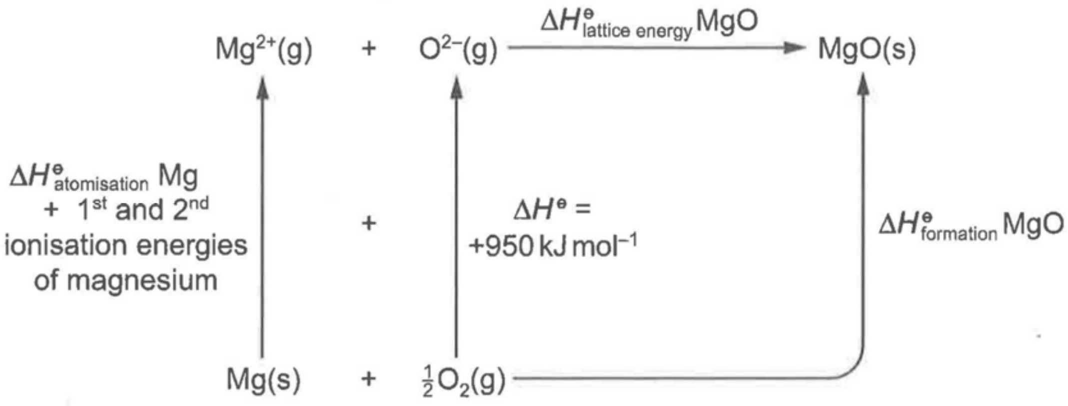
$\Delta H_r^{\theta} = \Delta H_f (H_2O_2) - [\, 2\, \Delta H_f (HN_3) + 2\, \Delta H_f (NO)]$

$-896.4 = -187.8 - (2\, \Delta H_f (HN_3) + 2 \times 90.3)$

$\Delta H_f (HN_3) = +264$ kJ mol^{-1}

11 A student calculated the lattice energy for magnesium oxide using the cycle shown.

The enthalpy change of atomisation of magnesium, $\Delta H^{\theta}_{\text{atomisation}}$ Mg, is the energy needed when 1 mol of gaseous magnesium atoms is formed from 1 mol of solid magnesium under standard conditions.



However, the value calculated by the student for the lattice energy was **less** exothermic than the correct value.

Which errors could have been made in the calculation?

1 omitting the enthalpy change of atomisation of magnesium

2 omitting the first ionisation energy of magnesium

3 using the standard enthalpy change of combustion of magnesium rather than the standard enthalpy change of formation of magnesium oxide

A 1 and 2 only

B 1 and 3 only

C 2 and 3 only

D 1, 2 and 3

Ans: A

By Hess's law,

Lattice energy = – [$\Delta H^{\theta}_{\text{atomisation}}$Mg] –[1st and 2nd I.E. of Mg] – 950
+ $\Delta H^{\theta}_{\text{formation}}$MgO

1 is correct as the lattice energy will be less exothermic if the enthalpy change of atomisation of Mg is omitted. This is because, the enthalpy change of atomisation of Mg is a positive term.

2 is correct as the lattice energy will be less exothermic if the first ionisation energy of Mg is omitted. This because, the first ionisation energy of Mg is a positive term

3 is incorrect as the replacing the standard enthalpy change of formation of MgO with the standard enthalpy change of combustion of Mg will have no effect on the value of the lattice energy. This is because both values are the same.

12 Which changes are accompanied by an increase in entropy of the system?

1 freezing of water
2 sublimation of iodine
3 vaporisation of ethanol
4 conversion of O_2(g) to O_3(g)

A 1 and 2 only

B 2 and 3 only

C 3 and 4 only

D 1 and 4 only

Answer: B

For option 2 and 3, there is an increase in the number of gaseous molecules (from solid to gas and from liquid to gas), there is an increase in the disorderness of the system, entropy increases.

For option 1, there is a decrease in the disorderness of the system (from liquid to solid) and similarly for that of option 4. $3O_2(g) \rightarrow 2O_3(g)$

13 The value of the ionic product of water, K_w, varies with temperature.

Temperature / °C	K_w / mol^2 dm^{-6}
25	1.0×10^{-14}
62	1.0×10^{-13}

What can be deduced from this information?

A The ionic dissociation of water is an exothermic process.

B The association of water molecules by hydrogen bonding increases as temperature increases.

C The pH of pure water increases with temperature.

D At 62 °C, water with a pH of 6.5 is neutral.

Answer: D

Option A is wrong as ionic dissociation of water involves bond breaking of water molecules, this is an endothermic reaction.

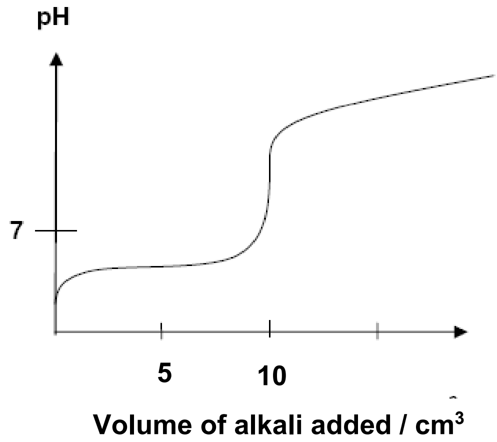
Option B is wrong. As temperature increases, more hydrogen bonds between molecules are broken.

Option C is wrong. The pH of pure water decreases with temperature. (pH = 7 at 25 °C and pH = 6.5 at 62 °C)

Option D is correct as water is neutral at all temperature as $[H^+] = [OH^-]$.

14 The following graph shows the changes in pH of 20.0 cm^3 of 1.0 mol dm^{-3} acid solution when excess 1.0 mol dm^{-3} alkali solution is added gradually.

Which one of the following pairs of solution with a suitable indicator could have resulted in the graph below?



	alkali	acid	indicator
A	NaOH	H_2SO_4	Methyl orange
B	NH_3	HNO_3	Phenolphthalein
C	KOH	CH_3CO_2H	Methyl orange
D	$Ba(OH)_2$	$CH_3CH_2CO_2H$	Phenolphthalein

Answer: D

Since the volume of alkali needed for neutralisation is half of that of acid, this indicates that there should be 2 OH^- per base molecules. Since this is a weak acid-strong base titration, pH at equivalence point should be greater than 7 as a basic salt is formed. Phenolphthalein is a suitable indicator as its working range is greater than 7.

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

The AgC*l* / Ag reference electrode is based on the following reaction:

$$\mathrm{AgC}l + e^- \rightleftharpoons \mathrm{Ag} + \mathrm{C}l^-$$

The reduction potential of the Fe^{2+} / Fe half−cell was found to be −0.64 V when measured using the AgC*l* / Ag reference electrode.

What is the reduction potential of the AgC*l* / Ag electrode with respect to the standard hydrogen electrode?

A –1.10 V **B** –0.20 V **C** +0.20 V **D** +1.10 V

Answer: C

The reduction potential of the Fe^{2+} / Fe half−cell was found to be −0.44 V when measured using the standard hydrogen electrode.

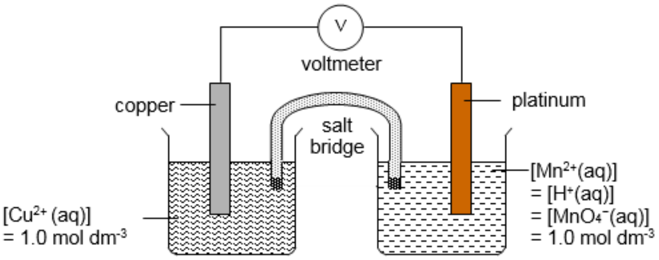
$E^o_{cell} = E^o_{red} - E^o_{ox}$

$-0.44\ V = E^o_{red} - 0.64$

$E^o_{red} = +\ 0.20\ V$

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

A cell is set up by connecting a Cu^{2+}/Cu half-cell and an acidified MnO_4^-/Mn^{2+} half-cell.



Which change in the set up will cause the corresponding effect on the e.m.f (potential difference) of the cell?

	change	effect on e.m.f of cell
A	addition of excess NH_3 (aq) into oxidation half-cell	increases
B	addition of concentrated H_2SO_4 into reduction half-cell	decreases
C	increase the size of the copper electrode	increases
D	replace copper with an alloy of copper and zinc	remains the same

Answer: A

$Cu^{2+} + 2e \rightleftharpoons Cu$ $\quad +0.34$ V
$MnO_4^- + 8H^+ + 5e \rightleftharpoons Mn^{2+} + 4H_2O$ $\quad +1.52$ V

$E^o_{cell} = E^o_{red} - E^o_{ox} = +1.52 – (+0.34) = +1.18$ V

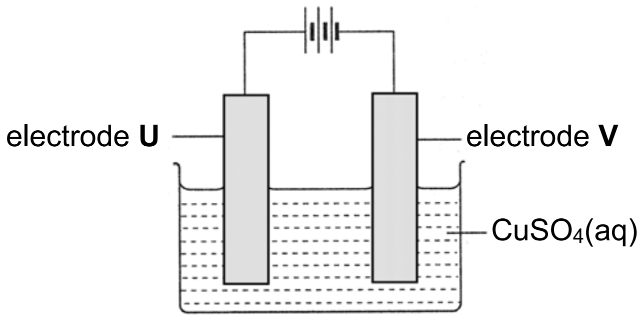
Option A is correct: when excess NH_3 (aq) into oxidation half-cell, $[Cu^{2+}]$ decreases as Cu^{2+} reacts with NH_3 to form $[Cu(NH_3)_4]^{2+}$. Since $[Cu^{2+}]$ decreases, equilibrium position shifts to the left, E^o_{ox} is less positive, E^o_{cell} becomes more positive.

Option B is wrong. When concentrated H_2SO_4 is added into reduction half-cell, $[H^+]$ increases. Since $[H^+]$ increases, equilibrium position shifts to the right, E^o_{red} is more positive, E^o_{cell} becomes more positive.

Option C is wrong. Increase the size of the copper electrode will not have effect on e.m.f. of the cell.

Option D is wrong. Replace copper with an alloy of copper and zinc will result in more positive E^o_{cell}. (+1.52 – (–0.76) = +2.28 V)

17 In an experiment, a cell was set up to obtain pure copper from a copper-silver alloy as shown below. Electrode **V** is pure copper and electrode **U** is the copper-silver alloy.



When a current of 40.0 A flows through the electrolyte for 26.8 minutes, the mass of the anode changes by 26.47 g.

What is the percentage of silver by mass in the electrode **U**?

A 20%

B 40%

C 60%

D 80%

Answer: A

$I \times t = n_e \times F$
$40 \times 26.8 \times 60 = n_e \times 96500$
$n_e = 0.6665$ mol

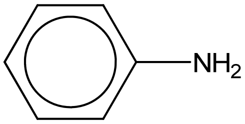
Since Cu : e = 1 : 2,
Amount of Cu formed = ½ x 0.6665 = 0.3332 mol
Mass of Cu formed = 0.3332 x 63.5 = 21.16 g

% silver by mass = (26.47-21.16)/26.47 x 100% = 20%

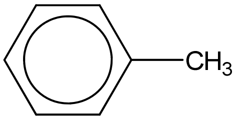
18 Which of the following is a planar molecule?

A $H{-}C{\equiv}C{-}CH_2CH_3$

B



C



D $H_2C{=}CH{-}CHO$

Answer: D

Option A is wrong. There are 2 sp^3 carbon atoms (tetrahedral around the C) in the molecule.

Option B is wrong. The molecule is trigonal pyramidal around the N atom.

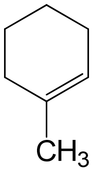
Option C is wrong. There are 1 sp^3 carbon atom (tetrahedral around the C) in the molecule.

Option D is correct. All the carbons are sp^2 carbon in the molecule.

19 A hydrocarbon, on heating with an excess of hot concentrated acidic $KMnO_4$ produces $HO_2CCH_2CH_2CH_2COCH_3$.

What could the hydrocarbon be?

1



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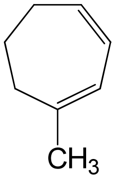

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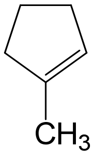


A 1 and 2 only

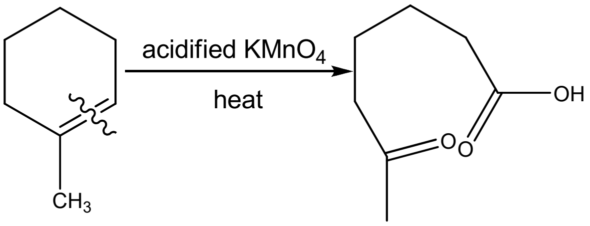
B 1 and 3 only

C 2 and 3 only

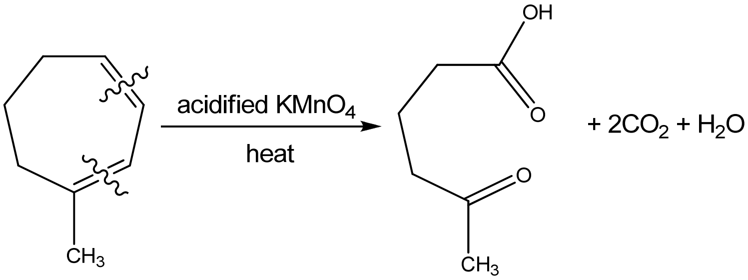
D 1, 2 and 3

Answer: C

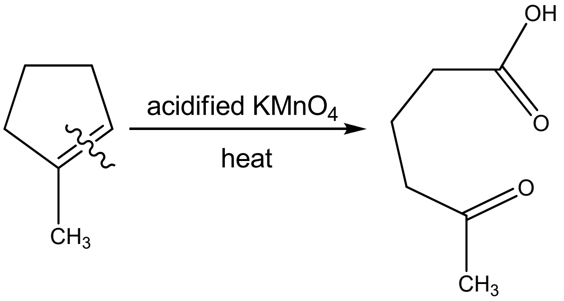
Option A is wrong.



Option B is correct.

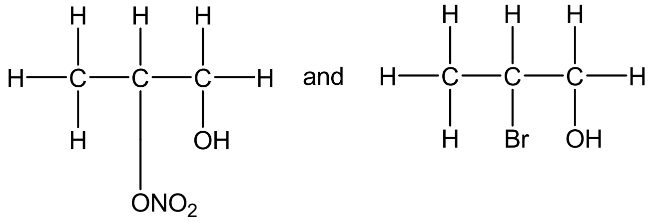


Option C is correct.

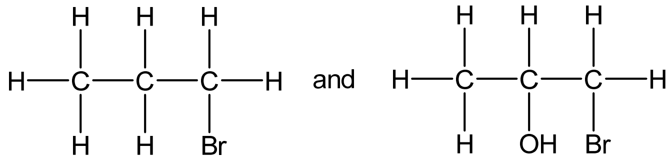


20 When propene reacts with Br_2 in the presence of excess aqueous KNO_3, what are the two major products formed?

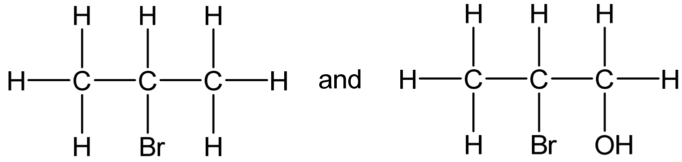
A



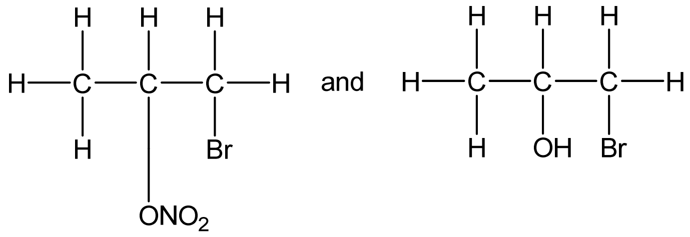
B



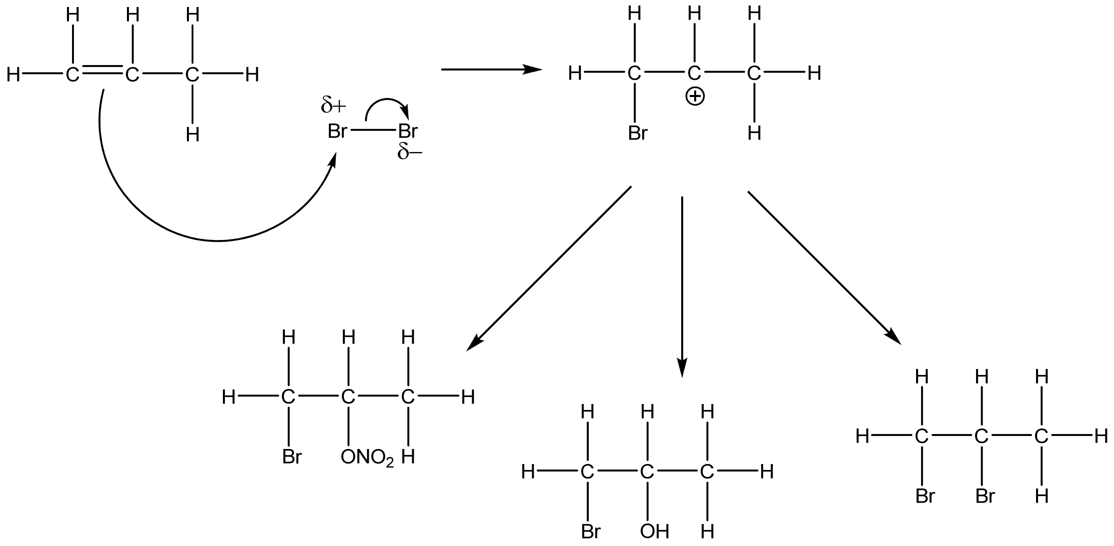
C



D



Answer: D



21 The molecule of benzene, C_6H_6 is a regular hexagon in which the π electrons are described as delocalised.

Which of the following statements are true for benzene?

1 It prevents benzene from undergoing addition reactions.

2 All C–C bonds lengths in benzene are intermediate between C–C bond in an alkane and C=C bond in an alkene.

3 The enthalpy change of hydrogenation of benzene is less exothermic than that predicted for cyclohexatriene.

4 The presence of π electrons enables benzene to be a good electrical conductor.

A 1 and 2 only

B 2 and 3 only

C 1, 2 and 3 only

D 1, 2 and 4 only

Answer: C

Option 1 is correct. Benzene undergoes substitution reaction to remain its aromaticity.

Option 2 is correct. As the π electrons are delocalised in the benzene ring, all the C-C bonds have partial double bond character.

Option 3 is correct. As the π electrons are delocalised in the benzene ring, benzene is more stable and it occupies lower energy level as it is more stable due to its aromaticity. As a result, less energy is released from hydrogenation of benzene.

Option 4 is wrong. Although the π electrons are delocalised in the benzene ring, there is no free mobile electrons and ions in liquid benzene, thus benzene is not a good conductor of electricity.

22 Some chlorobutanes were separately treated with hot ethanolic sodium hydroxide. Two of these gave the same hydrocarbon, C_4H_6.

From which pair of chlorobutanes was this hydrocarbon obtained?

A $CH_3CH_2CH_2CH_2Cl$ and $CH_3CH_2CH_2CHCl_2$

B $CH_3CH_2CH_2CH_2Cl$ and $ClCH_2CH_2CH_2CH_2Cl$

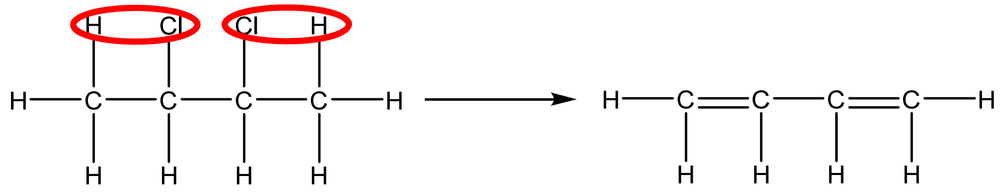
C $CH_3CH_2CCl_2CH_3$ and $ClCH_2CH_2CH_2CHCl_2$

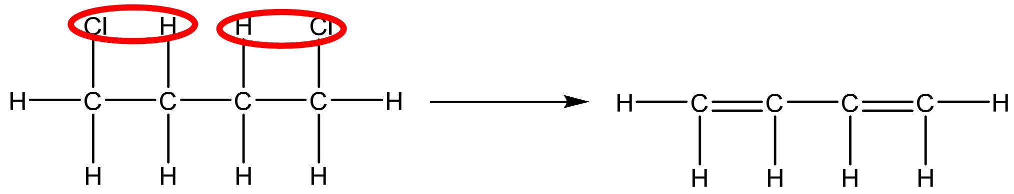
D $CH_3CHClCHClCH_3$ and $ClCH_2CH_2CH_2CH_2Cl$

Answer: D

For option A, B and C, there is at least one molecule in the option contain 1 or 3 Cl atoms which after elimination can only form 1 or 3 C=C bond.

For option D, the two compounds can produce the same compound, as shown below:





23 Deuterium, D, is the ${}^{2}_{1}H$ isotope of hydrogen.

Which of the following reactions yield a carbon compound containing deuterium?

1 $CH_3CH_2CN \xrightarrow[\text{heat}]{D_2,\ \text{Ni catalyst}}$

2 $CH_3CO_2CH_2CH_3 \xrightarrow[\text{heat}]{D_2SO_4,\ D_2O}$

3 $CH_3COCI_3 \xrightarrow[D_2O]{\text{NaOD}}$

4 $(CH_3)_3OH \xrightarrow[\text{heat}]{\text{conc } D_2SO_4}$

A 1 and 2 only

B 1 and 4 only

C 1, 2 and 3 only

D 2, 3 and 4 only

Answer: C

Option 1 is correct.

$$CH_3CH_2CN \xrightarrow[\text{heat}]{D_2,\ \text{Ni catalyst}} CH_3CH_2CD_2ND_2$$

Option 2 is correct.

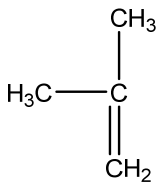
$$CH_3CO_2CH_2CH_3 \xrightarrow[\text{heat}]{D_2SO_4,\ D_2O} CH_3COOD + CH_3CH_2OD$$

Option 3 is correct.

$$CH_3COCI_3 \xrightarrow[D_2O]{\text{NaOD}} CH_3COO^- + CDI_3$$

Option 4 is wrong.

$$(CH_3)_3OH \xrightarrow[\text{heat}]{\text{conc } D_2SO_4}$$



$$H_3C-C(CH_3)=CH_2$$

24 Which of the following synthetic routes **does not** produce ethanoic acid?

A $CH_3Br \xrightarrow[\text{heat}]{\text{alcoholic KCN}} \xrightarrow[\text{heat}]{\text{dil HCl}}$

B $CH_3CHO \xrightarrow[\text{warm}]{[Ag(NH_3)_2]^+} \xrightarrow[\text{r.t.p.}]{H^+}$

C $CH_3CH(OH)CH_3 \xrightarrow[\text{warm}]{\text{aqueous alkaline iodine}} \xrightarrow[\text{r.t.p.}]{H^+}$

D $CH_3CH(OH)CH_2CH_3 \xrightarrow[180\ ^\circ C]{\text{excess conc } H_2SO_4} \xrightarrow[\text{heat}]{\text{acidic } K_2Cr_2O_7}$

Answer: D

Option A is correct.

$$CH_3Br \xrightarrow[\text{heat}]{\text{alcoholic KCN}} CH_3CN \xrightarrow[\text{heat}]{\text{dil HCl}} CH_3COOH$$

Option B is correct.

$$CH_3CHO \xrightarrow[\text{warm}]{[Ag(NH_3)_2]^+} CH_3COO^- \xrightarrow[\text{r.t.p.}]{H^+} CH_3COOH$$

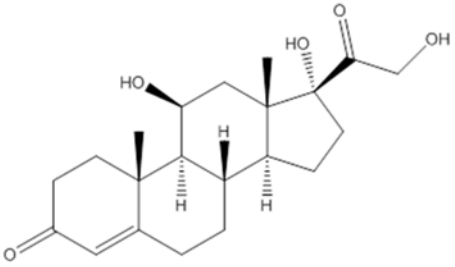
Option C is correct.

$$CH_3CH(OH)CH_3 \xrightarrow[\text{warm}]{\text{aqueous alkaline iodine}} CH_3COO^- \xrightarrow[\text{r.t.p.}]{H^+} CH_3COOH$$

Option D is wrong.

$$CH_3CH(OH)CH_2CH_3 \xrightarrow[180\ ^\circ C]{\text{excess conc } H_2SO_4} \begin{array}{c} CH_3CH{=}CH_2CH_3 \\ CH_2{=}CHCH_2CH_3 \end{array} \xrightarrow[\text{heat}]{\text{acidic } K_2Cr_2O_7} \text{no reaction}$$

25 Hydrocortisone is a steroid hormone produced by the adrenal gland and is released in response to stress. It is commonly used as an active ingredient in anti-inflammatory creams.



Hydrocortisone

Which of the following statements about hydrocortisone is true?

A When treated with $NaBH_4$ in the presence of methanol, it forms a compound containing 5 hydroxy groups.

B When warmed with aqueous alkaline iodine, a yellow precipitate is observed.

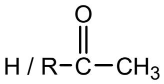
C When treated with cold dilute $KMnO_4$, it forms a compound containing 2 hydroxy groups.

D When treated with an excess of hot concentrated acidified $KMnO_4$, it forms a compound containing 7 chiral centres.

Answer: A

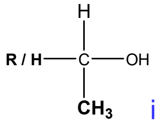
Option A is correct. The two ketone is reduced to secondary alcohol. Together with the other three alcohol in the molecule, the molecule has 5 hydroxy group.

Option B is wrong. There is no



$H / R-\overset{\displaystyle O}{\overset{\|}{C}}-CH_3$

or

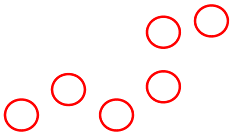


$R / H-\overset{\displaystyle H}{\overset{|}{\underset{\underset{\displaystyle CH_3}{|}}{C}}}-OH$

in the molecule.

Option C is wrong. When treated with cold dilute $KMnO_4$, the alkene in the molecule will be converted to diol. Together with the other three alcohol in the molecule, the molecule has 5 hydroxy group.

Option D is wrong. When treated with an excess of hot concentrated acidified $KMnO_4$, it forms a compound containing 6 chiral centres.



26 Equal amounts of compounds **P**, **Q**, **R** and **S** are separately shaken with 100 cm^3 of water. The pH of each resultant solution is then measured.

$CH_3CH_2CO_2H$	CH_3CH_2COCl	$ClCH_2CH_2CO_2H$	$BrCH_2CH_2CO_2H$
P	**Q**	**R**	**S**

Which of the following shows the correct order of increasing order of acidity of the solutions formed?

A P, R, S, Q

B P, S, R, Q

C Q, P, S, R

D Q, S, R, P

Answer: B

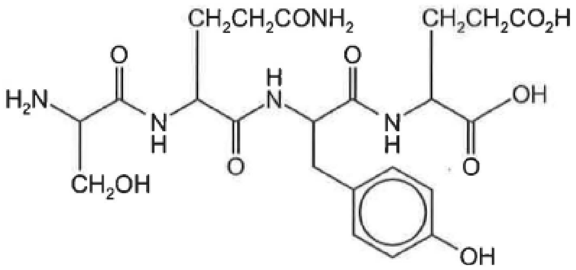
$CH_3CH_2COCl + H_2O \rightarrow CH_3CH_2CO_2H + HCl$

Solution is most acidic.

Cl group is more electronegative than Br and the negative charge of $ClCH_2CH_2CO_2^-$ is dispersed to a greater extent than $BrCH_2CH_2CO_2^-$. Thus, $ClCH_2CH_2CO_2^-$ is more stable than $BrCH_2CH_2CO_2^-$. $ClCH_2CH_2CO_2H$ is more acidic than $BrCH_2CH_2CO_2H$.

$CH_3CH_2CO_2H$ is the least acidic among the four compounds.

27 The diagram shows the structure of the tetrapeptide **T**.

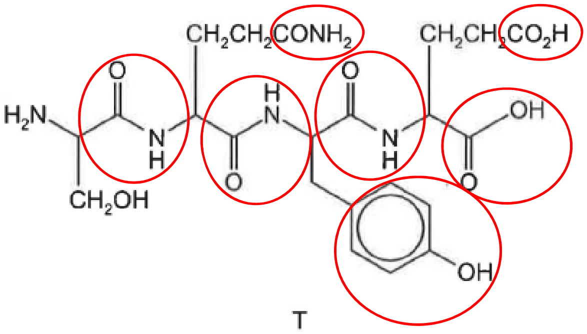


T

When 0.1 mole of **T** is heated under reflux with NaOH(aq) until no further reaction occurs, how many moles of NaOH will react?

A	0.4	**B**	0.5
C	0.6	**D**	0.7

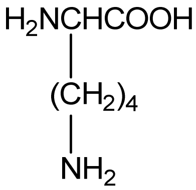
Answer: D



T

The circled functional group can react with NaOH(aq), heat with reflux.

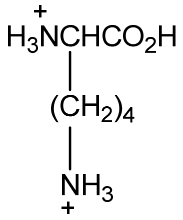
28 Lysine is an α-amino acid.



$$\begin{array}{l} H_2NCHCOOH \\ \quad\;| \\ \;(CH_2)_4 \\ \quad\;| \\ \;\;NH_2 \end{array}$$

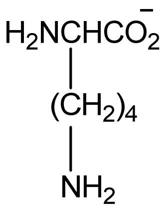
Which structure is predominant when lysine is in an aqueous solution of pH 9.5, given that lysine has three pK_a values of 2.2, 8.9 and 10.5?

A



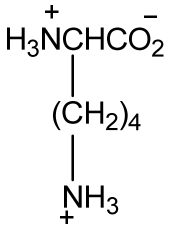
$$\begin{array}{l} H_3\overset{+}{N}CHCO_2H \\ \quad\;| \\ \;(CH_2)_4 \\ \quad\;| \\ \;\;\underset{+}{N}H_3 \end{array}$$

B



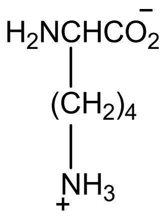
$$\begin{array}{l} H_2NCHCO_2^{-} \\ \quad\;| \\ \;(CH_2)_4 \\ \quad\;| \\ \;\;NH_2 \end{array}$$

C



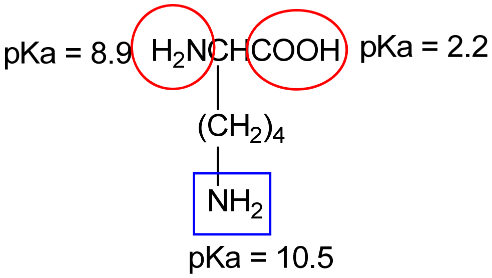
$$\begin{array}{l} H_3\overset{+}{N}CHCO_2^{-} \\ \quad\;| \\ \;(CH_2)_4 \\ \quad\;| \\ \;\;\underset{+}{N}H_3 \end{array}$$

D

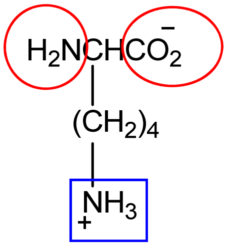


$$\begin{array}{l} H_2NCHCO_2^{-} \\ \quad\;| \\ \;(CH_2)_4 \\ \quad\;| \\ \;\;\underset{+}{N}H_3 \end{array}$$

Answer: D



When pH > pKa, the functional group circled will be deprotonated.
When pH < pKa, the functional group squared will be protonated.



$$\begin{array}{l} H_2NCHCO_2^{-} \\ \quad\;| \\ \;(CH_2)_4 \\ \quad\;| \\ \;\;\underset{+}{N}H_3 \end{array}$$

29 Element **J** is in Period 3 of the Periodic Table. The following three statements are the properties of element **J** or its compounds.

- Adding NaOH(aq) to the solution resulting from the reaction of a chloride of **J** with water produces a white precipitate which is soluble in an excess of NaOH(aq).
- Element **J** is a solid at room temperature.
- The oxide of element **J** is soluble in hydrochloric acid.

What is the identity of element **J**?

A	magnesium	**C**	silicon
B	aluminium	**D**	phosphorus

Answer: B

Based on the information provided, the only possible Period 3 element for **J** is Al.

$AlCl_3 + 3NaOH \rightarrow Al(OH)_3 + 3NaCl$
$Al(OH)_3 + NaOH \rightarrow NaAl(OH)_4$

Al is a solid at room temperature.

The oxide of Al is soluble in hydrochloric acid.
$Al_2O_3 + 6HCl \rightarrow 2AlCl_3 + 3H_2O$

30 *The use of the Data Booklet is relevant to this question.*

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

Oxidation state	V	IV	III	II
Ion	VO_2^+	VO^{2+}	V^{3+}	V^{2+}
Colour	yellow	blue	green	violet

What is the final colour of the solution when excess zinc powder is added to an acidified solution containing VO_2^+ ions?

A	yellow	**C**	green
B	blue	**D**	violet

Answer: D

$V^{3+} + e^- \rightleftharpoons V^{2+}$	–0.26
$VO^{2+} + 2H^+ + e^- \rightleftharpoons V^{3+} + H_2O$	+0.34
$VO_2^+ + 2H^+ + e^- \rightleftharpoons VO^{2+} + H_2O$	+1.00
$Zn^{2+} + 2e^- \rightleftharpoons Zn$	–0.76

$E^o_{cell} = E^o_{red} - E^o_{ox} = E^o_{red} - (-0.76)$

For reaction to be spontaneous, $E^o_{cell} > 0$ V. In order for E^o_{cell} to be > 0, E^o_{red} must be > –0.76
Thus, VO_2^+ will be eventually reduced to V^{2+}

End of Paper

INNOVA JUNIOR COLLEGE
JC2 PRELIMINARY EXAMINATION
in preparation for General Certificate of Education Advanced Level
Higher 2

CANDIDATE NAME

CLASS

INDEX NUMBER

CHEMISTRY 9729/02

Paper 2 Structured Questions **27 August 2018**

Candidates answer on the question paper. **2 hours**

Additional Materials: *Data Booklet*

READ THESE INSTRUCTIONS FIRST

Write your index number, name and civics group on all the work you hand in.
Write in dark blue or black pen.
You may use pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.

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

You are advised to show all working in calculations.
You are reminded of the need for good English and clear presentation in your answers.
You are reminded of the need for good handwriting.
Your final answers should be in 3 significant figures.

You may use a calculator.

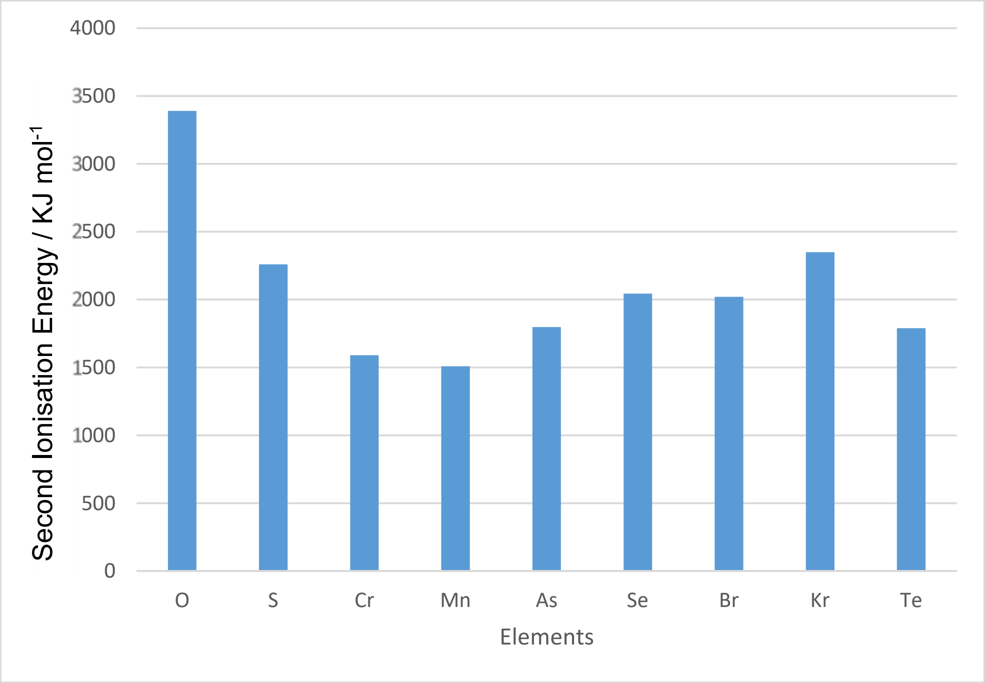
The number of marks is given in brackets [ ] at the end of each question or part question.

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

For Examiner's Use	
1	**9**
2	**8**
3	**6**
4	**15**
5	**13**
6	**12**
7	**12**
Significant Figures and Units	
Handwriting and Presentation	
Total	**75**

This document consists of **19** printed pages **1** blank page.

1 **(a)** The following diagram shows the second ionisation energy of some elements.



(i) Explain why the second ionisation energies of elements O, S, Se and Te show a decreasing trend.

……………………………………………………………………………………………

……………………………………………………………………………………………

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

(ii) Explain why the second ionisation energy of Br is lower than that of Se.

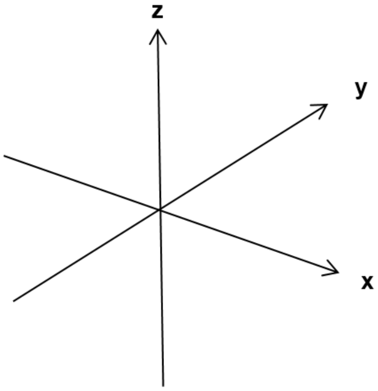
……………………………………………………………………………………………

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

(iii) Write the full ground state electronic configuration for Cr.

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

(iv) Draw the d_{xy} orbital in the axes provided below. [1]



(b) Oxygen–oxygen bond lengths in some molecules are given below:

Molecule	Bond Length
Oxygen, O_2	0.121 nm
Hydrogen peroxide, H_2O_2	0.149 nm
Ozone, O_3	0.128 nm

(i) Draw the structure of the molecule ozone, O_3. [1]

(ii) With reference to the data given above, comment and explain the oxygen–oxygen bond length in ozone as compared to oxygen and hydrogen peroxide.

………………………………………………………………………………………………

………………………………………………………………………………………………

………………………………………………………………………………………………

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

(iii) Explain clearly why hydrogen peroxide is a liquid while oxygen is a gas at room conditions in terms of structure and bonding.

…………………………………………………………………………………………

…………………………………………………………………………………………

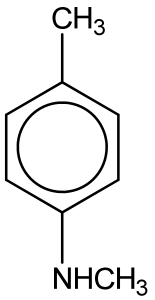
…………………………………………………………………………………………

…………………………………………………………………………………………[2]

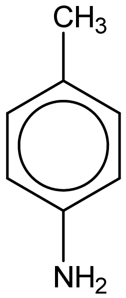
[Total: 9]

2 Compounds containing nitrogen are important to life and have applications in science and medicine.

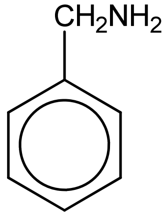
Three nitrogeneous bases have the following structures.



N,4-dimethylbenzenamine



4-methylphenylamine



benzylamine

(a) **(i)** Arrange the three bases above in increasing order of pK_b.

…………………………………………………………………………………………[1]

(ii) Explain in terms of their molecular structures why benzylamine and 4-methylphenylamine have different pK_b values.

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………[2]

(iii) Outline how *N*,4-dimethylbenzenamine may be produced from 4-methylphenylamine.

…………………………………………………………………………………………..

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

(b) The pK_b of benzylamine is 4.66.

25.0 cm^3 of 0.025 mol dm^{-3} benzylamine was completely neutralised by dilute hydrochloric acid of the same concentration. The salt formed reacts with water and the pH of the resultant solution is less than 7.

(i) Write the equation to show the reaction between the salt formed and water.

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

(ii) With reference to your equation in **(b)(i)**, write an expression for the acid dissociation constant of the salt.

[1]

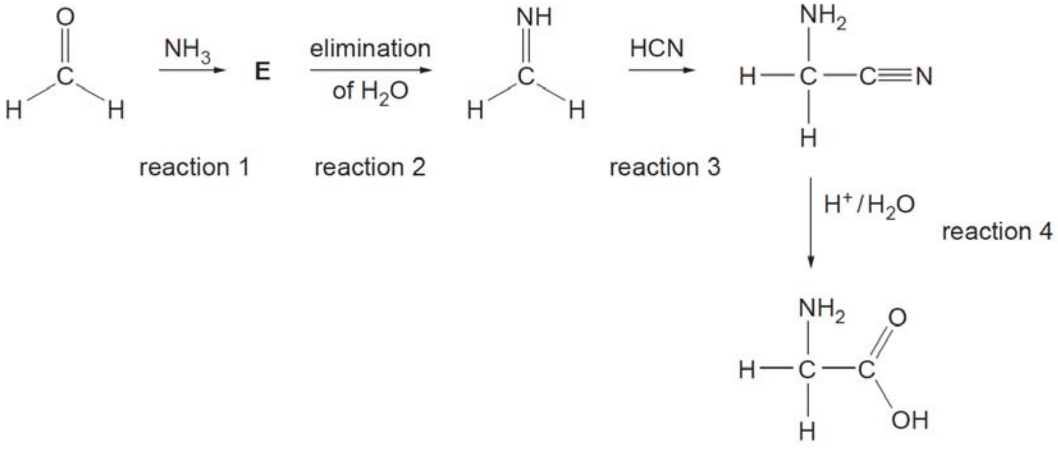
(iii) Hence, determine the pH of the resultant solution.

[2]

[Total: 8]

3 Methanal is a colorless, strong-smelling gas used in making building materials and many household products.

The Strecker synthesis is a route to preparing amino acids. Glycine, 2-aminoethanoic acid, can be prepared from methanal in this way. This is shown in the four steps reaction scheme below.



2-aminoethanoic acid

(a) **(i)** Suggest the role of ammonia in this synthesis.

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

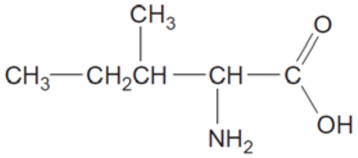
(ii) Compound **E** has the molecular formula CH_5NO.
Suggest a structure for compound **E**.

[1]

(iii) State the type of reaction for reaction 4.

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

(b) The amino acid shown below is isoleucine, 2-amino-3-methylpentanoic acid.



2-amino-3-methylpentanoic acid

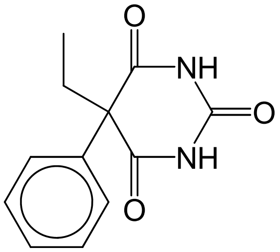
Molecule **F** can be used as the starting material to prepare this amino acid using a Strecker synthesis.

Draw the skeletal structure of **F**.

[1]

(c) An amide bond is formed when two amino acids react together.

Phenobarbital, which is a medication used to treat epilepsy, also has an amide bond in it.



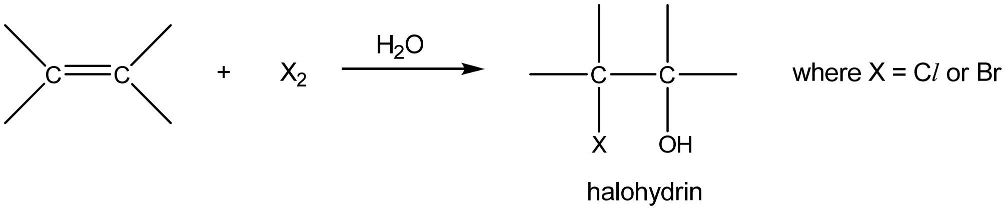
phenobarbital

Predict all the products formed when phenorbarbital undergoes acidic hydrolysis.

[2]

[Total: 6]

4 **(a)** Formation of 1,2-halo alcohols, also known as halohydrins, occurs via the addition reaction between an alkene and a halogen in the presence of water.



In a series of experiments, the reaction between propene and aqueous bromine was carried out with different concentrations of the two reagents, and the following relative initial rates were obtained.

Experiment	[$CH_3CH{=}CH_2$] / mol dm^{-3}	[Br_2] / mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}
1	0.020	0.020	1.00×10^{-3}
2	0.030	0.020	1.50×10^{-3}
3	0.040	0.030	3.00×10^{-3}

(i) Use these data to deduce the order of reaction with respect to each of the two reagents, showing how you arrive at your answers.

[2]

(ii) Hence write a rate equation for the reaction.

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

(iii) Calculate the rate constant for the reaction, giving its units.

[2]

(iv) State and explain how the rate of reaction may change if chlorine is used instead of bromine in the reaction with propene.

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

(b) **(i)** The mechanism of the addition reaction between propene and aqueous Br_2 involves three steps.

- There is an initial attack by the π electron pair of the alkene on Br_2 to yield a carbocation intermediate.
- This is followed by the nucleophilic attack of the lone pair of electrons on oxygen in water on the carbocation intermediate.
- The third step involves the loss of H^+ ion which then yields the neutral bromohydrin.

Using the information given above, describe a mechanism for this reaction.

[3]

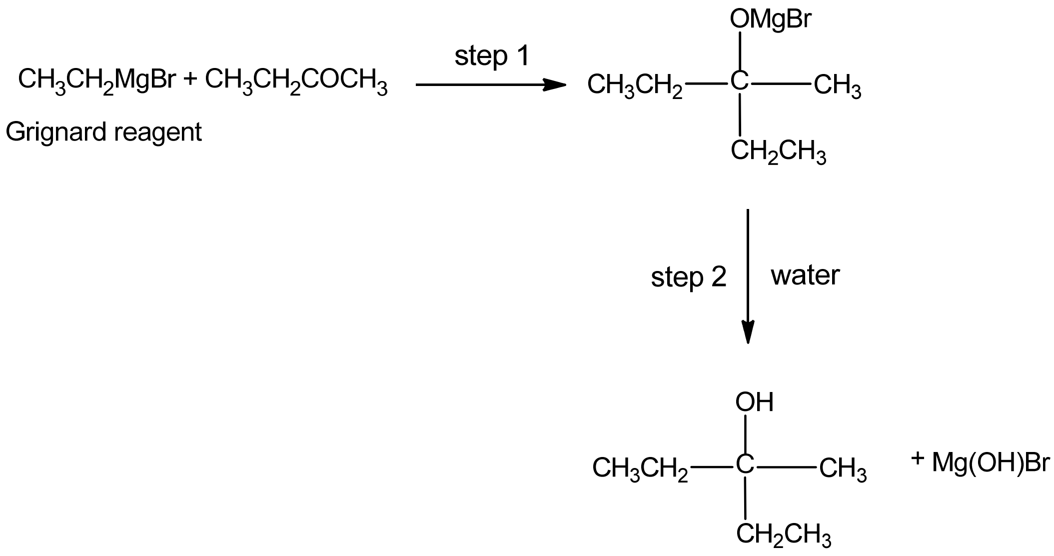
(ii) Based on your mechanism drawn, explain whether it is consistent with the rate equation proposed.

…………………………………………………………………………………………

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

(c) Grignard reagents are organo-magnesium halides, commonly used in synthesis to prepare a variety of organic compounds.

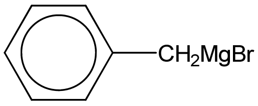
The carbon-magnesium bonds in Grignard reagents are highly polar and this makes it extremely useful in organic synthesis as it is able to react with other polar organic molecules to form carbon-carbon bonds. An example of the use of a Grignard reagent is the two-step reaction of CH_3CH_2MgBr with butanone, $CH_3CH_2COCH_3$, to form 3-methylpentan-3-ol.



3-methylpentan-3-ol

(i) Suggest the type of reaction that has taken place in step 1.

……………………………………………………………………………………[1]

(ii) Suggest the structural formula of the final organic product formed when  is reacted with propanone, CH_3COCH_3, in a similar two-step process.

[1]

(iii) Suggest a suitable Grignard reagent and another organic compound to be used if propan-2-ol is to be prepared using a similar two-step process.

[2]

(iv) The Grignard reagent $CH_3CH_2CH_2MgBr$ can be readily converted into a carboxylic acid by using carbon dioxide.

Suggest the structural formula for the organic product formed.

[1]

[Total: 15]

5 **(a)** Cobalt forms many coloured complexes. Cobalt(**III**) chloride combines with ammonia to form a pink coloured compound **A**, $CoCl_3.H_2O.5NH_3$ (M_r = 268.4) in which the coordination number of cobalt is 6.

1.00 g of **A** is dissolved in 25 cm^3 of water and the solution is titrated with 0.500 mol dm^{-3} silver nitrate solution. It is found that 22.40 cm^3 of silver nitrate is required for complete reaction.

(i) Calculate the number of moles of free chloride ions per mole of **A**.

[2]

(ii) Draw the structure of the complex ion in **A.**

[1]

(iii) When the pink compound **A** is heated, water vapour and ammonia were evolved to give a purple solid **B**.
A and **B** have the same coordination number.

Suggest the formula of the complex in the purple solid **B**.

....[1]

(iv) Account for the difference in the colour of **A** and **B**.

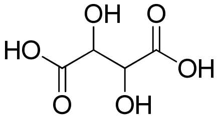
....

....

....

....[2]

(b) Aqueous hydrogen peroxide is fairly stable, but when a mixture of a cobalt(II) salt and tartaric acid is added to aqueous hydrogen peroxide, the initially pink solution slowly turns into a green cobalt(III) species.



tartaric acid

After a while, oxygen gas is vigorously evolved and the solution turns back to pink again.

(i) State the role of the cobalt(II) salt in this reaction and support your answer by referring to the observations.

Role of the cobalt(II) salt: …………………………….……………………………[1]

Observation with explanation:

………………..…………………………………………………………………………

………………..…………………………………………………………………………

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

(ii) Tartaric acid acts as a complexing agent in this reaction to stabilise the Co^{3+} cation.

With the aid of relevant data from the *Data Booklet*, show that Co^{3+} is not stable in aqueous solution.

………………..…………………………………………………………………………

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

(c) A student wanted to measure the standard cell potential, $E^{\varnothing}_{cell}$, between the Co^{2+}/Co half-cell and the Fe^{3+}/Fe^{2+} half-cell. She set up and connected the two half cells and obtained a reading.

(i) Calculate the value $E^{\varnothing}_{cell}$ that will be obtained by the student.

[1]

(ii) State and explain what happens to the standard cell potential, $E^{\varnothing}_{cell}$ when ammonia is added to the Co^{2+}/Co half-cell.

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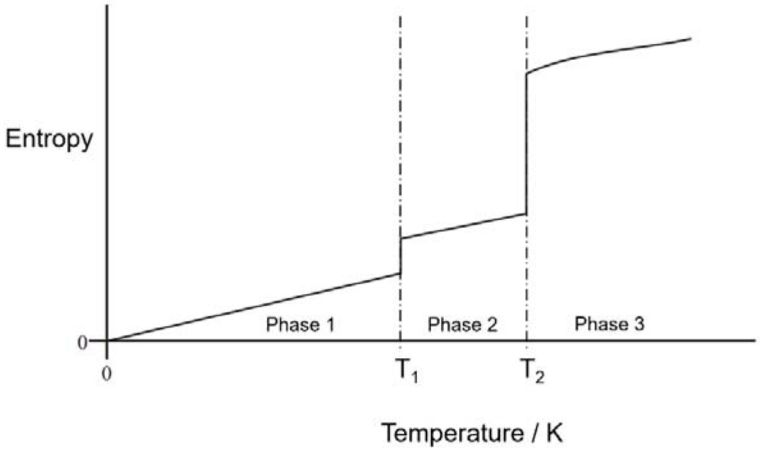
………………………………………………………………………………………[2]

[Total: 13]

6 A student plotted the sketch graph below to show how the entropy of a sample of H_2O varies with temperature.



(a) Identify the state of H_2O in Phase 2 and 3 respectively. Suggest a value of T_2.

In phase 2:……………… In phase 3: ……………… value of T_2: ……………… [1]

(b) Suggest why entropy of H_2O is zero at 0 K.

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

(c) Explain why the entropy change, ΔS, at temperature T_2 is much larger than that at temperature T_1.

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

(d) It requires 3.49 kJ of heat energy to convert 1.53 g of H_2O from the state in phase 2 to phase 3 at temperature T_2 and 100kPa.

Use these data and your value of T_2 in part **(a)** to calculate the value of ΔS, including units, for the conversion of one mole of H_2O from the state in phase 2 to phase 3 at temperature T_2.

[3]

(e) The student wants to find out if dissolving a salt, silver fluoride in water is always a spontaneous process. He must first find the enthalpy change of solution of silver fluoride in water.

Some enthalpy changes for silver fluoride are shown in the table.

	ΔH / kJ mol^{-1}
Lattice energy of silver fluoride	–950
Enthalpy change of hydration for silver ions	–464
Enthalpy change of hydration for fluoride ions	–506

(i) Use the data provided to calculate a value for the enthalpy change of solution of silver fluoride in water.

[2]

(ii) If entropy change for dissolving silver fluoride in water has a positive value, explain why dissolving of silver fluoride in water is always a spontaneous process.

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

(iii) Explain why the enthalpy change of hydration of the fluoride ions is more negative than the enthalpy change of hydration of the chloride ions.

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

[Total: 12]

7 The uses of carboxylic acids are so extensive that they can be divided into several industries, such as pharmaceuticals or food among others.

(a) Ethanol and ethanoic acid react reversibly to form ethyl ethanoate and water according to the equation:

$$CH_3COOH(l) + CH_3CH_2OH(l) \rightleftharpoons CH_3COOCH_2CH_3(l) + H_2O(l)$$

A student mixed 0.0800 mol of ethanoic acid and 0.120 mol of ethanol in a conical flask and the flask was sealed with a bung and allowed to reach equilibrium at 20 °C.

The equilibrium mixture is placed in a graduated flask and the volume made up to 250 cm^3 with distilled water. A 10.0 cm^3 sample of this equilibrium mixture was placed in a conical flask with a few drops of phenolphthalein and titrated with 0.100 mol dm^{-3} of sodium hydroxide from a burette. The indicator turned pink when 6.40 cm^3 of NaOH had been added.

(i) Calculate the amount of CH_3COOH in the 250 cm^3 equilibrium mixture.

[1]

(ii) Hence, calculate the value for K_c for the reaction of ethanoic acid and ethanol at 20 °C.

[2]

(b) The following table compares the pK_a values of two dicarboxylic acids with that of ethanoic acid.

Acid	Formula	pK_1	pK_2
ethanoic	CH_3COOH	4.8	–
malonic	$HOOCCH_2COOH$	2.8	5.7
succinic	$HOOC(CH_2)_2COOH$	4.2	5.6

(i) Suggest a reason why the pK_1 value of malonic acid is so much less than the pK_1 of ethanoic and succinic acid.

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

(ii) Suggest a reason why the pK_2 value of malonic and succinic acid is higher than its respective pK_1 value.

……………………………………………………………………………………………

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

(c) Malonic acid can undergo dehydration with P_4O_{10} to give a foul-smelling gas, **A**. At 30.5 kPa, 0.1057 g of A occupies 200 cm^3 at a temperature of 200°C. Determine the relative molecular mass of **A**.

[2]

(d) At high temperature, succinic acid can also undergo dehydration to produce a neutral compound **B**, $C_4H_4O_3$ which does not react with sodium metal or Brady's reagent.

Compound **B** reacts with ammonia to give a compound **C**, $C_4H_7NO_3$, which reacts with cold NaOH(aq), but not with cold HC*l*(aq).

Suggest structures for **B** and **C** and explain the observations.

[4]

[Total: 12]

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INNOVA JUNIOR COLLEGE
JC2 PRELIMINARY EXAMINATION
in preparation for General Certificate of Education Advanced Level
Higher 2

CANDIDATE NAME

CLASS

INDEX NUMBER

CHEMISTRY 9729/02

Paper 2 Structured Questions **27 August 2018**

Candidates answer on the question paper. **2 hours**

Additional Materials: *Data Booklet*

READ THESE INSTRUCTIONS FIRST

Write your index number, name and civics group on all the work you hand in.
Write in dark blue or black pen.
You may use pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.

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

You are advised to show all working in calculations.
You are reminded of the need for good English and clear presentation in your answers.
You are reminded of the need for good handwriting.
Your final answers should be in 3 significant figures.

You may use a calculator.

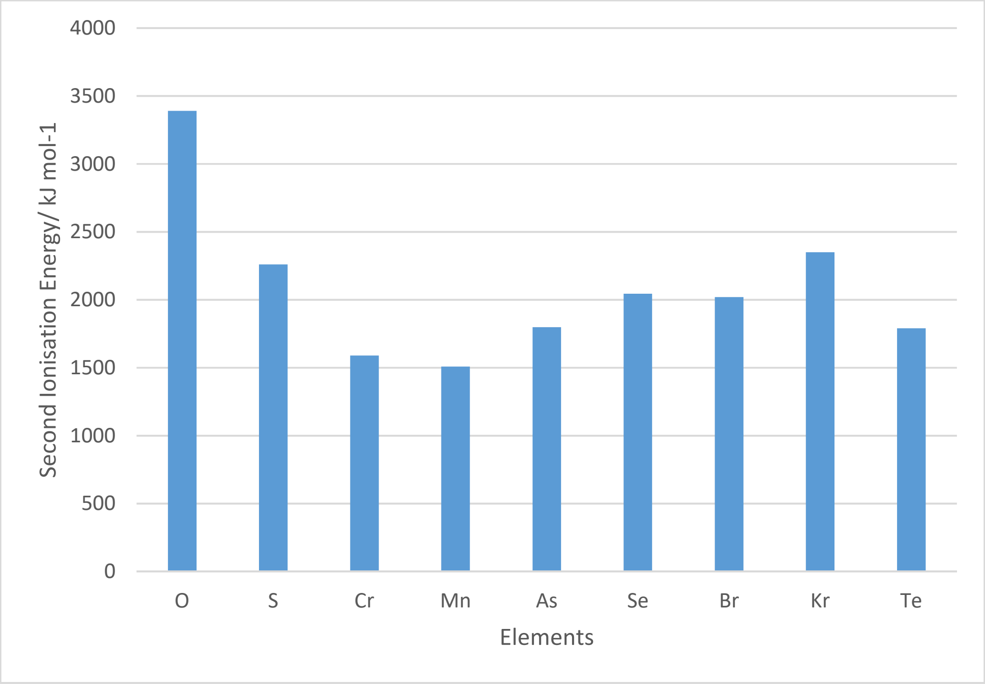
The number of marks is given in brackets [ ] at the end of each question or part question.

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

For Examiner's Use	
1	**9**
2	**8**
3	**6**
4	**15**
5	**13**
6	**12**
7	**12**
Significant Figures and Units	
Handwriting and Presentation	
Total	**75**

This document consists of **19** printed pages and **1** blank page.

1 **(a)** The following diagram shows the second ionisation energy of some elements.



(i) Explain why the second ionisation energies of elements O, S, Se and Te show a decreasing trend. [1]

The number of principal quantum shells increases/ The valence electrons are further away [√]
It is less strongly attracted to the nucleus OR Less energy is required to remove the valence electrons [√], hence second ionisation energy decreases.

(ii) Explain why the second ionisation energy is Br is lower than that of Se. [1]

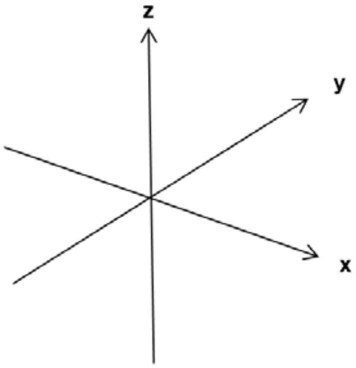
Se^+: $[Ar]4s^2 4p^3$ Br^+:$[Ar]4s^2 4p^4$

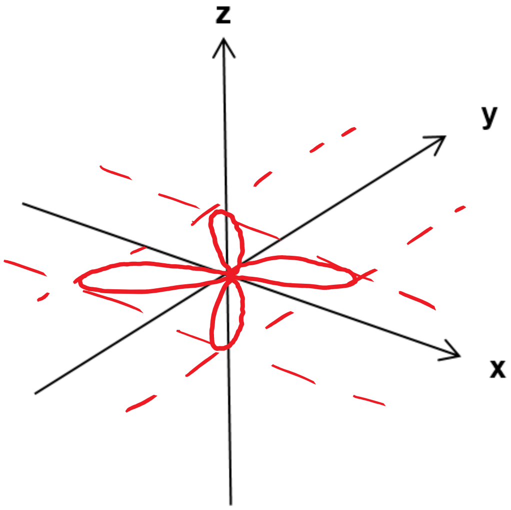
The paired 4p/np electrons[√] / 2 electrons in the same 4p orbital in Br^+ experience interelectronic repulsion [√], less energy is required to remove an electron from this orbital.

(iii) Write the full ground state electronic configuration for Cr. [1]

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^1$[1]

(iv) Draw the d_{xy} orbital in the axes provided below. [1]



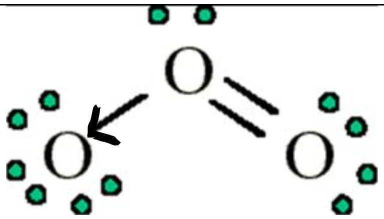


[1]

(b) Oxygen–oxygen bond lengths in some molecules are given below:

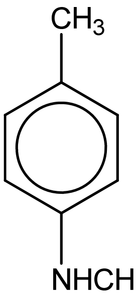
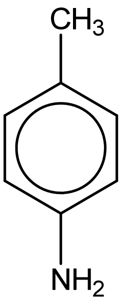
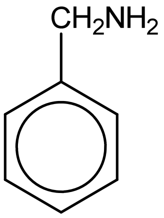
Molecule	Bond Length
Oxygen, O_2	0.121 nm
Hydrogen peroxide, H_2O_2	0.149 nm
Ozone, O_3	0.128 nm

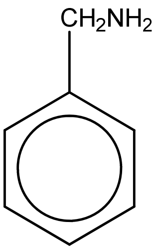
(i) Draw the structure of the molecule ozone, O_3. [1]



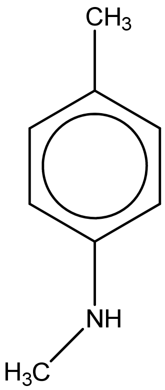
[1]

		(ii)	With reference to the data given above, comment and explain the oxygen–oxygen bond length in ozone as compared to oxygen and hydrogen peroxide. [2]
			Oxygen–oxygen bond length in ozone is longer than O=O in oxygen but shorter than O-O in hydrogen peroxide. [1] P orbital of oxygen overlap with π orbital of adjacent oxygen-oxygen double bond. OR Lone pair on oxygen atom can delocalised into the π electron cloud of adjacent oxygen- oxygen double bond [1]
		(iii)	Explain clearly why hydrogen peroxide is a liquid while oxygen is a gas at room conditions in terms of structure and bonding. [2]
			Both hydrogen peroxide and oxygen have simple molecular structure. [√] Oxygen have instantaneous dipole induced dipole forces of attraction between molecules [√] while hydrogen peroxide have hydrogen bonding between the molecules. [√] More energy is needed to overcome the stronger hydrogen bond [√], hence it has stronger intermolecular forces of attraction and exist as a liquid.
			[Total: 9]

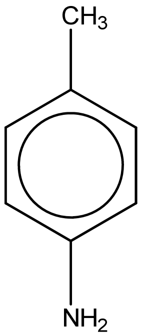
2	Compounds containing nitrogen are important to life and have applications in science and medicine. Three nitrogeneous bases have the following structures.  *N*,4-dimethylbenzenamine  4-methylphenylamine  benzylamine		
	(a)	**(i)**	Arrange the three bases above in increasing order of pK_b. [1]
			Lowest p*K*b ⟶ Highest p*K*b



benzylamine

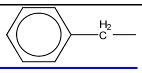


N,4-dimethyl benzenamine



4-methylphenylamine [1]

(ii) Explain in terms of their molecular structures why benzylamine and 4-methylphenylamine have different pK_b values. [2]

In benzylamine, the presence of electron donating  increases the electron density on N [✓], making the lone pair of electron on N more available [✓] to accept a proton. Hence, benzylamine is the most basic.

In 4-methylphenylamine, the lone pair of electron on N delocalised into the π orbital of the benzene ring, decreasing the electron density on N [✓], making the lone pair of electron on N less available [✓] to accept a proton. Hence, 4-methylphenylamine is the least basic.

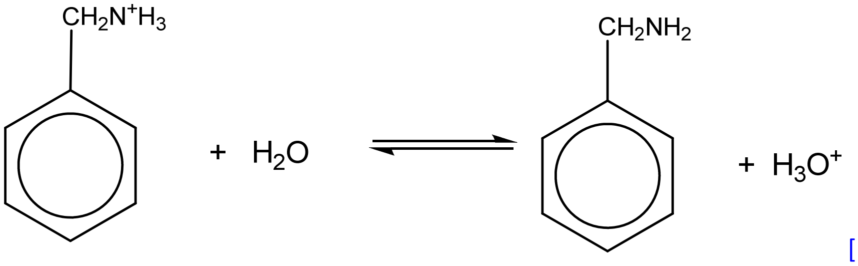
(iii) Outline how N,4-dimethylbenzenamine may be produced from 4-methylphenylamine. [1]

Heat 4-methylphenylamine with (ethanolic) CH_3Cl (in a sealed tube). [1]

(b) The pK_b of benzylamine is 4.66.

25.0 cm^3 of 0.025 mol dm^{-3} benzylamine was completely neutralised by dilute hydrochloric acid of the same concentration. The salt formed reacts with water and the pH of the resultant solution is less than 7.

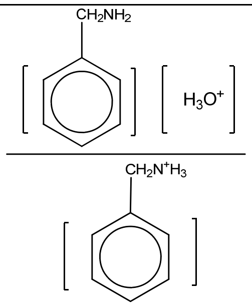
(i) Write the equation to show the reaction between the salt formed and water. [1]



[1]

(ii) With reference to your equation in (b)(i), write an expression for the acid dissociation constant of the salt. [1]

Ka =



[1]

(iii) Hence, determine the pH of the resultant solution. [2]

[salt] = $(6.25 \times 10^{-4}) \div (50/1000)$
= 0.0125 mol dm^{-3} [✓]

$K_a = K_w / K_b$
$= \frac{10^{-14}}{10^{-4.66}}$
$= 4.571 \times 10^{-10}$ [✓]

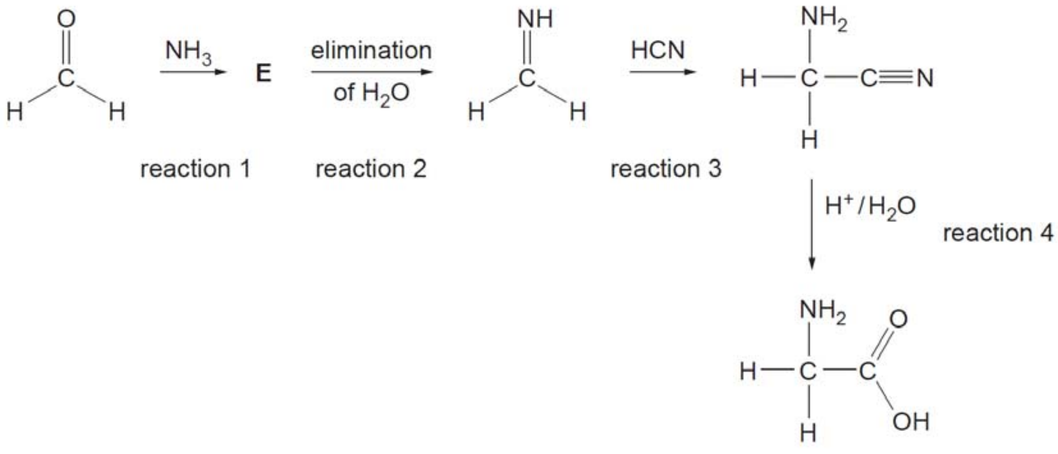
$[H^+] = \sqrt{Ka \times [salt]}$
$= \sqrt{4.571 \times 10^{-10} \times 0.0125}$
$= 2.390 \times 10^{-6}$ [✓]

pH = 5.62 [✓]

[Total: 8]

3 Methanal is a colorless, strong-smelling gas used in making building materials and many household products.

The Strecker synthesis is a route to preparing amino acids. Glycine, 2-aminoethanoic acid, can be prepared from methanal in this way. This is shown in the four steps reaction scheme below.

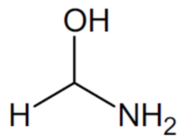


2-aminoethanoic acid

(a) **(i)** What is the role of ammonia, in the context of this synthesis? [1]

Nucleophile [1]
Allow Nucleophilic or Lewis base or Lone-pair donor

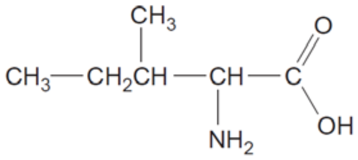
(ii) Compound **E** has the molecular formula CH_5NO.
Suggest a structure for compound **E**. [1]


[1]

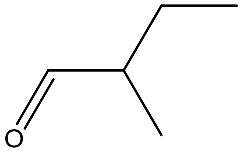
(iii) State the type of reaction for reaction 4. [1]

Acidic hydrolysis [1]

(b) The amino acid shown below is isoleucine, 2-amino-3-methylpentanoic acid.

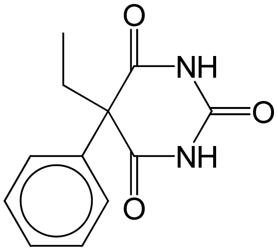


Molecule **F** can be used as the starting material to prepare this amino acid using a Strecker synthesis.
Draw the skeletal structure of **F**. [1]


[1]

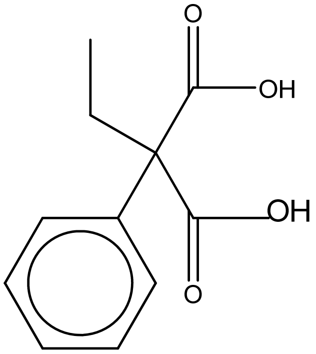
(c) An amide bond is formed when two amino acids react together.

Phenobarbital, which is a medication used to treat epilepsy, also has an amide bond in it.



phenobarbital

Predict all the products formed when phenorbarbital undergoes acidic hydrolysis.

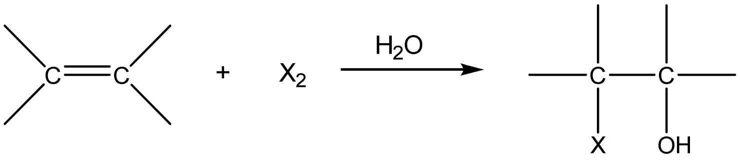


[1] , CO_2 [✓], NH_4^+ [✓]

[2]

[Total: 6]

4 **(a)** Formation of 1,2-halo alcohols, also known as halohydrins, occurs via the addition reaction between an alkene and a halogen in the presence of water.



halohydrin

where X = C*l* or Br

In a series of experiments, the reaction between propene and aqueous bromine was carried out with different concentrations of the two reagents, and the following relative initial rates were obtained.

Experiment	[$CH_3CH=CH_2$] / mol dm^{-3}	[Br_2] / mol dm^{-3}	initial rate / mol dm^{-3} s^{-1}
1	0.020	0.020	1.00×10^{-3}
2	0.030	0.020	1.50×10^{-3}
3	0.040	0.030	3.00×10^{-3}

(i) Use these data to deduce the order of reaction with respect to each of the two reagents, showing how you arrive at your answers. [2]

Let the rate equation be: Rate = k[$CH_3CH=CH_2$]^x[Br_2]^y

Comparing experiments 1 & 2,

$$\frac{Rate_1}{Rate_2} = \frac{k\,[CH_3CH=CH_2]^x\,[Br_2]^y}{k[CH_3CH=CH_2]^x\,[Br_2]^y}$$

$$\frac{1.00\times10^{-3}}{1.50\times10^{-3}} = \frac{k\,[0.020]^x\,[0.020]^y}{k\,[0.030]^x\,[0.020]^y}$$

x = 1 [1m]

Comparing experiments 1 & 3,

$$\frac{Rate_1}{Rate_3} = \frac{k\,[CH_3CH=CH_2]^x\,[Br_2]^y}{k[CH_3CH=CH_2]^x\,[Br_2]^y}$$

$$\frac{1.00\times10^{-3}}{3.00\times10^{-3}} = \frac{k\,[0.020]^x\,[0.020]^y}{k\,[0.040]^x\,[0.030]^y}$$

y = 1 [1m]

(ii) Hence write a rate equation for the reaction. [1]

Rate = k[$CH_3CH=CH_2$][Br_2]

(iii) Calculate the rate constant for the reaction, giving its units. [2]

Using experiment 1,

$$k = \frac{Rate}{[CH_3CH=CH_2]\,[Br_2]}$$

$$k = \frac{1.00\times10^{-3}}{[0.020]\,[0.020]}$$ = 2.50 [1m] $mol^{-1}dm^3s^{-1}$ [1m]

(iv) State and explain how the rate of reaction may change if chlorine is used instead of bromine in the reaction with propene. [1]

Rate will decrease [√] because C*l*-C*l* bond is stronger than Br-Br [√].

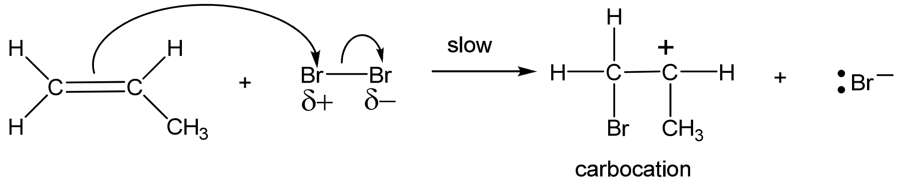
(b) **(i)** The mechanism of the addition reaction between propene and aqueous Br_2 involves three steps.

- There is an initial attack by the π electron pair of the alkene on Br_2 to yield a carbocation intermediate.

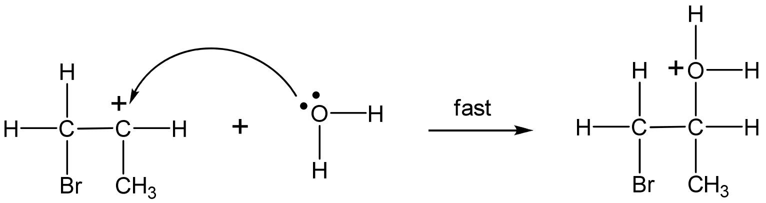
- This is followed by the nucleophilic attack of the lone pair of electrons on oxygen in water on the carbocation intermediate.
- The third step involves the loss of H^+ ion which then yields the neutral bromohydrin.

Using the information given above, describe a mechanism for this reaction.

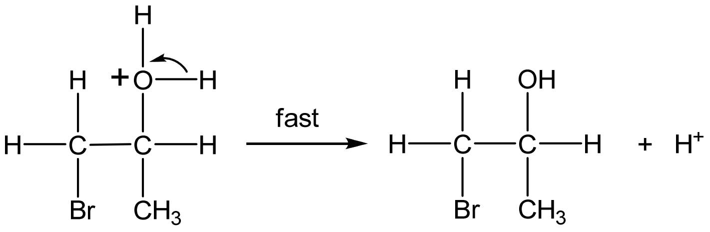
[3]



Dipoles [√], two curvy arrows [√], correct carbocation [√], label slow step [√], Br^- [√]



Lone pair + curvy arrow [√], intermediate [√], label fast step [√]



Curvy arrow [√], final organic product [√], H^+ [√]
11 [√] – 3m
6 to 10 [√] – 2m
3 to 5 [√] – 1m

(ii) Based on your mechanism drawn, explain whether it is consistent with the rate equation proposed. [1]

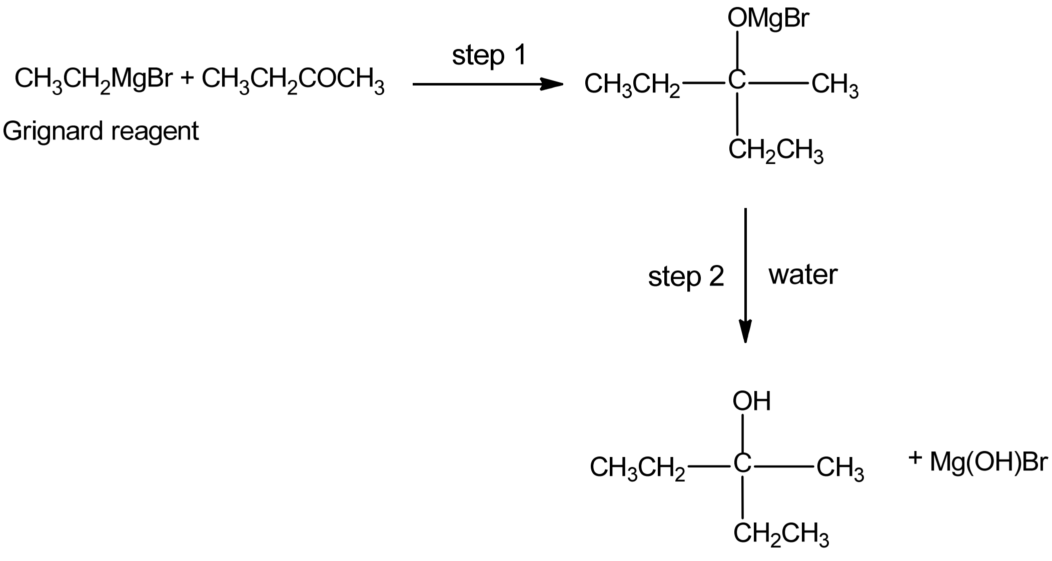
It is **consistent** as there is **1 propene molecule and 1 Br_2 molecule in the rate determining step**, which is consistent with the rate equation.

Or

To allow ecf if rate equation is wrong

(c) Grignard reagents are organo-magnesium halides, commonly used in synthesis to prepare a variety of organic compounds.

The carbon-magnesium bonds in Grignard reagents are highly polar and this makes it extremely useful in organic synthesis as it is able to react with other polar organic molecules to form carbon-carbon bonds. An example of the use of a Grignard reagent is the two-step reaction of CH_3CH_2MgBr with butanone, $CH_3CH_2COCH_3$, to form 3-methylpentan-3-ol.

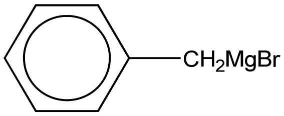


3-methylpentan-3-ol

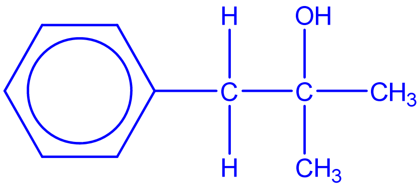
(i) Suggest the type of reaction that has taken place in step 1. [1]

Nucleophilic addition [1]

(ii) Suggest the structural formula of the final organic product formed when



is reacted with propanone, CH_3COCH_3, in a similar two-step process. [1]



[1]

(iii) Suggest a suitable Grignard reagent and another organic compound to be used if propan-2-ol is to be prepared using a similar two-step process. [2]

CH_3MgBr [1] CH_3CHO [1]

(iv) The Grignard reagent $CH_3CH_2CH_2MgBr$ can be readily converted into a carboxylic acid by using carbon dioxide.

Suggest the structural formula for the organic product formed. [1]

$CH_3CH_2CH_2COOH$

[Total: 15]

5 **(a)** Cobalt forms many coloured complexes. Cobalt(**III**) chloride combines with ammonia to form a pink coloured compound **A**, $CoCl_3.H_2O.5NH_3$ (M_r = 268.4) in which the coordination number of cobalt is 6.

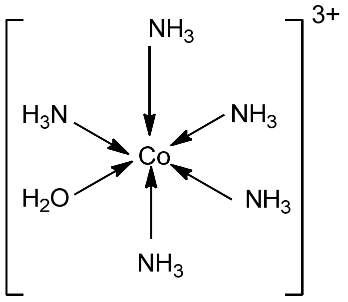
1.00 g of **A** is dissolved in 25 cm^3 of water and the solution is titrated with 0.500 mol dm^{-3} silver nitrate solution. It is found that 22.40 cm^3 of silver nitrate is required for complete reaction.

(i) Calculate the number of moles of free chloride ions per mole of **A**.

no. of moles of $AgNO_3$ = 0.500 x (22.40/1000) = 1.12×10^{-2} mol [1]
no. of moles of Cl^- = 1.12×10^{-2} mol
no. of moles of **A** = 1.00/268.4 = 3.73×10^{-3} mol
no. of moles of free Cl^- ions per mole of **A** = $(1.12 \times 10^{-2})/(3.73 \times 10^{-3})$ = 3 [1]

[2]

(ii) Draw the structure of the complex ion in **A.**



[1]

[1]

(iii) When the pink compound **A** is heated, water vapour and ammonia were evolved to give a purple solid **B**.
A and **B** have the same coordination number.
Suggest the formula of the complex in the purple solid **B**.

$[Co(NH_3)_4Cl_2]^+$ or $[Co(NH_3)_3Cl_3]$ [1]

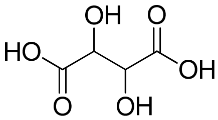
[1]

(iv) Account for the difference in the colour of **A** and **B**.

The **different ligands** in **A** and **B** cause the **energy gap between the split d–orbitals to be different**. **[1]** The **wavelength of light absorbed is different [1]** for **A** and **B** and thus the colour observed are different.

[2]

(b) Aqueous hydrogen peroxide is fairly stable, but when a mixture of a cobalt(II) salt and tartaric acid is added to aqueous hydrogen peroxide, the initially pink solution slowly turns into a green cobalt(III) species.



tartaric acid

After a while, oxygen gas is vigorously evolved and the solution turns back to pink again.

(i) State the role of the cobalt(II) salt in this reaction and support your answer by referring to the observations.

Role of the cobalt(II) salt: catalyst [1]

Observation with explanation:

- The **oxygen gas is vigorously evolved** showing that the **reaction speeds up** [1] OR
- The solution turns from **pink to green to pink (WTTE)** showing that **Co^{2+} is regenerated** [1]

[2]

(ii) Tartaric acid acts as a complexing agent in this reaction to stabilise the Co^{3+} cation.

With the aid of relevant data from the *Data Booklet*, show that Co^{3+} is not stable in aqueous solution.

$Co^{3+} + e \rightleftharpoons Co^{2+}$ $E_{red} = +1.89V$
$O_2 + 4H^+ + 4e \rightleftharpoons 2H_2O$ $E_{red} = +1.23V$
E^o cell = +1.89 – (+1.23) = + 0.66 V [1]
Co^{3+} oxidises water readily to form Co^{2+} / Co^{3+} is readily reduced by water to form Co^{2+}. [1]

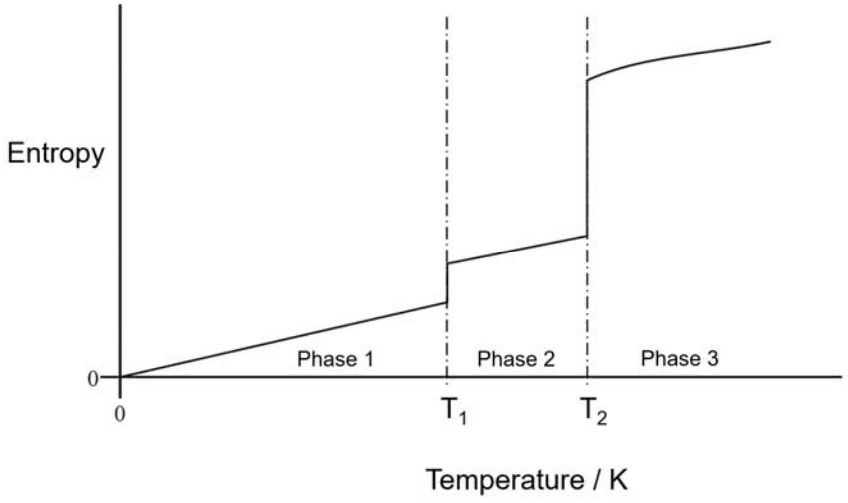
[2]

(c) A student wanted to measure the standard cell potential, $E^{\emptyset}_{cell}$, between the Co^{2+}/Co half-cell and the Fe^{3+}/Fe^{2+} half-cell. She set up and connected the two half cells and obtained a reading.

(i) Calculate the value $E^{\emptyset}_{cell}$ that will be obtained by the student.

[R] $Fe^{3+} + e \rightleftharpoons Fe^{2+}$ $E_{red} = +0.77V$
[O] $Co^{2+} + 2e \rightleftharpoons Co$ $E_{red} = -0.28V$

			$E^{\varnothing}_{cell}$ = +0.77 – (–0.28) = +1.05 V [1] [1]
		(ii)	State and explain what happens to the standard cell potential, $E^{\varnothing}_{cell}$ when ammonia is added to the Co^{2+}/Co half-cell.
			When NH_3 is added, the following equilibrium is set up in the Co^{2+}/Co half-cell: Either: $[Co(NH_3)_6]^{2+} + 2e \rightleftharpoons Co + 6NH_3 \quad E_{red} = -0.43V$ **[1]** (Give B.O.D. if the value -0.43V is not quoted in the answer) **OR $[Co^{2+}]$ decreases** as $Co(OH)_2(s)$ is formed. **[1]** the E_{ox} of Co^{2+}/Co **will become more negative/ position of the equilibrium** $Co^{2+} + 2e \rightleftharpoons Co$ **will shift left** Hence, the $E^{\varnothing}_{cell}$ becomes **more positive**. **[1]** [2]
			[Total: 13]

6	A student plotted the sketch graph below to show how the entropy of a sample of H_2O varies with temperature.	
		
	(a)	Identify the state of H_2O in Phase 2 and 3 respectively. Suggest a value of T_2.
		In phase 2:……………… In phase 3: ……………… value of T_2: ……………… [1]
		In phase 2: liquid In phase 3: gas T_2 : 373K
	(b)	Suggest why entropy of H_2O is zero at 0 K.
		……………………………………………………………………………………[1]
		It is at maximum state of order or no disorder or perfectly ordered or pure crystalline structure.

(c) Explain why the entropy change, ΔS, at temperature T_2 is much larger than that at temperature T_1.

…………………………………………………………………………………………………

…………………………………………………………………………………………………

…………………………………………………………………………………………………

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

At T_2, the increase form phase 2 to 3 is much larger as the gas molecules in phase 3 have more ways in which the particles can be arranged than particles in liquid. [1]

At T_1, the particles in phase 2 (liquid) are still orderly arranged compared to the ordered arrangement of particles in phase 1. [1] Thus, the increase in disorder is smaller from phase 1 to 2.
(2nd marking point: mention of smaller increase from phase 1 to 2 as it is from an ordered arrangement to slightly disordered arrangement in liq.)

(d) It requires 3.49 kJ of heat energy to convert 1.53 g of H_2O from the state in phase 2 to phase 3 at temperature T_2 and 100kPa.

Use these data and your value of T_2 in part **(a)** to calculate the value of ΔS, including units, for the conversion of one mole of H_2O from the state in phase 2 to phase 3 at temperature T_2.

[3]

Amt of water = $\frac{1.53}{18} = 0.0850$

enthalpy change reaction per mole of water = $\frac{3.49}{0.0850} = +41.1$ kJ mol^{-1} **[1]**
award if + sign is omitted, but penalise negative sign is included

$\Delta G = \Delta H - T\Delta S = 0$
$+41.1 - (373)\Delta S = 0$ equate ΔG =0, substitute ΔH, T_2 into equation **[1]** ecf

$\Delta S = 0.110$ kJ K^{-1} mol^{-1} correct computation (allow ecf) and units **[1]** ecf

(e) The student wants to find out if dissolving a salt, silver fluoride in water is always a spontaneous process. He must first find the enthalpy change of solution of silver fluoride in water.

Some enthalpy changes for silver fluoride are shown in the table.

	Δ*H* / kJ mol^{-1}
Lattice energy of silver fluoride	–950
enthalpy change of hydration for silver ions	–464
enthalpy change of hydration for fluoride ions	–506

(i) Use the data provided to calculate a value for the enthalpy change of solution of silver fluoride in water.

			[2]
			$\Delta H_{solution} = \Delta H_{hyd}\ Ag^+ + \Delta H_{hyd}\ F^- - LE$ $= (-464) + (-506) - (-950)$ [1] working $= -20\ kJ\ mol^{-1}$ [1] answer
		(ii)	If entropy change for dissolving silver fluoride in water has a positive value, explain why dissolving of silver fluoride in water is always a spontaneous process.
			[2]
			$\Delta G = \Delta H - T\Delta S$ Relate to signs of ΔS and ΔH [1]: Since ΔS is positive, the term (– TΔS) is always negative. Thus, since ΔH is negative, ΔG is always negative at all temperature. [1]
		(iii)	Explain why the enthalpy change of hydration of the fluoride ions is more negative than the enthalpy change of hydration of the chloride ions.
			[1]
			$\Delta H_{hydration}$ α charge density [√] Fluoride (ions) are smaller (than chloride), with **higher charge density [√]**
			[Total: 12]

7	The uses of carboxylic acids are so extensive that they can be divided into several industries, such as pharmaceuticals or food among others.		
	(a)	Ethanol and ethanoic acid react reversibly to form ethyl ethanoate and water according to the equation: $CH_3COOH(l) + CH_3CH_2OH(l) \rightleftharpoons CH_3COOCH_2CH_3(l) + H_2O(l)$ A student mixed 8.00×10^{-2} mol of ethanoic acid and 1.20×10^{-1} mol of ethanol in a conical flask and the flask was sealed with a bung and allowed to reach equilibrium at 20 °C. The equilibrium mixture is placed in a graduated flask and the volume made up to 250 cm^3 with distilled water. A 10.0 cm^3 sample of this equilibrium mixture was placed in a conical flask with a few drops of phenolphthalein and titrated with 0.100 mol dm^{-3} of sodium hydroxide from a burette. The indicator turned pink when 6.40 cm^3 of NaOH had been added.	
		(i)	Calculate the amount of CH_3COOH in the equilibrium mixture. Amount of NaOH = $0.100 \times \frac{6.40}{1000} = 0.00064$ mol Amount of CH_3COOH in 10.0 cm^3 = 0.00064 mol Amount of CH_3COOH in 250 cm^3 = $\frac{250}{10} \times 0.00064 = 0.016$ mol **[1]**

[1]

(ii) Hence, calculate the value for K_c for the reaction of ethanoic acid and ethanol at 20 °C.

	CH_3CO_2H (l)	C_2H_5OH (l)	$CH_3CO_2C_2H_5$ (l)	H_2O (l)
Initial amt / mol	0.08	0.12	0	0
Equilibrium amt / mol	**0.016**	**0.056**	**0.064**	**0.064**

Equilibrium amount **[1]**

$$K_c = \frac{[H_2O][CH_3COOC_2H_5]}{[CH_3COOH][C_2H_5OH]}$$

$$= \frac{(\frac{0.064}{V})(\frac{0.064}{V})}{(\frac{0.016}{V})(\frac{0.056}{V})}$$

= 4.57 [1]

[2]

(b) The following table compares the pK_a values of two dicarboxylic acids with that of ethanoic acid.

acid	Formula	pK_1	pK_2
ethanoic	CH_3COOH	4.8	–
malonic	$HOOCCH_2COOH$	2.8	5.7
succinic	$HOOC(CH_2)_2COOH$	4.2	5.6

(i) Suggest a reason why the pK_1 value of malonic acid is so much less than the pK_1 of ethanoic and succinic acid.

Malonic acid is **more acidic** than ethanoic or succinic acid **[1]** as **its monoanion is stabilised by intra hydrogen bonds between the COO^- group and unionised COOH group [1]**.

[2]

(ii) Suggest a reason why the pK_2 value of malonic and succinic acid is higher than its respective pK_1 value.

The removal of an H^+ from the monoanion that already carries a negative charge would be electrostatically unfavourable. **[1]**

[1]

(c) Malonic acid can undergo dehydration with P_4O_{10} to give a foul-smelling gas, **A**. At 30.5 kPa, 0.1057 g of A occupies 200 cm^3 at a temperature of 200°C. Determine the relative molecular mass of **A**.

pV = nRT

$$30.5 \times 10^3 \times \frac{200}{10^6} = \frac{0.1057}{M_r} \times 8.31 \times (200 + 273)$$ **[1]**

M_r = 68.1 (1 d.p) **[1]**

[2]

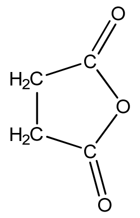
(d) At high temperature, succinic acid can also undergo dehydration to produce a neutral compound **B**, $C_4H_4O_3$ which does not react with sodium metal or Brady's reagent.

Compound **B** reacts with ammonia to give a compound **C**, $C_4H_7NO_3$, which reacts with cold NaOH(aq), but not with cold HCl(aq).

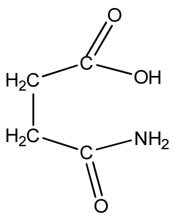
Suggest structures for **B** and **C** and explain the observations.

- **B** does not react with Na; **absence of –OH group**. **[√]**
- **B** does not react with Brady's reagent; **absence of carbonyl group**. **[√]**
- **C** does not react with cold HCl(aq); **absence of basic group [√]**, **amide** likely to be present **[√]**.
- **C** undergoes **acid base** with cold NaOH(aq) **[√]**; it contains an **acidic group** (carboxylic acid). **[√]**

Max [2] for explanations



compound B



compound C

[1] each

[4]

[Total: 12]

INNOVA JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
in preparation for General Certificate of Education Advanced Level
Higher 2

CHEMISTRY 9729/03

Paper 3 Free Response **10 September 2018**

2 hours

Candidates answer on separate paper.

Additional Materials: Writing Papers
Data Booklet
Cover Page

READ THESE INSTRUCTIONS FIRST

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

Section A
Answer **all** questions.

Section B
Answer **one** question.

You are advised to show all working in calculations.
You are reminded of the need for good English and clear presentation in your answers.
You are reminded of the need for good handwriting.
Your final answers should be in 3 significant figures.

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

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

Section A

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

1 This question is about the chemistry of ethene and its derivatives.

(a) Ethene is the starting material to form ethanedioic acid.

(i) Suggest the synthetic route for the formation of ethanedioic acid from ethene. [2]

(ii) 0.200 mol of ethene is stored in a 20.0 dm^3 flask with 0.800 mol of ethane at 127 °C.

Calculate the total pressure in the flask. Hence or otherwise, calculate the partial pressure of ethene in the flask. [2]

(iii) The total pressure that you calculated in **(a)(ii)** is different from the actual pressure exerted. Suggest an explanation for the difference. [1]

(iv) Ethene reacts with hydrogen in the presence of nickel catalyst to form ethane.

Explain why nickel can be used as a catalyst in this reaction. [2]

(v) Outline the mode of action of the catalyst in this reaction. [2]

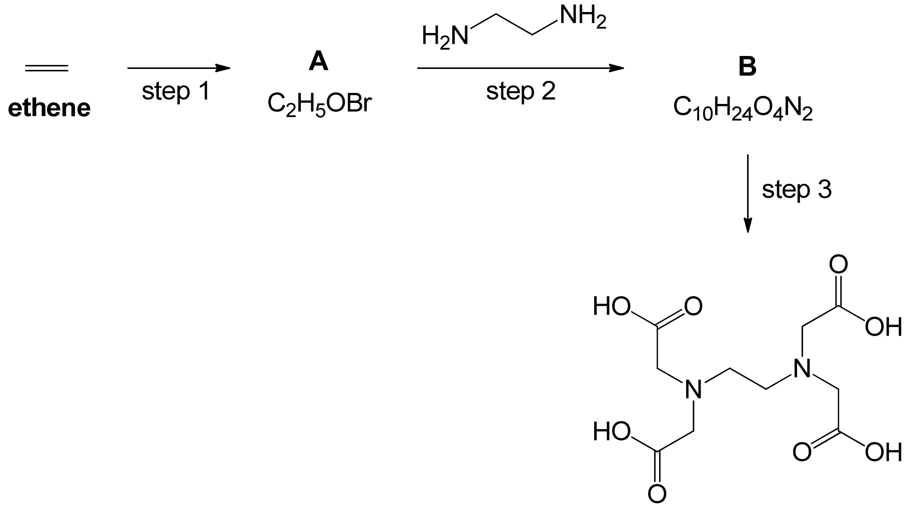
(b) Dissolving 4.82×10^{-5} mol calcium ethanedioate, CaC_2O_4, in 1 dm^3 of water forms a saturated solution.

(i) Write an expression for the solubility product of calcium ethanedioate and state its units. [1]

(ii) Calculate the solubility product of calcium ethanedioate. [1]

(iii) 50.0 cm^3 of 0.100 mol dm^{-3} $CaCl_2$ and 50.0 cm^3 of 0.300 mol dm^{-3} $Na_2C_2O_4$ are mixed together. Determine if CaC_2O_4 will be precipitated out. [2]

(c) Synthesis of the unionised form of EDTA (H_4Y) can be carried out in the laboratory using ethene as the starting material.



unionised form of EDTA (H_4Y)

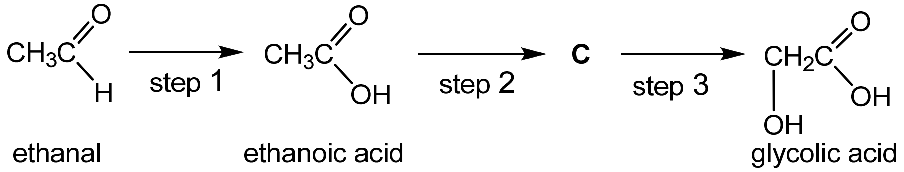
(i) Draw the structures of **A** and **B**.

[2]

(ii) Suggest appropriate reagents and conditions for step 3.

[1]

(d) Ethene can be used to form ethanal. Ethanal in turn is used to synthesize glycolic acid via the reaction shown below.



(i) Identify the intermediate **C** and state the reagent and condition for step 3.

[2]

(ii) Explain the difference in acidity between glycolic acid and ethanoic acid.

[2]

(iii) Two molecules of glycolic acid can react with one another under suitable conditions to form a neutral compound with the loss of two water molecules.

Suggest a possible structure for the compound formed.

[1]

(iv) Suggest a simple chemical test to distinguish between ethanoic acid and glycolic acid.

[2]

[Total: 23]

2 Iron is the fourth most common element in the Earth's crust. It is a d-block element which is known to exhibit different characteristics from the s-block elements. Since ancient times, iron has been widely employed in a variety of applications.

(a) **(i)** One well-known property of iron and its compounds is the ability to catalyse reactions. For example, aqueous iron(II) chloride can be used to catalyse the reaction between I^- and $S_2O_8^{2-}$, to form I_2 and SO_4^{2-} ions.

Using relevant $E^\ominus$ values from the *Data Booklet*, explain why iron(II) chloride can be used as a catalyst for this reaction.

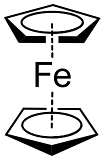
[2]

(ii) A sample of iron was vapourised, ionised and passed through an electric field. Analysis of deflection occurring at the electric field region revealed that a sample of $^{32}S^{2-}$ ions would be deflected by +20° towards the positive potential.

What is the angle, and direction of deflection for a sample of $^{56}Fe^{3+}$ ions passing through the same electric field?

[2]

(b) Ferrocene, $Fe(C_5H_5)_2$, is an orange solid which is known to exhibit anti-cancer activity. In this complex, $C_5H_5^-$ is the ligand and it donates π electrons from the ring to the vacant 3d orbital of Fe. The structure of ferrocene is given below.



ferrocene

(i) State the oxidation number of Fe in ferrocene.

[1]

(ii) Suggest why ferrocene is a coloured complex.

[2]

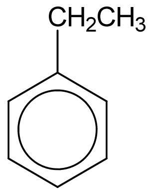
(iii) Light of a longer wavelength is lower in energy than light of a shorter wavelength. The following table shows the spectral colours and the corresponding wavelengths.

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

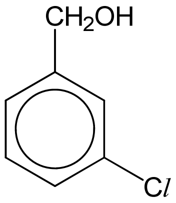
Given that aqueous Fe^{2+} ion is green in colour, suggest and explain if water causes a larger split between the two groups of 3d orbitals as compared to $C_5H_5^-$.

[2]

(c) Ethylbenzene is used to synthesize (3-chlorophenyl)methanol which is used as a general solvent for inks, paints, lacquers, epoxy resin coatings and as a degreasing agent.



ethylbenzene



(3-chlorophenyl)methanol

Starting with ethylbenzene, outline a three-step reaction scheme to obtain (3-chlorophenyl)methanol. Your answer should include clearly the reagents and conditions in each step, and the structures of all intermediates formed.

[3]

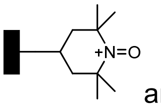
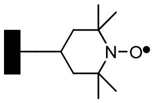
(d) **D** is an achiral organic compound with the molecular formula C_2H_7NO. It can be formed from the reaction between a primary amide and lithium aluminium hydride. In the presence of a suitable catalyst, 1 mole of **D** reacts with 1 mole of benzoic acid to form **E**, $C_9H_{11}NO_2$. However, 1 mole of **D** requires 2 moles of benzoyl chloride to react completely to form **F**, $C_{16}H_{15}NO_3$ and copious white fumes. 2 moles of **D** can also react with gaseous PCl_5 to form a cyclic **G**, $C_4H_{10}N_2$, which contains a 6-membered ring.

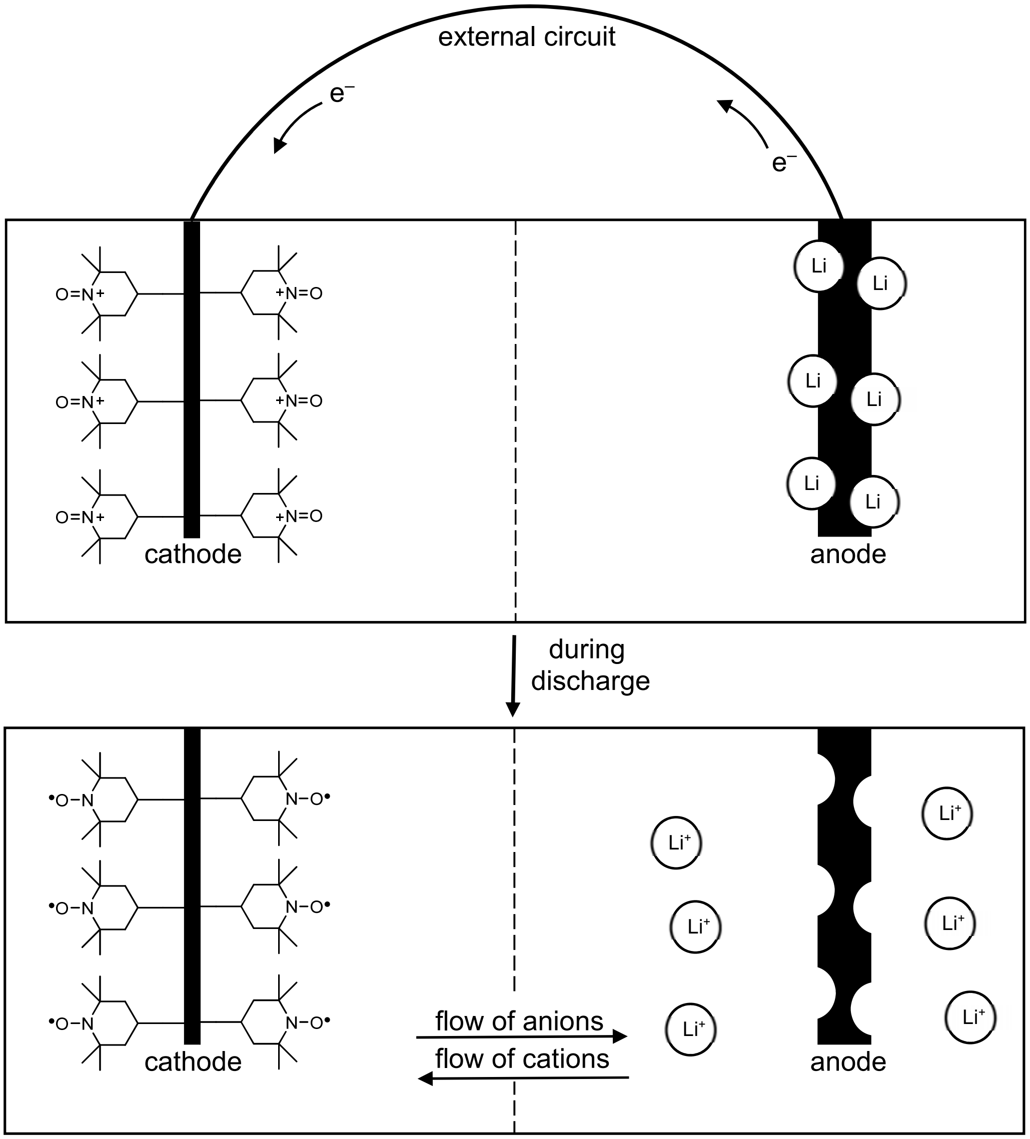
Deduce the structures of **D**, **E**, **F** and **G** and explain the reactions described.

[7]

[Total: 19]

3 An organic radical battery (ORB) is a relatively new type of battery which uses flexible plastics, to provide electrical power. One type of hybrid ORB/Li-ion battery consists of: a cathode made from solid organic polymer containing oxoammonium ion formed from (2,2,6,6-Tetramethylpiperidin-1-yl)oxyl (TEMPO) nitroxide radicals; an anode made from graphite with Li atoms inserted between the graphite layers; and an electrolyte of $LiPF_6$ dissolved in organic solvent.

During discharge, Li atoms give up electrons at the anode to become Li^+ ions. The electrons travel round the external circuit, and are picked up by the cathode. The anions and cations in the electrolyte move to the anode and cathode respectively. This is illustrated in the following diagram in which  and  are simplified representations of the polymer containing oxoammonium ion and TEMPO nitroxide radicals respectively.



(a) **(i)** Graphite is often mixed in the polymer used for making the cathode electrode.

Suggest a reason for this. [1]

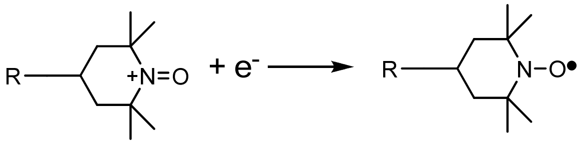
(ii) Calculate the oxidation number of N in the cathode **before** discharge. [1]

(iii) The E_{cell} generated by the hybrid ORB/Li-ion battery under standard conditions is 2.17 V.

Use relevant $E^{\ominus}$ value from the *Data Booklet* to calculate the electrode potential generated by the cathode half-cell.

[1]

(iv) During discharge, the following reaction occurs at the cathode.



where R represents the organic polymer cathode.

Write an equation for the overall process that occurs during discharge.

[1]

(v) Draw the dot-and-cross diagram of the PF_6^- ion and state its shape.

[2]

(vi) Suggest whether $LiPF_6$ or LiF has a lower melting point. Explain your answer.

[2]

(b) The hybrid ORB/Li-ion battery is a secondary battery, i.e., it is rechargeable.

During charging, 1.22 g of Li is regenerated from Li^+ ions at the cathode.

(i) Calculate the amount of electrons required to form 1.22 g of Li. [1]

Besides the generation of Li, there is a competing side-reaction that occurs at the cathode.

In this side-reaction, ethylene carbonate, $C_3H_4O_3$ undergoes reduction in the presence of Li^+ ions to form ethene and lithium carbonate.

(ii) Write the half-equation for the side-reaction occurring at the cathode.

[1]

A current of 5.0 A is supplied over 2 hours during charging.

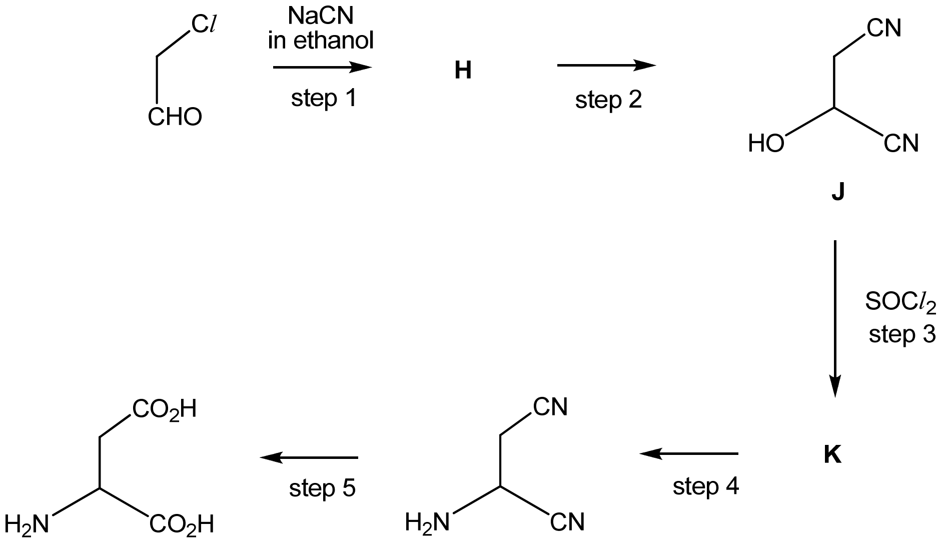
(iii) Use the information given and your answer in **(b)(i)** to calculate the amount of electrons consumed by the side-reaction.

[1]

(iv) Suggest why the battery needs to be replaced after about 1000 charge-discharge cycles.

[1]

(c) Chloroethanal is the starting material in the synthesis of aspartic acid.



(i) Suggest structures for the intermediates **H** and **K**.

[2]

(ii) Suggest reagents and conditions for step 2 and for step 4.

[2]

(iii) The reaction in step 2 produces sample **J**, which does not show optical activity. Explain the observation.

[2]

[Total: 18]

Section B

Answer **one** question from this section

4 **(a)** For many compounds the enthalpy change of formation cannot be calculated directly. An indirect method based on enthalpy changes of combustion can be used.

The enthalpy change of combustion can be found by a calorimetry experiment in which the heat energy given off during combustion is used to heat a known mass of water and the temperature change recorded.

(i) Define the term *standard enthalpy change of combustion.*

[1]

(ii) Write the equation for the complete combustion of ethanol, CH_3CH_2OH.

[1]

In an experiment to determine the enthalpy change of combustion of ethanol, 0.23 g of ethanol was burned and the heat given off raised the temperature of 100 g of water by 16.3 °C.

(iii) Calculate the heat energy change during the combustion of ethanol.

[1]

(iv) Hence, calculate the enthalpy change on burning 1 mole of ethanol.

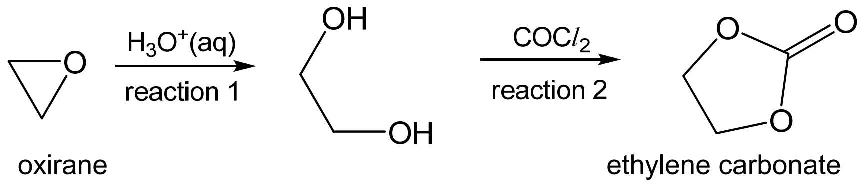
[2]

(v) Suggest one reason why the value for the enthalpy change of combustion of ethanol determined by a simple laboratory calorimetry experiment is likely to be lower than the true value.

[1]

(b) Epoxides are cyclic ethers commonly used in organic reactions.

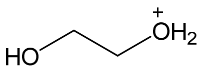
Ethylene carbonate can be prepared from an epoxide, oxirane by the following reactions.



(i) Suggest the type of reaction for reaction 2.

[1]

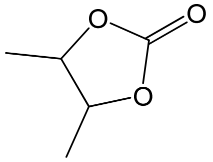
(ii) Reaction 1 is an acid-catalysed reaction that proceeds via a three-step mechanism:

1) Protonation of oxirane by H_3O^+.
2) Ring opening of protonated oxirane due to nucleophilic attack by H_2O to yield an oxonium ion,  .
3) Deprotonation of the oxonium ion to yield the product, with the regeneration of H_3O^+.

Suggest the mechanism for Reaction 1.

[3]

Compound **L** can be synthesised from an epoxide in a similar manner as ethylene carbonate.



Compound **L**

(iii) Draw the structure of the epoxide used for synthesising compound **L**.

[1]

(iv) Suggest why compound **L** is able to exhibit cis-trans isomerism.

[1]

(c) A number of isomers with the formula $Fe(H_2O)_6Cl_3$ exist. Their general formula is $[Fe(H_2O)_{6-n}Cl_n]Cl_{3-n}.nH_2O$.

Each isomer contains a six co-ordinated Fe(III) ion in an octahedral complex. Water molecules not directly bonded with the Fe atom are held in the crystal lattice as water of crystallisation.

(i) Similar to organic compounds, octahedral complexes can also exhibit stereoisomerism depending on the orientation of the ligands.

One such example will be the iron complex when *n* is 2. It can exist in two isomeric forms where only one of them has a dipole moment.

Name the type of isomerism shown by the complex.

[1]

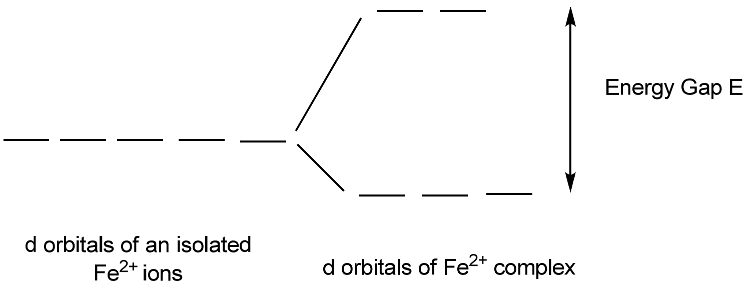
(ii) Draw the structures of the two isomeric forms of the complex.

[2]

(iii) State which isomer has a dipole moment. Explain your answer.

[2]

(iv) The following diagram shows how the d-orbitals are split in an octahedral environment.



When the H_2O ligand is changed to a C*l* ligand, the Fe^{2+} ion changes the electronic configuration from a 'high spin' to a 'low spin' state.

In a 'high spin' state, the electrons occupy all the d-orbitals singly, before starting to pair up in the lower energy d-orbitals.

In a 'low spin' state, the lower energy d-orbitals are filled first, by pairing up if necessary, before the higher energy d-orbitals are used.

Use diagrams like the one above to show the electronic distribution of a Fe^{2+} ion in a high spin state, and in a low spin state.

[2]

(v) State and explain which ligand will result in a larger energy gap, E, between its d-orbitals.

[1]

[Total: 20]

5 Carbonyl compounds are common in our everyday lives. They are mainly used as solvents, perfumes and flavouring agents or as intermediates in the manufacture of plastics and pharmaceuticals.

(a) The characteristic smell of cherries and fresh almonds is due to benzaldehyde.

(i) Benzaldehyde can react with chloromethane to form 3-methylbenzaldehyde. Describe the mechanism for this reaction.

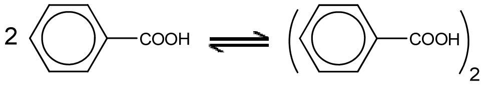
[3]

(ii) Benzene can also react under a similar reaction with chloromethane.

State and explain whether benzene or benzaldehyde would react with chloromethane more readily.

[2]

(b) Benzaldehyde can also react with hot acidified dichromate(VI) to give benzoic acid. In benzene, benzoic acid associates to form dimers.



(i) Draw a diagram to illustrate the bonding in the dimer.

[1]

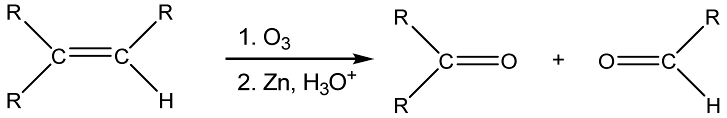
(ii) Predict and explain whether the dimerisation is favoured at a high or low temperature.

[2]

(iii) Suggest why the above equilibrium cannot be established in an aqueous medium.

[1]

(c) Carbonyl compounds can be prepared from alkenes via the ozonolysis reaction as shown below.



An alkene **M**, $C_{11}H_{14}$ was treated with O_3, followed by Zn and H_3O^+ to give **N** C_4H_8O and **P**, C_7H_6O. **N** gives a yellow precipitate with aqueous alkaline iodine while **P** gives a grey precipitate with ammonical silver nitrate solution. In the presence of OH^-, **P** undergoes a reaction to give **Q**, $C_7H_6O_2$ and **S**, C_7H_8O. Both **Q** and **S** react with Na metal, but only **Q** reacts with $NaHCO_3$.

Suggest the structures of **M, N, P, Q** and **S**.

[5]

(d) **T, U, V** and **W** are four consecutive elements in the **fourth** period of the Periodic Table. (The letters are **not** the actual symbols of the elements.)

T is a soft, silvery metal with a melting point just above room temperature. Its amphoteric oxide, $\mathbf{T}_2O_3$, has a melting point of 1900 °C and can be formed by heating **T** in oxygen.

W is a solid that can exist as several allotropes, most of which contain $\mathbf{W}_8$ molecules. **W** burns in air to form $\mathbf{W}O_2$ and $\mathbf{W}O_3$**,** which dissolves in water to form an acidic solution. The acidic solutions react with sodium hydroxide to form the salt $Na_2\mathbf{W}O_3$ and $Na_2\mathbf{W}O_4$ respectively.

(i) Suggest the identities of **T** and **W**.

[2]

(ii) Write equations for the reactions of $\mathbf{T}_2O_3$ with

- hydrochloric acid,
- sodium hydroxide

[2]

(iii) Suggest the structure in $\mathbf{T}_2O_3$.

[1]

(iv) Write an equation for the formation of the acidic solution when $\mathbf{W}O_3$ dissolves in water.

[1]

[Total: 20]

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INNOVA JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
in preparation for General Certificate of Education Advanced Level
Higher 2

CHEMISTRY

9729/03

Paper 3 Free Response

10 September 2018

2 hours

Candidates answer on separate paper.

Additional Materials: Writing Papers
Data Booklet
Cover Page

READ THESE INSTRUCTIONS FIRST

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

Section A
Answer **all** questions.

Section B
Answer **one** question.

You are advised to show all working in calculations.
You are reminded of the need for good English and clear presentation in your answers.
You are reminded of the need for good handwriting.
Your final answers should be in 3 significant figures.

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

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

Section A

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

1 This question is about the chemistry of ethene and its derivatives.

(a) Ethene is the starting material to form ethanedioic acid.

(i) Suggest the synthetic route for the formation of ethanedioic acid from ethene.

[2]

CH_2CH_2 → $CH_2(OH)CH_2(OH)$ [1m] → ethanedioic acid

Step 1: cold, KMnO4, NaOH(aq) [✓]

Step 2: $K_2Cr_2O_7$, dil H_2SO_4, heat [✓]

(ii) 0.200 mol of ethene is stored in a 20.0 dm^3 flask with 0.800 mol of ethane at 127^{0}C.

Calculate the total pressure in the flask. Hence or otherwise, calculate the partial pressure of ethene in the flask.

[2]

$P(20.0 \times 10^{-3}) = (0.200 + 0.800)(8.31)(127 + 273)$
P = 166200 Pa [1]

Partial pressure of ethene = 0.2/1.0 x 166200 = 33240
= 33.2×10^3 Pa [1]

(iii) The total pressure that you calculated in **(a)(ii)** is different from the actual pressure exerted. Suggest an explanation for the difference.

[1]

There is <u>significant intermolecular forces of attraction</u> present between the gases OR intermolecular forces of attraction between the gases are not negligible [1].

(iv) Ethene reacts with hydrogen in the presence of nickel catalyst to form ethane.

Explain why nickel can be used as a catalyst in this reaction.

[2]

Nickel has **available 3d electrons for bond formation** with the reactant molecules (ie. ethene and hydrogen) [1] and **available low lying vacant orbitals or energetically accessible orbitals which can accept electron** pairs from the reactant molecules. [1]

(v) Outline the mode of action of the catalyst in this reaction.

[2]

The catalyst is in a solid state and it functions as a **<u>heterogeneous catalyst</u>** **[√]** as it is in a different phase than ethene and hydrogen. Ethene and hydrogen **<u>(reactants) will be adsorbed to the surface of the Ni catalyst.</u>** **[√]** **<u>Bonds in the reactant molecules are weakened</u>** **[√]** which lowers the activation energy. New bonds are then formed between adjacent reactant molecules to form ethane (product). **<u>The product formed will be desorbed from the surface of the Ni catalyst.</u>** **[√]**

(b) Dissolving 4.82×10^{-5} mol calcium ethanedioate, CaC_2O_4, in 1 dm^3 of water forms a saturated solution.

(i) Write an expression for the solubility product of calcium ethanedioate and state its units.

[1]

$K_{sp}(CaC_2O_4) = [Ca^{2+}][C_2O_4^{2-}]$ unit: $mol^2\ dm^{-6}$ [1]

(ii) Calculate the solubility product of calcium ethanedioate.

[1]

$K_{sp} = (4.82 \times 10^{-5})^2$
$= 2.32 \times 10^{-9}$ [1]

[units not nec. as already stated in (i)]

(iii) 50.0 cm^3 of 0.100 mol dm^{-3} $CaCl_2$ and 50.0 cm^3 of 0.300 mol dm^{-3} $Na_2C_2O_4$ are mixed together. Determine if CaC_2O_4 will be precipitated out.

[2]

For precipitation to occur, IP of CaC_2O_4 must exceed Ksp of CaC_2O_4
Since the volume used is the same, the new concentration is halved the original concentration.

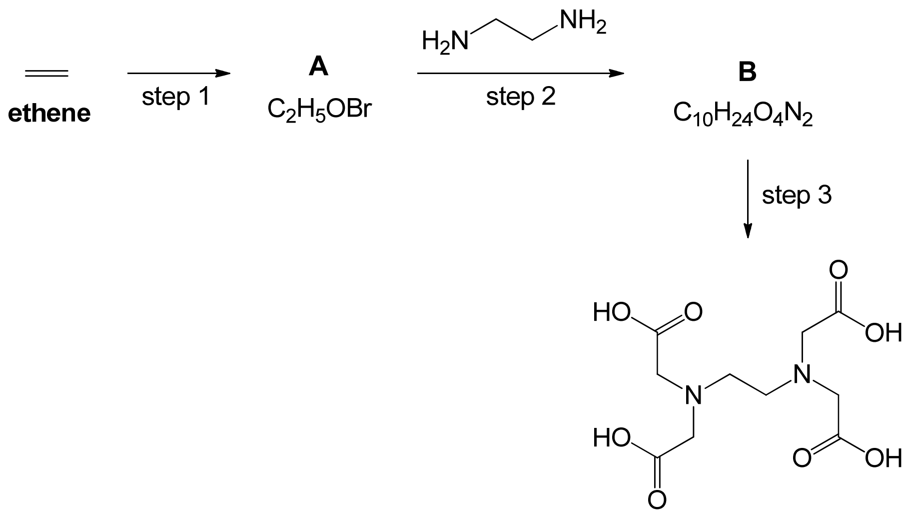
New $[Ca^{2+}] = 0.100 / 2 = 0.05$ [✓]

New $[C_2O_4^{2-}] = 0.300 / 2 = 0.15$ [✓]

IP of $CaC_2O_4 = (0.05)(0.15) = 7.50 \times 10^{-3}$ [✓]

Since IP > Ksp, CaC_2O_4 will ppt out. [✓][ECF with student's Ksp value from (ii)]

(c) Synthesis of the unionised form of EDTA (H_4Y) can be carried out in the laboratory using ethene as the starting material.

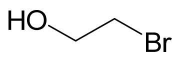


unionised form of EDTA (H_4Y)

(i) Draw the structures of **A** and **B**.

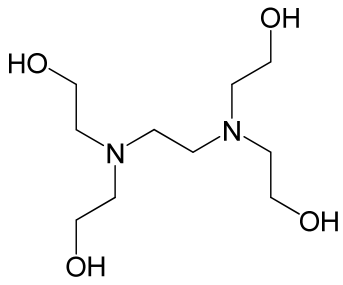
[2]

A:



[1]

B:



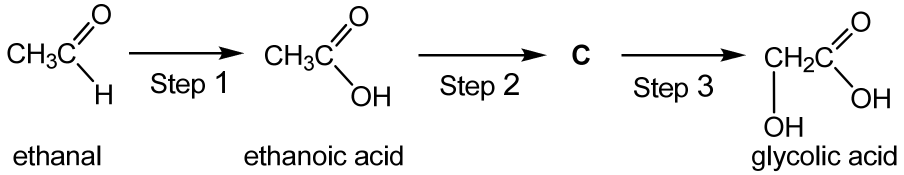
[1]

(ii) Suggest appropriate reagents and conditions for step 3.

[1]

Step 3: dilute H_2SO_4, $KMnO_4$(aq)/$K_2Cr_2O_7$(aq), heat under reflux [1] (followed by careful addition of NaOH(aq))

(d) Ethene can be used to form ethanal. Ethanal in turn is used to synthesize glycolic acid via the reaction shown below.

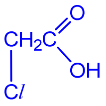


(i) Identify the intermediate **C** and state the reagent and condition for Step 3.

[2]

Step 3: NaOH(aq), heat under reflux; followed by aq. HCl [1]

C:



[1]

(ii) Explain the difference in acidity between glycolic acid and ethanoic acid.

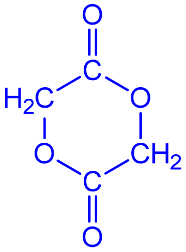
[2]

In glycolic acid, the electron withdrawing –OH [✓] group reduces the negative charge on $-COO^-$ [✓] of the conjugate base of glycolic acid, thus making the anion of glycolic acid is more stable that the ethanoate anion [✓]. Hence, glycolic acid is a stronger acid [✓].

(iii) Two molecules of glycolic acid can react with one another under suitable conditions to form a neutral compound with the loss of two water molecules.

Suggest a possible structure for the compound formed.

[1]



[1]

(iv) Suggest a simple chemical test to distinguish between ethanoic acid and glycolic acid.

[2]

Test: $K_2Cr_2O_7$, dil H_2SO_4, heat [1]
Ethanoic acid: orange $K_2Cr_2O_7$ turns green [✓]
Glycolic acid: orange $K_2Cr_2O_7$ remains [✓]

OR
Test: $KMnO_4$, dil H_2SO_4, heat
Ethanoic acid: purple $KMnO_4$ remains
Glycolic acid: purple $KMnO_4$ decolorised. Effervescence observed. gas produced forms white ppt with $Ca(OH)_2$

[Total: 23]

2 Iron is the fourth most common element in the Earth's crust. It is a d-block element which is known to exhibit different characteristics from the s-block elements. Since ancient times, iron has been widely employed in a variety of applications.

(a) **(i)** One well-known property of iron and its compounds is the ability to catalyse reactions. For example, aqueous iron(II) chloride can be used to catalyse the reaction between I^- and $S_2O_8^{2-}$, to form I_2 and SO_4^{2-} ions.

Using relevant $E^\ominus$ values from the *Data Booklet*, explain why iron(II) chloride can be used as a catalyst for this reaction.

[2]

$S_2O_8^{2-} + 2Fe^{2+} \rightarrow 2Fe^{3+} + SO_4^{2-}$

Ecell = +2.01 – (0.77)
= +1.24 V (reaction is energetically feasible) [1]

$2\,I^- + 2Fe^{3+} \rightarrow 2Fe^{2+} + I_2$
Ecell = +0.77 – (+0.54)
= +0.23 V (reaction is energetically feasible) [1]

(ii) A sample of iron was vapourised, ionised and passed through an electric field. Analysis of deflection occurring at the electric field region revealed that a sample of $^{32}S^{2-}$ ions would be deflected by +20° towards the positive potential.

What is the angle, and direction of deflection for a sample of $^{56}Fe^{3+}$ ions passing through the same electric field?

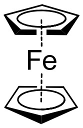
[2]

Angle of deflection of $^{32}S^{2-}$ = 20
20 = k (-2 / 32)
k = - 320

Angle of deflection of $^{56}Fe^{3+}$ = (-320) (3 / 56)
= -17.1° [1 for final answer; 1m for indication of direction]

or 17.1° [1m] towards the negative potential [1m]

(b) Ferrocene, $Fe(C_5H_5)_2$, is an orange solid which is known to exhibit anti-cancer activity. In this complex, $C_5H_5^-$ is the ligand and it donates π electrons from the ring to the vacant 3d orbital of Fe. The structure of ferrocene is given below.



ferrocene

(i) State the oxidation number of Fe in ferrocene. [1]

+2

(ii) Suggest why ferrocene is a coloured complex. [2]

There is partially filled 3d orbitals in Fe^{2+}. [√]

In the presence of ligands, 3d orbitals of iron are split into 2 groups with small energy gap (d–d splitting). [√]

Some light energy is used to promote an electron [√] from a d-orbital of lower energy to a d-orbital of a higher energy [√].

(Colour observed is complementary to the colour absorbed.)

(iii) Light of a longer wavelength is lower in energy than light of a shorter wavelength. The following table shows the spectral colours and the corresponding wavelengths.

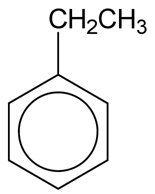
Colour	**Wavelength / nm**
Violet	380 – 450
Blue	450 – 495
Green	495 – 570
Yellow	570 – 590
Orange	590 – 620
Red	620 – 750

Given that aqueous Fe^{2+} ion is green in colour, suggest and explain if water causes a larger split between the two groups of 3d orbitals as compared to $C_5H_5^-$. [2]

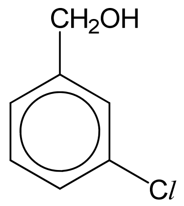
Water causes a smaller split between the 3d orbitals. [1]

With water as the ligand, electromagnetic waves with energy corresponding to red is absorbed which has a lower energy than blue, which is absorbed when $C_5H_5^-$ is the ligand. [1]

(c) Ethylbenzene is used to synthesize (3-chlorophenyl)methanol which is used as a general solvent for inks, paints, lacquers, epoxy resin coatings and as a degreasing agent.



ethylbenzene

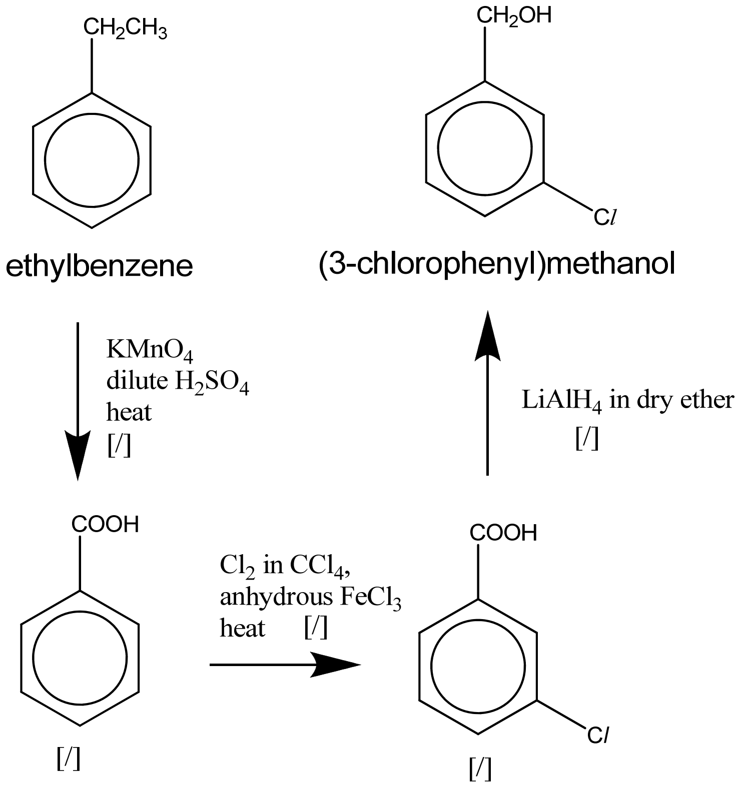


(3-chlorophenyl)methanol

Starting with ethylbenzene, outline a three-step reaction scheme to obtain (3-chlorophenyl)methanol. Your answer should include clearly the reagents and conditions in each step, and the structures of all intermediates formed.

[3]

Ans:



5 [√] – 3m
3 to 4 [√] – 2m
2 [√] – 1m

(d) **D** is an achiral organic compound with the molecular formula C_2H_7NO. It can be formed from the reaction between a primary amide and lithium aluminium hydride. In the presence of a suitable catalyst, 1 mole of **D** reacts with 1 mole of benzoic acid to form **E,** $C_9H_{11}NO_2$. However, 1 mole of **D** requires 2 moles of benzoyl chloride to react completely to form **F,** $C_{16}H_{15}NO_3$ and copious white fumes. 2 moles of **D** can also react with gaseous PCl_5 to form a cyclic **G**, $C_4H_{10}N_2$, which contains a 6-membered ring.

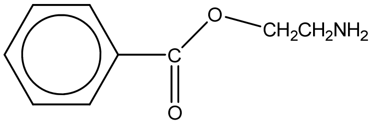
Deduce the structures of **D**, **E**, **F** and **G** and explain the reactions described.

[7]

Info	Deduction
D is formed from reaction between primary amide and LiAlH4	**D** contains a primary amine [√]
1 mol **D** reacts with 1 mol of benzoic acid to form **E,** $C_9H_{11}NO_2$	• **D** undergoes condensation / nucleophilic acyl substitution [√] • **E** is an ester [√] • **D** contains alcohol [√]
1 mol **D** require 2 mol benzoyl chloride to react completely to form Compound **F,** $C_{16}H_{15}NO_3$ and copious white fumes.	• **D** undergoes condensation/ nucleophilic acyl substitution [√] • Copious white fumes are HCl [√] • **F** contains an amide [√] and an ester [√]
2 mol **D** reacts with gaseous PCl_5 to form a cyclic Compound **G**, $C_4H_{10}N_2$	• **D** undergoes nucleophilic substitution [√] • **G** contains an amine [√]
8 - 10 [√] – 3m 5 - 7 [√] – 2m 2 – 4 [√] – 1m	

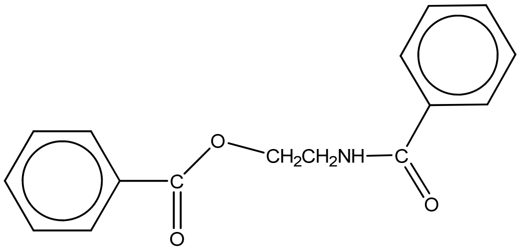
D (C_2H_7NO) : $NH_2CH_2CH_2OH$ [1]

Compound **E** ($C_9H_{11}NO_2$) :



[1]

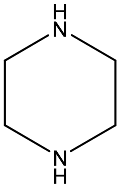
Compound **F** ($C_{16}H_{15}NO_3$) :



[1]

ECF for structure E and F based on wrong structure D, $H_2NCH(OH)CH_3$.

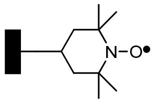
Compound **G** ($C_4H_{10}N_2$) :

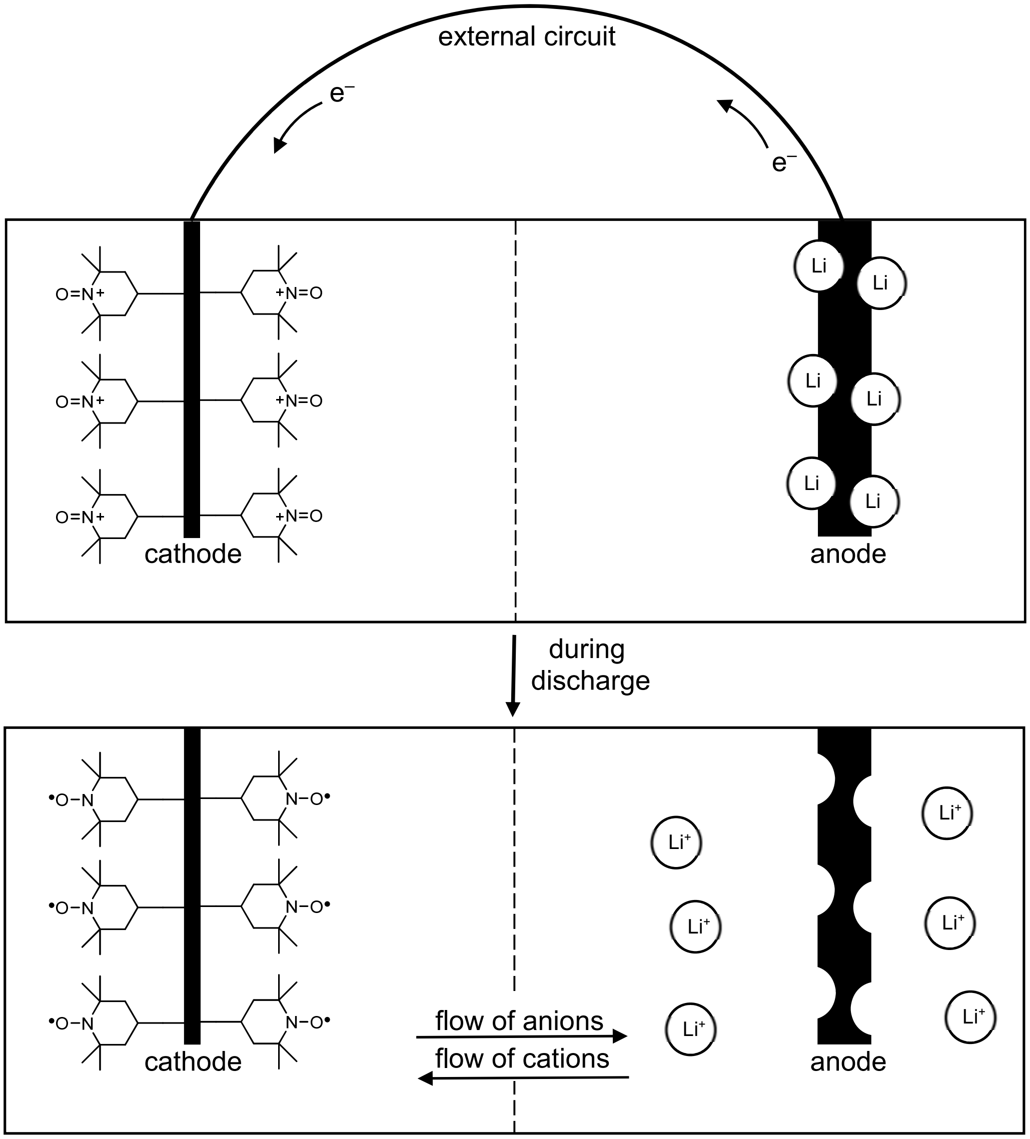


[1]

[Total: 19]

3 An organic radical battery (ORB) is a relatively new type of battery which uses flexible plastics, to provide electrical power. One type of hybrid ORB/Li-ion battery consists of: a cathode made from solid organic polymer containing oxoammonium ion formed from (2,2,6,6-Tetramethylpiperidin-1-yl)oxyl (TEMPO) nitroxide radicals; an anode made from graphite with Li atoms inserted between the graphite layers; and an electrolyte of $LiPF_6$ dissolved in organic solvent.

During discharge, Li atoms give up electrons at the anode to become Li^+ ions. The electrons travel round the external circuit, and are picked up by the cathode. The anions and cations in the electrolyte move to the anode and cathode respectively. This is illustrated in the following diagram in which and  are simplified representations of the polymer containing oxoammonium ion and TEMPO nitroxide radicals respectively.



(a) **(i)** Graphite is often mixed in the polymer used for making the cathode electrode.

Suggest a reason for this. [1]

To increase the electrical conductivity of the electrode
Or (good) conductor of electricity [1]

(ii) Calculate the oxidation number of N in the cathode **before** discharge. [1]

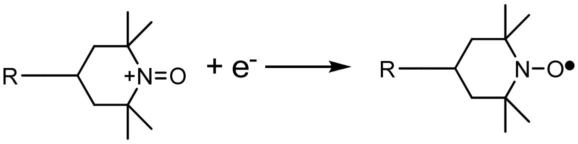
Oxidation number of N is +1 [**1**]

(iii) The E_{cell} generated by the hybrid ORB/Li-ion battery under standard conditions is 2.17 V.

Use relevant $E^{\ominus}$ value from the *Data Booklet* to calculate the electrode potential generated by the cathode half-cell. [1]

Ecell = E_{red} – E_{ox}
+2.17 = E_{red} – (-3.04)
= -0.87 V [1, with correct working and sign]

(iv) During discharge, the following reaction occurs at the cathode.

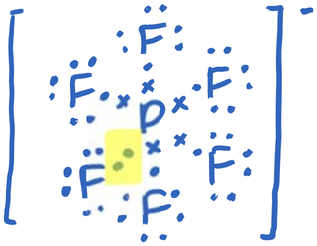


where R represents the organic polymer cathode.

Write an equation for the overall process that occurs during discharge. [1]

Li + → + Li^+ [1]

(v) Draw the dot-and-cross diagram of the PF_6^- ion and state its shape. [2]



[1, check for dative bond and overall charge]

Shape: **Octahedral [1]**

(vi) Suggest whether $LiPF_6$ or LiF has a lower melting point. Explain your answer. [2]

$LiPF_6$. [1, conditional provided student considered LE)
PF_6^- has a **larger anionic radius** [✓] than F^-, giving rise to a **lower magnitude of LE**[✓] (since L.E. $\propto \left|\frac{q_+ \times q_-}{r_+ + r_-}\right|$). Hence, $LiPF_6$ has a lower ionic bond strength and less energy is required to overcome the ionic bond, giving rise to lower mp.

-

(b) The hybrid ORB/Li-ion battery is a secondary battery, i.e., it is rechargeable.

During charging, 1.22 g of Li is regenerated from Li$^+$ ions at the cathode.

(i) Calculate the amount of electrons required to form 1.22 g of Li. [1]

Amount of Li formed = 1.22 / 6.9 = 0.1768 mol

Li+ + e → Li

Amount of electrons consumed = 0.1768 = 0.177 mol [1].

Besides the generation of Li, there is a competing side-reaction that occurs at the cathode.

In this side-reaction, ethylene carbonate, $C_3H_4O_3$ undergoes reduction in the presence of Li$^+$ ions to form ethene and lithium carbonate.

(ii) Write the half-equation for the side-reaction occurring at the cathode. [1]
$C_3H_4O_3 + 2Li^+ + 2e \rightarrow C_2H_4 + Li_2CO_3$ [1]

A current of 5.0 A is supplied over 2 hours during charging.

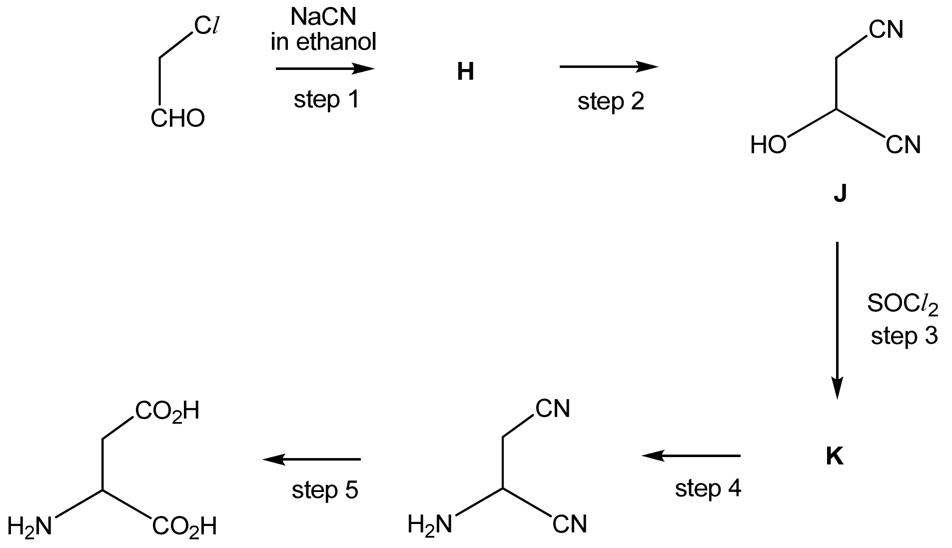
(iii) Use the information given and your answer in **(b)(i)** to calculate the amount of electrons consumed by the side-reaction. [1]
Amount of electrons supplied = (5.0) (2 x 3600) / 96500 = 0.3731 mol [✓].

Hence, amount of electrons consumed by side-reaction
= 0.3731 – 0.1768
= 0.196 mol [✓, **allow ecf from (i)**].

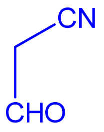
(iv) Suggest why the battery needs to be replaced after about 1000 charge-discharge cycles. [1]

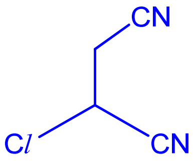
Some of the **Li ions are depleted** / **not all the Li metal is regenerated** during charging **due to the side-reaction** [1].

(c) Chloroethanal is the starting material in the synthesis of aspartic acid.



(i) Suggest structures for the intermediates **H** and **K**. [2]

H:  **[1]**

K:  **[1]**

(ii) Suggest reagents and conditions for step 2 and for step 4. [2]

Step 2: HCN, trace NaOH(aq)/NaCN, cold **[1]**

Step 4: excess, concentrated ethanolic NH_3, heat in sealed tube **[1]**

(iii) The reaction in step 2 produces sample **J**, which does not show optical activity. Explain the observation. [2]

The **nucleophile, CN^-, has equal chances of attacking either above or below the plane of the electron-deficient carbonyl carbon in compound H** **[1]**. Thus, the product mixture contains 50% of each of the enantiomer, forming a **racemic mixture**[√]. Hence, the **optical activity of the 2 enantiomers cancels out**[√]. Thus, sample **J** produced does not show optical activity.

[Total: 18]

Section B

Answer **one** question from this section

4 **(a)** For many compounds the enthalpy change of formation cannot be calculated directly. An indirect method based on enthalpy changes of combustion can be used.

The enthalpy change of combustion can be found by a calorimetry experiment in which the heat energy given off during combustion is used to heat a known mass of water and the temperature change recorded.

(i) Define the term *standard enthalpy change of combustion.* [1]

Standard enthalpy change of combustion, ΔH_c^{θ}, of a compound is the enthalpy change (heat evolved) when **1 mole of the substance** is **completely burnt in oxygen** under standard conditions of 298K and 1 bar. [1]

(ii) Write the equation for the complete combustion of ethanol, CH_3CH_2OH. [1]

$CH_3CH_2OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$[1] (ss not required)

In an experiment to determine the enthalpy change of combustion of ethanol, 0.23 g of ethanol was burned and the heat given off raised the temperature of 100 g of water by 16.3 °C.

(iii) Calculate the heat energy change during the combustion of ethanol. [1]

$$\begin{aligned}\text{Heat change} &= mc\Delta T \\ &= (100)(4.18)(16.3) \\ &= 6813.4\end{aligned}$$

= 6810 J[1]
(no mark awarded if unit given is wrong)

(iv) Hence, calculate the enthalpy change on burning 1 mole of ethanol. [2]

Amount of ethanol = 0.23 / (2x12.0 + 6.0 + 16.0)
= 5.00×10^{-3} mol

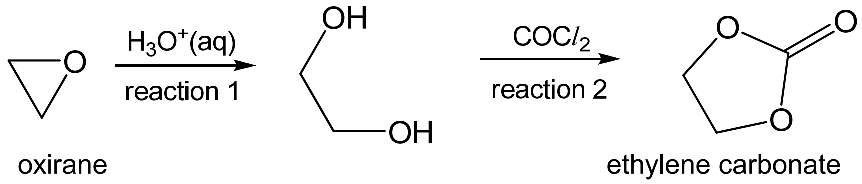
Enthalpy change = - ($6813.4/5.00 \times 10^{-3}$) [1m; ECF from (iii)]
= - 1362680 J mol^{-1}
= - 1360 kJ mol^{-1} [1m include unit & sign]

(v) Suggest one reason why the value for the enthalpy change of combustion of ethanol determined by a simple laboratory calorimetry experiment is likely to be lower than the true value. [1]

Heat loss to the surrounding. / Incomplete combustion/ Ethanol is volatile and evaporated./ Ethanol is impure. / Not all energy is absorbed by the water.
(Any answer 1 mark)

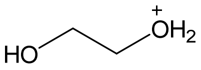
(b) Epoxides are cyclic ethers commonly used in organic reactions.

Ethylene carbonate can be prepared from an epoxide, oxirane by the following reactions.



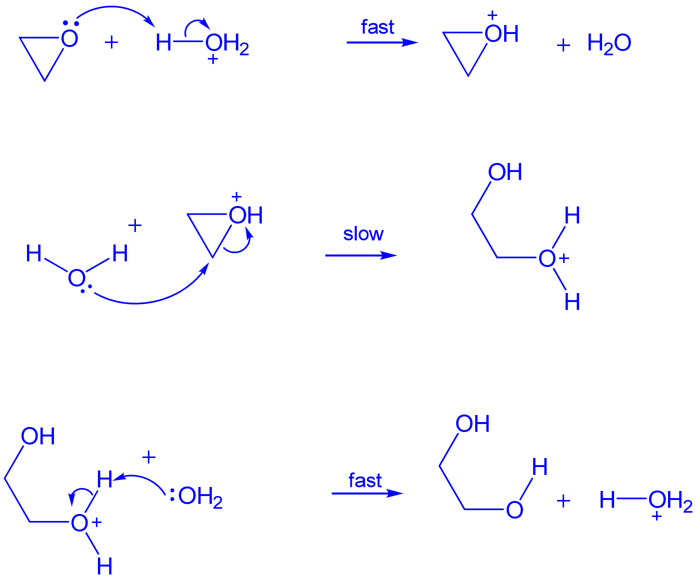
(i) Suggest the type of reaction for reaction 2. [1]
Condensation/ nucleophilic acyl substitution [1]

(ii) Reaction 1 is an acid-catalysed reaction that proceeds via a three-step mechanism:

1) Protonation of oxirane by H_3O^+.
2) Ring opening of protonated oxirane due to nucleophilic attack by H_2O to yield an oxonium ion,  .

3) Deprotonation of the oxonium ion to yield the product, with the regeneration of H_3O^+.

Suggest the mechanism for Reaction 1.
[3]

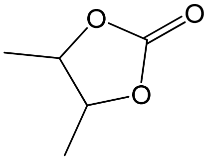


✓ - correct half-arrows and lone pairs for step 1
✓ - formation of H_2O in step 1
✓ - correct structure for protonated epoxide in step 1
✓ - correct half-arrows and lone pair for step 2
✓ - correct half-arrows and regeneration of H_3O^+ for step 3

(fast & slow labels not marked for)

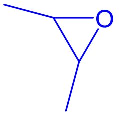
3m – all 5 ✓ ; 2m – 3 to 4 ✓ ; 1m – 2 ✓

Compound **L** can be synthesised from an epoxide in a similar manner as ethylene carbonate.



Compound **L**

(iii) Draw the structure of the epoxide used for synthesising compound **L**. [1]



[1]

(iv) Suggest why compound **L** is able to exhibit cis-trans isomerism. [1]
Restricted C-C bond rotation [1] due to **ring strain/ rigidity of ring**
(and both C atoms of the ring is attached to 2 different groups or atoms)

(c) A number of isomers with the formula $Fe(H_2O)_6Cl_3$ exist. Their general formula is $[Fe(H_2O)_{6-n}Cl_n]Cl_{3-n}.nH_2O$.

Each isomer contains a six co-ordinated Fe(III) ion in an octahedral complex. Water molecules not directly bonded with the Fe atom are held in the crystal lattice as water of crystallisation.

(i) Similar to organic compounds, octahedral complexes can also exhibit stereoisomerism depending on the orientation of the ligands.

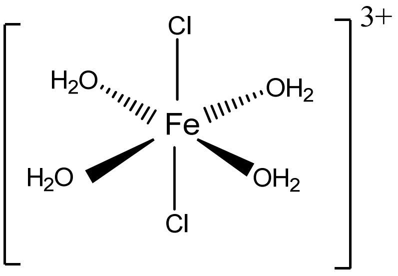
One such example will be the iron complex when *n* is 2. It can exist in two isomeric forms where only one of them has a dipole moment.

Name the type of isomerism shown by the complex

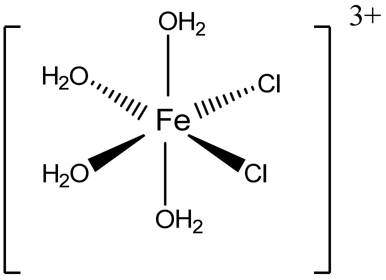
[1]

Cis- Trans isomerism

(ii) Draw the structures of the two isomeric forms of the complex. [2]



trans



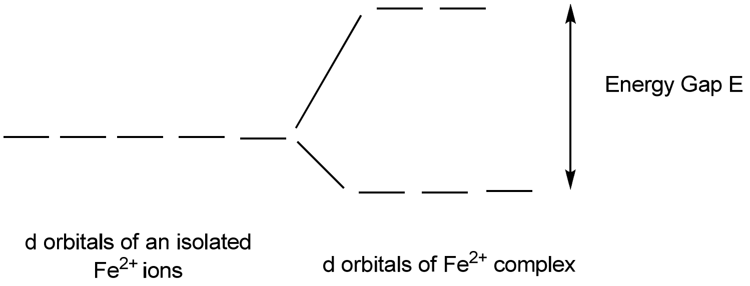
cis

[1 mark each] (labelling of cis-trans not required)

(iii) State which isomer has a dipole moment. Explain your answer. [2]

Cis isomer has a dipole moment. [1] (student need not mention "cis". Marks are awarded as long as student identify the correct isomer)
Cl^- on the same side of the complex/ overall dipole moment does not cancel out.[1]

(iv) The following diagram shows how the d-orbitals are split in an octahedral environment.



When the H_2O ligand is changed to a C*l* ligand, the Fe^{2+} ion changes the electronic configuration from a 'high spin' to a 'low spin' state.

In a 'high spin' state, the electrons occupy all the d-orbitals singly, before starting to pair up in the lower energy d-orbitals.

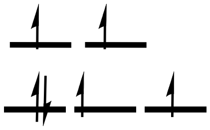
In a 'low spin' state, the lower energy d-orbitals are filled first, by pairing up if necessary, before the higher energy d-orbitals are used.

Use diagrams like the one above to show the electronic distribution of a Fe^{2+} ion in a high spin state, and in a low spin state.

[2]

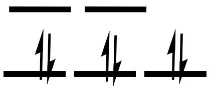
Fe^{2+} : $3d^6$

'High spin' state



[1]

'Low spin' state



[1]

(v) State and explain which ligand will result in a larger energy gap, E, between its d-orbitals.

[1]

(Complex with) Cl ligand [/]
Electrons will only pair up in the lower orbitals when the energy gap was greater than the interelectronic repulsion between the two electrons in the same orbital. (wttse) [/]

[Total: 20]

5 Carbonyl compounds are common in our everyday lives. They are mainly used as solvents, perfumes and flavouring agents or as intermediates in the manufacture of plastics and pharmaceuticals.

(a) The characteristic smell of cherries and fresh almonds is due to benzaldehyde.

(i) Benzaldehyde can react with chloromethane to form 3-methylbenzaldehyde. Describe the mechanism for this reaction.

[3]

Electrophilic Substitution **[1]**
$CH_3Cl + FeCl_3 \longrightarrow CH_3^+ + [FeCl_4]^-$

$H^+ + [FeCl_4]^- \longrightarrow FeCl_3 + HCl$
1 [√] for each step

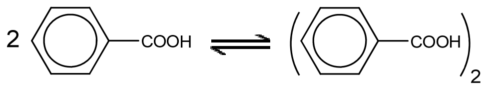
(ii) Benzene can also react under a similar reaction with chloromethane.

State and explain whether benzene or benzaldehyde would react with chloromethane more readily.

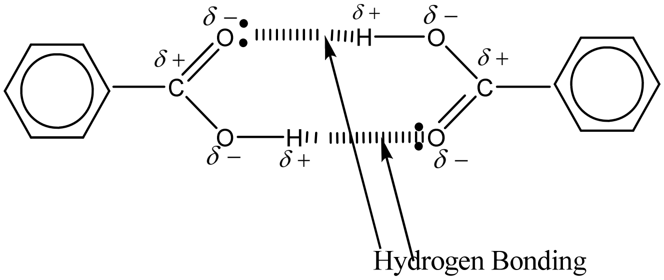
[2]

Benzene would react **more readily [√]** with chloromethane.
Benzaldehyde contains an **electron withdrawing CHO group [√]** which **decreases the electron density of the benzene ring [√]**, making it **less susceptible to electrophilic attacks [√]**.

(b) Benzaldehyde can also react with hot acidified dichromate(VI) to give benzoic acid. In benzene, benzoic acid associates to form dimers.



(i) Draw a diagram to illustrate the bonding in the dimer. [1]



All details included (dipoles, lone pair, hydrogen bonds) – **[1]**

(ii) Predict and explain whether the dimerisation is favoured at a high or low temperature.

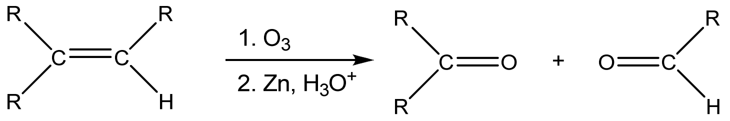
[2]

Low temperature [1, conditional]. At low temperature, the position of equilibrium shifts to the right to favour the **exothermic reaction [1]** to release heat.

(iii) Suggest why the above equilibrium cannot be established in an aqueous medium.
In aqueous medium, **benzoic acid would form hydrogen bonds with the water molecules instead** of forming a dimer, **[1]**

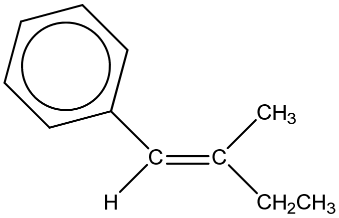
[1]

(c) Carbonyl compounds can be prepared from alkenes via the ozonolysis reaction as shown below.

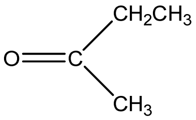


An alkene **M**, $C_{11}H_{14}$ was treated with O_3, followed by Zn and H_3O^+ to give **N** C_4H_8O and **P**, C_7H_6O. **N** gives a yellow precipitate with aqueous alkaline iodine while **P** gives a grey precipitate with ammonical silver nitrate solution. In the presence of OH^-, **P** undergoes a reaction to give **Q**, $C_7H_6O_2$ and **S**, C_7H_8O. Both **Q** and **S** react with Na metal, but only **Q** reacts with $NaHCO_3$.

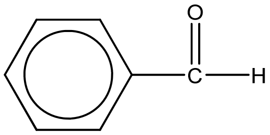
Suggest the structures of **M, N, P, Q** and **S**. [5]



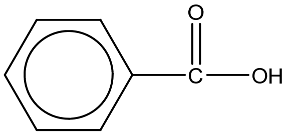
M



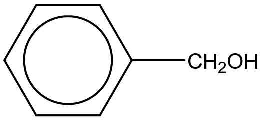
N



P



Q



S

[1] each

(d) **T, U, V** and **W** are four consecutive elements in the **fourth** period of the Periodic Table. (The letters are **not** the actual symbols of the elements.)

T is a soft, silvery metal with a melting point just above room temperature. Its amphoteric oxide, **T**$_2$O$_3$, has a melting point of 1900 °C and can be formed by heating **T** in oxygen.

W is a solid that can exist as several allotropes, most of which contain **W**$_8$ molecules. **W** burns in air to form **W**O$_2$ and **W**O$_3$**,** which dissolves in water to form an acidic solution. The acidic solutions react with sodium hydroxide to form the salt Na$_2$**W**O$_3$ and Na$_2$**W**O$_4$ respectively.

(i) Suggest the identities of **T** and **W**. [2]

T = Ga [1]   **W** = Se [1]

(ii) Write equations for the reactions of **T**$_2$O$_3$ with

- hydrochloric acid,
- sodium hydroxide [2]

$T_2O_3 + 6HCl \rightarrow 2TCl_3 + 3H_2O$ [1]

$T_2O_3 + 2NaOH + 3H_2O \rightarrow 2NaT(OH)_4$ [1]

(in writing the equations, students can replace **T** with Ga)

(iii) Suggest the structure in **T**$_2$O$_3$. [1]

Giant Ionic Structure [1]

(iv) Write an equation for the formation of the acidic solution when **W**O$_3$ dissolves in water. [1]

$WO_3 + H_2O \rightarrow H_2WO_4$ [1]

(in writing the equation, students can replace **W** with Se)

[Total: 20]

H

INNOVA JUNIOR COLLEGE
JC2 PRELIMINARY EXAMINATION
in preparation for General Certificate of Education Advanced Level
Higher 2

CANDIDATE NAME	

CLASS		INDEX NUMBER	

CHEMISTRY 9729/04

Paper 4 Practical **14 Aug 2018**

2 hours 30 minutes

Candidates answer on the Question Paper.

READ THESE INSTRUCTIONS FIRST

Write your index number, name and class on all the work you hand in.
Give details of the practical shift and laboratory when 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 18 and 19.
An **insert** is printed on **page 21**.

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

Shift
Laboratory

For Examiner's Use	
1	**7**
2	**21**
3	**27**
Total	**55**

This document consists of **20** printed pages and **2** blank pages.

1 You will find the relative atomic mass, A_r, of magnesium by measuring the volume of hydrogen produced when a known mass of metal reacts with an excess of acid.

$$Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$$

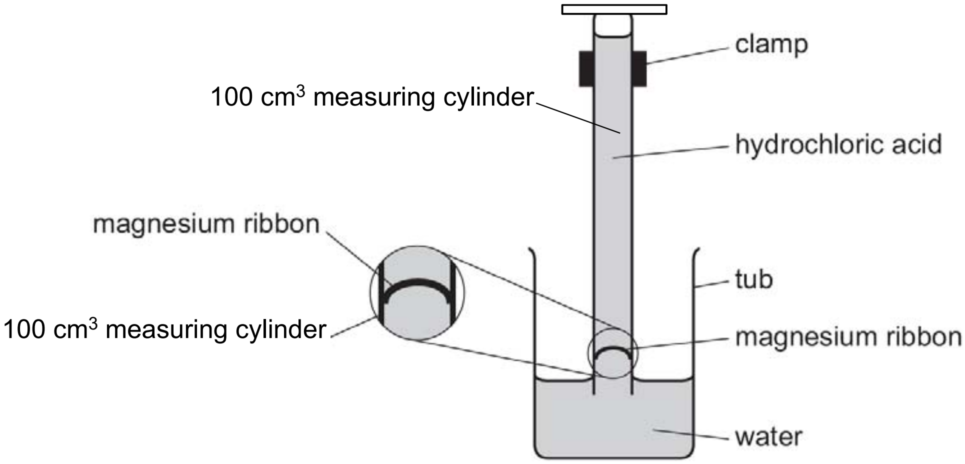
FA 1 is 2.00 mol dm^{-3} hydrochloric acid, HC*l*.

FA 2 is magnesium, Mg.

(a) Method

Read through the whole method before starting any practical work.

- Fill the tub with water to a depth of about 5 cm.
- Weigh the magnesium, **FA 2** and note its mass below.
- Fill the 100 cm^3 measuring cylinder to about 30 cm^3 mark with hydrochloric acid, **FA 1**.
- Gently, with minimal disturbance to the surface of the solution, top up the measuring cylinder containing **FA 1** with distilled water to about 4 to 5 cm above the 100-cm^3 mark.
- Bend the **FA 2** strip into a U-shape.
- Carefully place the **FA 2** strip about half a centimeter into the measuring cylinder so that it is above the liquid and friction holds it in position.
- Hold a piece of paper towel over the open end of the measuring cylinder, invert the measuring cylinder and immediately place it in the tub of water. Remove the paper towel and clamp the measuring cylinder as shown in the diagram.



- The liquid level should now be on the scale of the measuring cylinder. If it is not, repeat the above procedure to set up your experiment again.
- Record the initial reading on the measuring cylinder. Remember that the scale is now upside down.
- Leave the apparatus so that the acid from the measuring cylinder diffuses around the **FA 2** and reacts.
- You should start **Question 2 or Question 3** while waiting for the reaction to complete.
- When all the **FA 2** has reacted, note and record the final reading on the measuring cylinder.
- Calculate the volume of hydrogen produced.

Results

[2]

M1	
M2	

(b) **Calculations**
Show your working and appropriate significant figures in the final answer to **each** step of your calculations.

(i) Calculate the number of moles of hydrogen produced.
(Assume that 1 mole of gas occupies 24.0 dm^3 under these conditions.)

(If you are unable to calculate the volume of hydrogen produced in **(a)**, you may assume that the volume of hydrogen produced is 70 cm^3 for the calculation here. Note: this is a hypothetic value.)

Amount of H_2 = ………………………… [1]

M3	

(ii) Use your answer to **(i)** and the mass of magnesium used to calculate the A_r of magnesium.

A_r of Mg = ………………………… [1]

M4	

(c) What would be the effect on the value of the A_r of magnesium calculated if the temperature of the room was much lower than that for your experiment? Explain your answer.

……………………………………………………………………………………………………

……………………………………………………………………………………………………

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

M5	
M6	

(d) A similar experiment was repeated using aluminium instead. The reaction was much slower. Explain why aluminium took a longer time to react completely.

……………………………………………………………………………………………………

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

M7	

[Total: 7]

2 Sodium thiosulfate reacts with acid to produce a pale yellow precipitate of sulfur.

$$S_2O_3^{2-}(aq) + 2H^+(aq) \longrightarrow S(s) + SO_2(aq) + H_2O(l)$$

You will investigate how the rate of this reaction varies with the concentration of thiosulfate ions.
To do this, you will measure the time taken for a fixed amount of sulfur to be formed.

FA 3 is 0.10 moldm^{-3} sodium thiosulfate, $Na_2S_2O_3$.
FA 4 is 1.00 moldm^{-3} hydrochloric acid, HC*l*.

(a) Experiment 1

- Use the larger measuring cylinder to transfer 40 cm^3 of **FA 3** into the 100 cm^3 conical flask.
- Use the smaller measuring cylinder to measure 25 cm^3 of **FA 4**.
- Pour the **FA 4** into the **FA 3** in the conical flask and start timing **immediately**.
- Stir the mixture in the conical flask once and place the conical flask on top of the printed insert (page **21**) provided.
- Look down through the solution in the conical flask at the print on the insert.
- Stop timing as soon as the precipitate of sulfur makes the print on the insert **just** invisible.
- Record the reaction time to the nearest second.
- Empty, rinse and dry the conical flask so it is ready for use in **Experiment 2**.
- Rinse the sink with tap water to wash away the products of the reaction.

Experiment 2

- Use the larger measuring cylinder to transfer 30 cm^3 of **FA 3** into the 100 cm^3 conical flask.
- Use the same measuring cylinder to add 10 cm^3 of distilled water to the conical flask.
- Use the smaller measuring cylinder to add 25 cm^3 of **FA 4** to the mixture in the beaker and start timing **immediately.**
- Stir the mixture in the conical flask once and place the conical flask on top of the printed insert provided.
- Look down through the solution in the conical flask at the print on the insert.
- Stop timing as soon as the precipitate of sulfur makes the print on the insert **just** invisible.
- Record the reaction time to the nearest second.
- Empty, rinse and dry the conical flask so it is ready for use in **Experiment 3**.
- Rinse the sink with tap water to wash away the products of the reaction.

Experiment 3

Repeat **Experiment 2** using 20 cm^3 of **FA 3**, 20 cm^3 of distilled water and 25 cm^3 of **FA 4**.

Experiments 4 and 5

Choose suitable volumes that will enable you to investigate further the effect of changing the concentration of thiosulfate ions on the rate of the reaction. You should not use a volume of less than 10 cm^3 of **FA 3**.

Results

The relative rate of the reaction can be calculated as shown.

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

In an appropriate format in the space provided, record:

- all measurements of volumes used,
- the reaction time, to the nearest second,
- the relative rate of the reaction, to 3 significant figures, for each of the five experiments

M8	
M9	
M10	
M11	
M12	

[5]

(b) On the grid, plot a graph of rate of reaction (y-axis) against volume of **FA 3** (x-axis).
Circle any points that you consider anomalous and draw a line of best fit to show how the rate of the reaction depends on the volume of **FA 3**. [3]

M13	
M14	
M15	

(c) **Use your graph** to calculate the time that the reaction would have taken if 8 cm^3 of **FA 3** had been used. Show **on the grid** how you obtained your answer.

time = ……………………….. [1]

M16	

(d) It has been claimed that the reaction is non-zero order with respect to [$S_2O_3^{2-}$].

State whether you agree or disagree with this claim. Use evidence from your graph to support your answer.

……………………………………………………………………………………………………

……………………………………………………………………………………………………

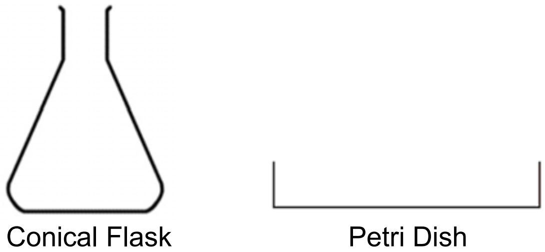
……………………………………………………………………………………………………

……………………………………………………………………………………………………

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

M17	
M18	

(e) A student broke the 100 cm^3 conical flask when carrying out the experiment and decided to use a petri dish instead. This has a different shape.



State and explain what effect this would have on the student's result.

……………………………………………………………………………………………………

……………………………………………………………………………………………………

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

M19	
M20	

(f) A student suggested that the temperature at which the experiment was carried out would also affect the rate of the reaction.

Plan an investigation, based on the experiment described in **2(a)**, to determine the effect of temperature on the rate of reaction.

You may assume that you are provided with

- 0.10 moldm^{-3} sodium thiosulfate, $Na_2S_2O_3$.
- 1.00 moldm^{-3} hydrochloric acid, HCl
- the equipment normally found in a school or college laboratory

Give a step-by step description of how you would carry out the experiment by considering

- what you would keep constant in all the experiments,
- an suitable number of experiments you would do, and a reasonable temperature range(minimum and maximum temperatures),
- the apparatus that you would use in addition to that specified in **2(a),**
- the procedure that you would follow and the measurements that you would take.

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.... [4]

M21	
M22	
M23	
M24	

(g) State a hazard that must be considered when planning the experiment and describe precautions that should be taken to keep risks to a minimum.

....

.... [1]

M25	

[Total: 21]

M26	
M27	
M28	

3 Qualitative Analysis

At each stage of any test, you are to record details of the following.

- colour changes seen
- the formation of any precipitate
- the solubility of such precipitates in an excess of the reagent added.

Where gases are released, they should be identified by a test, **described in the appropriate place in your observations.**

You should indicate clearly at what stage in a test a change occurs.
Marks are **not** given for chemical equations.
No additional tests for ions present should be attempted.

If any solution is warmed, a boiling tube MUST be used.

Rinse and reuse test-tubes and boiling tubes where possible.

Where reagents are selected for use in a test, the name or correct formula of the element or compound must be given.

Question 3 consists of two tasks.

In the first task, you are to explore the chemistry of some compounds of an unknown transition element **W** and determine its identities.

FA 5 is a solid sample of a common dioxide of the unknown transition element **W**,
FA 6 is dilute sulfuric acid, H_2SO_4,
FA 7 is a solid sample of sodium ethanedioate, $Na_2C_2O_4$,
FA 8 is a solution of pure compound **X**, which is the product formed in **(a)(i)**.

(a) **(i)**

Test	Observations
Transfer all of the solid sample of **FA 7** into a small conical flask. Add 25 cm^3 of **FA 6** to this flask. Gently heat the flask until the temperature of the mixture reaches about 60 °C. Swirl the mixture carefully. Place the flask on the heat proof mat. Using a spatula, add **FA 5** to the mixture in small portions. Between each addition, stir the mixture carefully with the thermometer and observe any changes in the temperature of the mixture. Stop adding **FA 5** to the mixture when you think the reaction is complete.	

Filter the mixture into a boiling tube and leave the filtrate to stand. The filtrate is compound **X**. Retain this filtrate for use in **(a)(ii).**	
While you are waiting for (a)(i) to be complete, continue with (c). The colour of the filtrate may change on standing.	

[3]

M29	
M30	
M31	

(a) **(ii)** In this part, you are to investigate the effect of the addition of aqueous sodium hydroxide, to separate portions of the filtrate from **(a)(i)** and **FA 8**.

In the space below, prepare a suitable table and in it record details of the tests performed and the observations made.

[3]

M32	
M33	
M34	

(b) **(i)** Give **two** conclusions you can draw about the nature of the reaction occurring in **(a)(i).**

In each case, support your conclusion by referring to your observations.

Conclusion **1**…………………………………………………………………...

Evidence………………………………………………………………………..

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…………………………………………………………………………………..

Conclusion **2**…………………………………………………………………...

Evidence………………………………………………………………………..

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………………………………………………………………………………… [2]

M35	
M36	

(ii) Explain why you decided to stop the addition of **FA 5** at the point you chose in **(a)(i)**.

You should support your answer by referring to your observations.

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…………………………………………………………………………………… [1]

M37	

(iii) Consider your observations in **(a)(ii).**

Identify the transition metal ion formed in **(a)(i)** and suggest an explanation for the differences between your observations when you added aqueous sodium hydroxide to the filtrate from **(a)(i)**, and to **FA 8**.

Ion present is …………………………………..

Explanation for difference ..……………………………………………………..

……………………………………………………………………………………..

…………………………………………………………………………………… [1]

M38	

(iv) In **(a)(i)**, the reaction between **FA 5** and **FA 7** occurs under acidic conditions.

Write an ionic equation for this reaction. Use the letter '**W**' to represent the transition metal in this equation.

…………………………………………………………………………………… [1]

M39	

In the second task, you are to perform a series of test to deduce the structure of the unknown hydrocarbon, **FA 9**.

FA 9 is a simple hydrocarbon compound,
FA 10 is bromine water.

(c)

	Test	observations
(i)	Place 5 cm^3 of aqueous sodium hydroxide in a test-tube. Add **1 drop** of **FA 9** to this test-tube. Add aqueous potassium manganate(VII), dropwise with shaking, until no further change is seen. Do not exceed 15 drops.	
	Note: Eventually, this reaction will produce a brown MnO_2 precipitate. There is no need for you to wait for this to happen.	
(ii)	Place 5 cm^3 of dilute sulfuric acid in a test–tube. Add **1 drop** of **FA 9** to this test–tube. Add aqueous potassium manganate(VII), dropwise with shaking, until no further change is seen. Do not exceed 15 drops.	
(iii)	Place 5 cm^3 of water in a test–tube. Add **1 drop** of **FA 9** to this test–tube. Add **FA 10,** dropwise with shaking, until no further change is seen.	

[3]

M40	
M41	
M42	

Conclusions

(d) Consider the identities of the Mn-containing reactant and eventual product in **(c)(i).**

Suggest a value for the oxidation number of Mn in the coloured ion produced in **(c)(i).** Explain your reasoning.

Oxidation number of Mn………………………………..

Explanation………………………………………………………………………

…………………………………………………………………………………….

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

M43	

(e) Compound **Y** is the main organic product in **(c)(i)**, when **FA 9** reacts with $KMnO_4$ under alkaline conditions. The molecular formula of **Y** is $C_6H_{12}O_2$.

(i) Deduce the molecular formula of **FA 9**.

Explain your deduction. Your explanation must be supported by evidence from your observations in **(c)**.

Molecular formula of **FA 9** is ………………………………………………

Explanation……………………………………………………………………

………………………………………………………………………………..

………………………………………………………………………………..

………………………………………………………………………………..

……………………………………………………………………………… [2]

M44	
M45	

(ii) Draw the structural formulae for **FA 9** and compound **Y**.

Explain how you deduced the structure of **FA 9**.

Structure of **FA 9**	Structure of **Y**

Explanation……………………………………………………………………

………………………………………………………………………………..

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………………………………………………………………………………..

……………………………………………………………………………… [2]

M46	
M47	

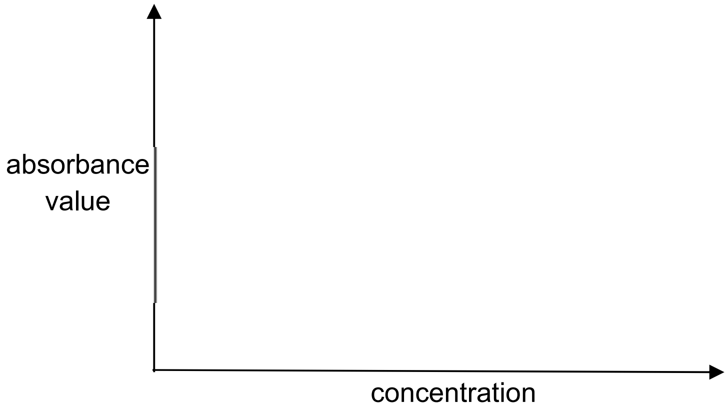
(f) **Planning**

Many transition metal complex ions are coloured. It is possible to use this property to determine the concentration of a solution of a coloured complex ion. A few cm^3 of the solution is placed inside a machine, known as a spectrometer. This machine measures the amount of light that is absorbed when a specific wavelength of visible light is shone through a coloured solution. It does this by comparing the amount of light passing through the sample with the amount of light passing through the pure solvent. The amount of light absorbed is expressed as an *absorbance value.* The more concentrated the solution, the higher the absorbance value, i.e., the absorbance value is directly proportional to the concentration of the solution.

This technique can be used to determine the concentration of a solution of aqueous $\mathbf{W}O_4^-$. A series of known, but different, concentration of solution containing $\mathbf{W}O_4^-$ is prepared. A spectrometer is used to measure the absorbance of each solution. A graph of absorbance against concentration is then plotted. This graph is known as a calibration line.

The experiment is then repeated using a solution of unknown concentration. By comparing the absorbance of this solution with the calibration line, the concentration of $\mathbf{W}O_4^-$ in the unknown solution can be determined.

(i) Sketch the calibration line for the graph of absorbance against concentration that you would expect to obtain.



[1] **M48**

(ii) Using the information given above, you are required to write a plan to determine the concentration of **W**O_4^- in a solution of **Z**.

You may assume that you are provided with:

- solution **Z**, of unknown **W**O_4^- concentration less than 2 mol dm^{-3};
- a standard solution containing 5.00 mol dm^{-3} of **W**O_4^-;
- access to a spectrometer and instructions for its use;
- graph paper;
- the apparatus and chemicals normally found in a school or college laboratory.

Your plan should include details of:

- the preparation of 100.0 cm^3 of 2.00 mol dm^{-3} aqueous **W**O_4^-;
- the preparation of a suitable range of diluted solutions of accurate concentrations;
- an outline of how the results would be obtained;
- how the calibration line would be used to determine the concentration of **W**O_4^- in solution **Z**.

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.... [7]

M49	
M50	
M51	
M52	
M53	
M54	
M55	

[Total: 21]

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 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 A*l* foil
nitrite, NO_2^- (aq)	NH_3 liberated on heating with OH^-(aq) and A*l* 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

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INSERT

Please detach the insert from the question paper for use in **Question 2**.

Innova junior college Innova junior

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INNOVA JUNIOR COLLEGE
JC2 PRELIMINARY EXAMINATION
in preparation for General Certificate of Education Advanced Level
Higher 2

CANDIDATE NAME			
CLASS		INDEX NUMBER	

CHEMISTRY 9729/04

Paper 4 Practical **14 Aug 2018**

2 hours 30 minutes

Candidates answer on the Question Paper.

READ THESE INSTRUCTIONS FIRST

Write your index number, name and class on all the work you hand in.
Give details of the practical shift and laboratory when 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 18 and 19.
An **insert** is printed on **page 21**.

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

Shift
Laboratory

For Examiner's Use	
1	**7**
2	**21**
3	**27**
Total	**55**

This document consists of **20** printed pages and **2** blank pages.

1 You will find the relative atomic mass, A_r, of magnesium by measuring the volume of hydrogen produced when a known mass of metal reacts with an excess of acid.

$$Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$$

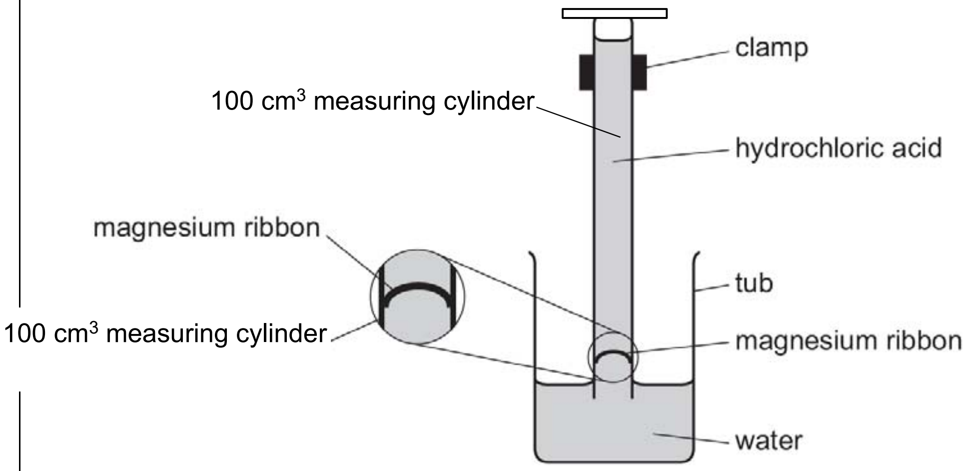
FA 1 is 2.00 mol dm^{-3} hydrochloric acid, HC*l*.

FA 2 is magnesium, Mg.

(a) **Method**

Read through the whole method before starting any practical work.

- Fill the tub with water to a depth of about 5 cm.
- Weigh the magnesium, **FA 2** and note its mass below.
- Fill the 100 cm^3 measuring cylinder to about 30 cm^3 mark with hydrochloric acid, **FA 1**.
- Gently, with minimal disturbance to the surface of the solution, top up the measuring cylinder containing **FA 1** with distilled water to about 4 to 5 cm above the 100-cm^3 mark.
- Bend the **FA 2** strip into a U-shape.
- Carefully place the **FA 2** strip about half a centimeter into the measuring cylinder so that it is above the liquid and friction holds it in position.
- Hold a piece of paper towel over the open end of the measuring cylinder, invert the measuring cylinder and immediately place it in the tub of water. Remove the paper towel and clamp the measuring cylinder as shown in the diagram.



- The liquid level should now be on the scale of the measuring cylinder. If it is not, repeat the above procedure to set up your experiment again.
- Record the initial reading on the measuring cylinder. Remember that the scale is now upside down.
- Leave the apparatus so that the acid from the measuring cylinder diffuses around the **FA 2** and reacts.
- You should start **Question 2 or Question 3** while waiting for the reaction to complete.
- When all the **FA 2** has reacted, note and record the final reading on the measuring cylinder.
- Calculate the volume of hydrogen produced.

Results

Mass of Mg used /g	0.069
Initial reading on measuring cylinder / cm^3	10.0
Final reading on measuring cylinder / cm^3	85.0
Volume of H_2 produced /cm^3	75.0

M1 mass of magnesium, initial and final readings and **volume of hydrogen** with **unambiguous headings** and **correct unit.**
M2 mass recorded to 3d.p. and readings recorded to nearest 0.5 cm^3.

[2]

M1	
M2	

(b) **Calculations**

Show your working and appropriate significant figures in the final answer to **each** step of your calculations.

(i) Calculate the number of moles of hydrogen produced.
(Assume that 1 mole of gas occupies 24.0 dm^3 under these conditions.)

(If you are unable to calculate the volume of hydrogen produced in **(a)**, you may assume that the volume of hydrogen produced is 70 cm^3 for the calculation here. Note: this is a hypothetic value.)

M3 Correct calculation moles H_2 = volume collected / 24000 mol

Amount of H_2 = 75/24000
= 3.125 x 10^{-3}
= 3.13 x 10^{-3} mol

Amount of H_2 = ... [1]

M3	

(ii) Use your answer to **(i)** and the mass of magnesium used to calculate the *A*$_r$ of magnesium.

M4 Correctly calculation using $A_r = \dfrac{\text{mass used}}{\text{amount of } H_2}$

Ar = 0.0690/ 3.125 x 10^{-3}
= 22.08
= 22.1

A_r of Mg = ... [1]

M4	

(c) What would be the effect on the value of the A_r of magnesium calculated if the temperature of the room was much lower than that for your experiment? Explain your answer.

....

		…………………………………………………………………………………… …………………………………………………………………………………… [2]	**M5** **M6**	
		M5 Volume (gas) measured/**or** moles/amount gas/H_2 would have been less **M6** *correct link betw Ar and amt/vol i.e* A_r greater (conditional: must follow from smaller **moles** of H_2/Mg) **or** **M5** Use correct molar volume for new room temperature **M6** A_r unchanged (but must follow from V_m smaller)		
	(d)	A similar experiment was repeated using aluminium instead. The reaction was much slower. Explain why aluminium took a longer time to react completely.		
		…………………………………………………………………………………… …………………………………………………………………………………… [1]	**M7**	
		M7 Aluminium has a protective **oxide layer** Or Al is **less reactive** than Mg. Hence, slower.		
		[Total: 7]		

2 Sodium thiosulfate reacts with acid to produce a pale yellow precipitate of sulfur.

$$S_2O_3^{2-}(aq) + 2H^+(aq) \longrightarrow S(s) + SO_2(aq) + H_2O(l)$$

You will investigate how the rate of this reaction varies with the concentration of thiosulfate ions.
To do this, you will measure the time taken for a fixed amount of sulfur to be formed.

FA 3 is 0.10 moldm^{-3} sodium thiosulfate, $Na_2S_2O_3$.
FA 4 is 1.00 moldm^{-3} hydrochloric acid, HC*l*.

(a) **Experiment 1**

- Use the larger measuring cylinder to transfer 40 cm^3 of **FA 3** into the 100 cm^3 conical flask.
- Use the smaller measuring cylinder to measure 25 cm^3 of **FA 4**.
- Pour the **FA 4** into the **FA 3** in the conical flask and start timing **immediately**.
- Stir the mixture in the conical flask once and place the conical flask on top of the printed insert (page **21**) provided.
- Look down through the solution in the conical flask at the print on the insert.
- Stop timing as soon as the precipitate of sulfur makes the print on the insert **just** invisible.
- Record the reaction time to the nearest second.
- Empty, rinse and dry the conical flask so it is ready for use in **Experiment 2**.
- Rinse the sink with tap water to wash away the products of the reaction.

Experiment 2

- Use the larger measuring cylinder to transfer 30 cm^3 of **FA 3** into the 100 cm^3 conical flask.
- Use the same measuring cylinder to add 10 cm^3 of distilled water to the conical flask.
- Use the smaller measuring cylinder to add 25 cm^3 of **FA 4** to the mixture in the beaker and start timing **immediately.**
- Stir the mixture in the conical flask once and place the conical flask on top of the printed insert provided.
- Look down through the solution in the conical flask at the print on the insert.
- Stop timing as soon as the precipitate of sulfur makes the print on the insert **just** invisible.
- Record the reaction time to the nearest second.
- Empty, rinse and dry the conical flask so it is ready for use in **Experiment 3**.
- Rinse the sink with tap water to wash away the products of the reaction.

Experiment 3

Repeat **Experiment 2** using 20 cm^3 of **FA 3**, 20 cm^3 of distilled water and 25 cm^3 of **FA 4**.

Experiments 4 and 5

Choose suitable volumes that will enable you to investigate further the effect of changing the concentration of thiosulfate ions on the rate of the reaction. You should not use a volume of less than 10 cm^3 of **FA 3**.

Results

The relative rate of the reaction can be calculated as shown.

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

In an appropriate format in the space provided, record:

- all measurements of volumes used,
- the reaction time, to the nearest second,
- the relative rate of the reaction, to 3 significant figures, for each of the five experiments

Expt No	Volume of **FA 3** / cm^3	Volume of water / cm^3	Reaction time/ s	Rate of reaction/ s^{-1}
1	40.0	0.0	27	37.0
2	30.0	10.0	36	27.8
3	20.0	20.0	60	16.7
4	25.0	15.0	43	23.3
5	10.0	30.0	136	7.35

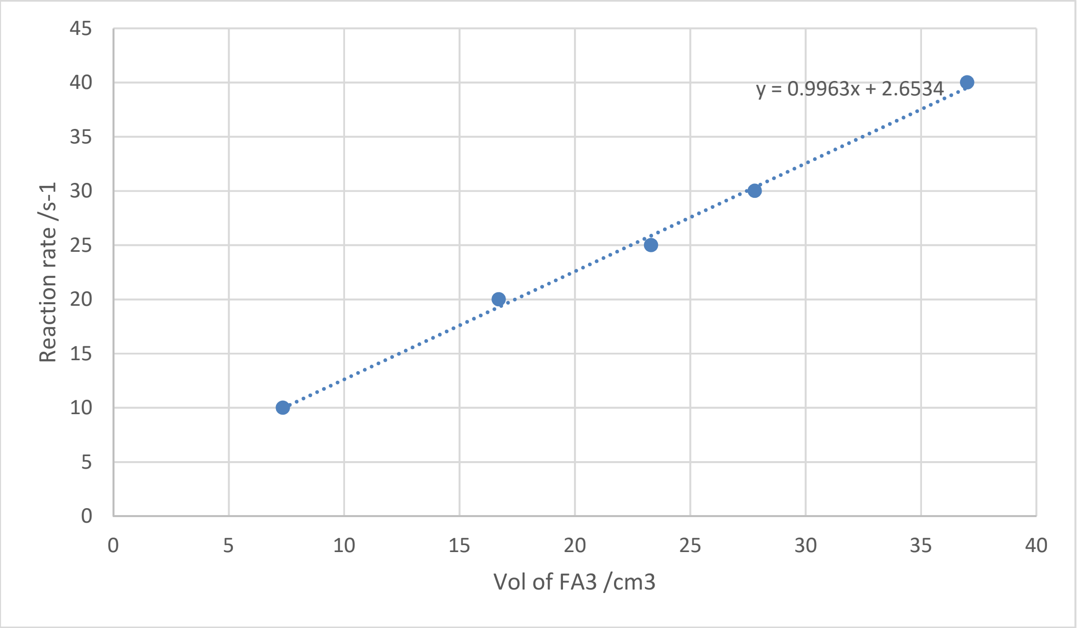
M8– Table that shows volume of FA 3, volume of water, time and rate for 5 experiments. Correct unit for all data: volume(cm^3), time(s), rate(s^{-1})
M9 – all times recorded to the nearest second **(whole number)**, all volume to 1 dp
M10 – Two additional experiments with volume FA 3 not less than 10 cm^3, not more than 40 cm^3 and no volume $\leq$ 2cm^3 close to another volume. Volume of water chosen so that FA 3 + water = 40 cm^3 for the additional experiments. 40cm3, 30cm3, 20cm3 must be present in the table.
M11 – Correctly calculates rate for all experiments and shown to 3 sf.
M12 – Award if candidate's (time for FA3 = 20)/(time for FA3 = 40) is between 1.90 and 2.40.

M8	
M9	
M10	
M11	
M12	

[5]

(b) On the grid, plot a graph of rate of reaction (y-axis) against volume of **FA 3** (x-axis).
Circle any points that you consider anomalous and draw a line of best fit to show how the rate of the reaction depends on the volume of **FA 3**. [3]

M13	
M14	
M15	



M13 – scales that cover more than half the space in both directions and axes labelled correctly with units.
M14 – points plotted correctly. Points must be within half a small square of the correct position.
M15 – line of best fit drawn which ignores anomalous results identified by the candidate

(c) **Use your graph** to calculate the time that the reaction would have taken if 8 cm^3 of **FA 3** had been used. Show **on the grid** how you obtained your answer.

M16 – correct line drawn within 1 small square (horizontal line must be shown) and correctly calculates (1000/ rate)

When 8 cm3 of FA3 is used,
Reaction rate = 10.6

Reaction time = 1000/10.6
= 94.3s

time = ………………………… [1]

M16	

(d) It has been claimed that the reaction is non-zero order with respect to [$S_2O_3^{2-}$].

State whether you agree or disagree with this claim. Use evidence from your graph to support your answer.

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		.... [2]
		Agree or disagree (conditional) **M17** **discuss shape of graph/ gradient compared to zero order or finding $t_{\frac{1}{2}}$ to prove first order and thus is non-zero. M18**
	(e)	A student broke the 100 cm^3 conical flask when carrying out the experiment and decided to use a petri dish instead. This has a different shape.  Conical Flask  Petri Dish State and explain what effect this would have on the student's result.
		.... [2]
		The time recorded will be **longer. M19 (Conditional; provided understanding that more sulfur is required is shown in explanation)** **More sulfur is required** to be formed in order to cover the mark. **M20**

M17	
M18	

M19	
M20	

(f) A student suggested that the temperature at which the experiment was carried out would also affect the rate of the reaction.

Plan an investigation, based on the experiment described in **2(a)**, to determine the effect of temperature on the rate of reaction.

You may assume that you are provided with

- 0.10 moldm^{-3} sodium thiosulfate, $Na_2S_2O_3$.
- 1.00 moldm^{-3} hydrochloric acid, HC*l*
- the equipment normally found in a school or college laboratory

Give a step-by step description of how you would carry out the experiment by considering

- what you would keep constant in all the experiments,
- an suitable number of experiments you would do, and a reasonable temperature range(minimum and maximum temperatures),
- the apparatus that you would use in addition to that specified in **2(a),**
- the procedure that you would follow and the measurements that you would take.

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.... [4]

1. Use the larger measuring cylinder to transfer 40 cm^3 of **FA 3** into the 100 cm^3 beaker.
2. Use the smaller measuring cylinder to measure 25 cm^3 of **FA 4** into another 100 cm^3 beaker.
3. Place both of them in a water bath set at 30°C/ Heat and maintain both solution at 30°C.
4. Ensure that both solutions have reached 30°C by using a thermometer to measure their initial temperature.
5. Pour the **FA 4** into the beaker containing **FA 3** and start timing immediately.
6. Stir the mixture in the beaker once and place the beaker on top of the printed insert provided.
7. Look down through the solution in the beaker at the print on the insert.
8. Stop timing as soon as the precipitate of sulphur makes the print on the insert just invisible.
9. Record the reaction time to the nearest second.
10. Repeat the experiment with the same volume of **FA 3** and **FA 4** used but at temperature 35°C, 40°C, 45°C, 50°C and 55°C.

M21– at least 5 experiments (not repeats of the same expt)
M22 – experiments covering at least a 25°C range (no greater than 100°C)
M23 – Maintaing the volumes of both reagents to be the same for all experiment. (Marks can be awarded if students repeat same experiment but volume is kept the same) ;
M24– Indication of **changing** and **maintaining** temperature either via direct heating or water bath.

(g) State a hazard that must be considered when planning the experiment and describe precautions that should be taken to keep risks to a minimum.

....

.... [1]

		Reference to “hot” apparatus/ sulfur dioxide evolved/ HCl acid (ignore any reference to possible effects) **with** use of **heat proof(thick)** gloves/ use of tongs/ use of fume cupboard. **M25** Spillages and goggles not accepted.
		Shows working in **all** calculations in **1(b)(i) and (ii)**, **2(c).** All calculations must be relevant although they may not be complete or correct. *Any calculation not attempted loses this mark.* **M26** Shows appropriate significant figures (3 ~~or 4 sf~~) in **all** final answers in **1(b)(i)**, **2(c)** and 1 dp in **1(b)(ii)** *Any calculation not attempted loses this mark.* **M27** Shows correct and appropriate units in **all** answers in **1(b)(i) (mol)**, **2(c)(s).** *Any calculation not attempted loses this mark.* **M28**
		[Total: 21]

M21	
M22	
M23	
M24	

M25	

M26	
M27	
M28	

3 **Qualitative Analysis**

At each stage of any test, you are to record details of the following.

- colour changes seen
- the formation of any precipitate
- the solubility of such precipitates in an excess of the reagent added.

Where gases are released, they should be identified by a test, **described in the appropriate place in your observations.**

You should indicate clearly at what stage in a test a change occurs.
Marks are **not** given for chemical equations.
No additional tests for ions present should be attempted.

If any solution is warmed, a boiling tube MUST be used.

Rinse and reuse test-tubes and boiling tubes where possible.

Where reagents are selected for use in a test, the name or correct formula of the element or compound must be given.

Question 3 consists of two tasks.

In the first task, you are to explore the chemistry of some compounds of an unknown transition element **W** and determine its identities.

FA 5 is a solid sample of a common dioxide of the unknown transition element **W**,
FA 6 is dilute sulfuric acid, H_2SO_4,
FA 7 is a solid sample of sodium ethanedioate, $Na_2C_2O_4$,
FA 8 is a solution of pure compound **X**, which is the product formed in **(a)(i)**.

(a)	**(i)**	Test	Observations
		Transfer all of the solid sample of **FA 7** into a small conical flask. Add 25 cm^3 of **FA 6** to this flask.	
		Gently heat the flask until the temperature of the mixture reaches about 60 °C.	White solid $Na_2C_2O_4$ dissolves (completely). [/]
		Swirl the mixture carefully. Place the flask on the heat proof mat.	
		Using a spatula, add **FA 5** to the mixture in small portions. Between each addition, stir the mixture carefully with the thermometer and observe any changes in the temperature of the mixture.	Effervescence/ bubbles after each addition. [/] $C_2O_4^{2-} \rightarrow 2CO_2 + 2e$ Gas produced white ppt in $Ca(OH)_2$ [/] Temperature of mixture rises (even though no heat is applied) [/]
		Stop adding **FA 5** to the mixture when you think the reaction is complete.	Temperature rise stops/ Temperature falls / mixture starts to cool/

Filter the mixture into a boiling tube and leave the filtrate to stand. The filtrate is compound **X**. Retain this filtrate for use in **(a)(ii).**	effervescence much less vigorous on addition of more **FA 5**. (reaction is complete)[/] 4 - 5[/] – 3 mark 2 - 3[/] – 2 mark 1[/] – 1 mark **M29, M30, M31**

M29	
M30	
M31	

While you are waiting for (a)(i) to be complete, continue with (c). The colour of the filtrate may change on standing.

[3]

(a) **(ii)** In this part, you are to investigate the effect of the addition of aqueous sodium hydroxide, to separate portions of the filtrate from **(a)(i)** and **FA 8**.

In the space below, prepare a suitable table and in it record details of the tests performed and the observations made.

Test	Filtrate	**FA 8**
To a 1 cm depth of filtrate from **(a)(i)**in a test tube, add **NaOH(aq) (dropwise),** with shaking, until in **excess**.	A light brown ppt is formed and the ppt is insoluble in excess NaOH(aq) [/]. On standing, the ppt turns brown. [/]	A off-white ppt is formed and the ppt is insoluble in excess NaOH(aq) [/]. On standing, the ppt turns brown. [/]
	$Mn^{2+} + 2OH^{-} \rightarrow Mn(OH)_2$ $Mn(OH)_2 \rightarrow Mn(OH)_3$	

[3]

M32	
M33	
M34	

Both procedure 1 mark (Students can combine both procedure into one) The procedure should describe the addition of a **small volume**/ (dropwise addition), and the addition of an **excess**, of NaOH (aq), both with shaking, to separate samples. **M32**	2[/] – **M33** 4[/] – **M33, M34**

(b) **(i)** Give **two** conclusions you can draw about the nature of the reaction occurring in **(a)(i).**

In each case, support your conclusion by referring to your observations.

Conclusion **1**………………………………………………………………………...

Evidence………………………………………………………………………….

…………………………………………………………………………………….

…………………………………………………………………………………………

Conclusion **2**……………………………………………………………………………

Evidence………………………………………………………………………………

…………………………………………………………………………………………

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

M35	
M36	

Conclusion 1: the reaction is exothermic.
Evidence: the temperature increased, (without further heating), as **FA 5** was added. **M35**

Conclusion 2: It is a redox reaction
Evidence: Positive limewater test shows that CO_2 is evolved because $C_2O_4^{2-}$ is oxidised (by **FA 5**) **M36**

(ii) Explain why you decided to stop the addition of **FA 5** at the point you chose in **(a)(i)**.

You should support your answer by referring to your observations.

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

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

Either a convincing explanation based on the cessation of effervescence/bubbles (on addition of more **FA 5)**

OR

A convincing explanation based on the temperature stops rising/starts to fall/remain constant (on addition of more **FA 5) M37**

(iii) Consider your observations in **(a)(ii).**

Identify the transition metal ion formed in **(a)(i)** and suggest an explanation for the differences between your observations when you added aqueous sodium hydroxide to the filtrate from **(a)(i)**, and to **FA 8**.

Ion present is ……………………………………..

Explanation for difference ………………………………………………………………

M37

……………………………………………………………………………………

…………………………………………………………………………………… [1]

Ion present is Mn^{2+}

Some Mn^{2+} in the filtrate is partially oxidised on standing/ in air (to Mn^{3+}, hence resulting in formation of $Mn(OH)_3$.) **M38**

(iv) In **(a)(i)**, the reaction between **FA 5** and **FA 7** occurs under acidic conditions.

Write an ionic equation for this reaction. Use the letter '**W**' to represent the transition metal in this equation.

M38

…………………………………………………………………………………… [1]

$\mathbf{W}O_2(s) + 4H^+(aq) + C_2O_4^{2-}(aq) \rightarrow \mathbf{W}^{2+}(aq) + 2H_2O(l) + 2CO_2(g)$

Accept:
$2\mathbf{W}O_2(s) + 8H^+(aq) + C_2O_4^{2-}(aq) \rightarrow 2\mathbf{W}^{3+}(aq) + 4H_2O(l) + 2CO_2(g)$ **M39**

M39

In the second task, you are to perform a series of test to deduce the structure of the unknown hydrocarbon, **FA 9**.

FA 9 is a simple hydrocarbon compound,
FA 10 is bromine water.

		Test	observations
(c)	**(i)**	Place 5 cm^3 of aqueous sodium hydroxide in a test-tube. Add **1 drop** of **FA 9** to this test-tube. Add aqueous potassium manganate(VII), dropwise with shaking, until no further change is seen. Do not exceed 15 drops.	(Purple KMnO4 decolourises) Solution turns green/ blue green [/] Colour deepens as more drops added. [/]
		Note: Eventually, this reaction will produce a brown MnO_2 precipitate. There is no need for you to wait for this to happen.	
	(ii)	Place 5 cm^3 of dilute sulfuric acid in a test–tube. Add **1 drop** of **FA 9** to this test–tube. Add aqueous potassium manganate(VII), dropwise with shaking, until no further change is seen. Do not exceed 15 drops.	Purple **FA 6** decolourise. [/] $MnO_4^- + 8H^+ + 5e \rightarrow Mn^{2+} + 4H_2O$ Colourless solution turns progressively darker brown. [/]
	(iii)	Place 5 cm^3 of water in a test–tube. Add **1 drop** of **FA 9** to this test–tube. Add **FA 10,** dropwise with shaking, until no further change is seen.	Brown bromine water decolourise. (Brown solution turns yellow) [/] 5[/] – 3 marks 3 -4 [/] – 2 marks 1 -2 [/] – 1 mark **M40, M41, M42**
			[3]

Conclusions

(d) Consider the identities of the Mn-containing reactant and eventual product in **(c)(i).**

Suggest a value for the oxidation number of Mn in the coloured ion produced in **(c)(i).** Explain your reasoning.

Oxidation number of Mn……………………………….

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

		…………………………………………………………………………………… ……………………………………………………………………………… [1]	**M43**
		Allow oxidation numbers of +5 or +6 And An explanation along the lines of - The oxidation numbers of Mn in MnO_4^- and in MnO_2 are +7 and +4 respectively. - So, as the reaction in **(c)(i)** involves a change of oxidation number from +7 to +4, The oxidation number of the coloured ion will be between these value. **M43**	

(e) Compound **Y** is the main organic product in **(c)(i)**, when **FA 9** reacts with $KMnO_4$ under alkaline conditions. The molecular formula of **Y** is $C_6H_{12}O_2$.

(i) Deduce the molecular formula of **FA 9**.

Explain your deduction. Your explanation must be supported by evidence from your observations in **(c)**.

Molecular formula of **FA 9** is ....

Explanation..

....

....

....

.... [2]

M44	
M45	

Explanations based on the following points

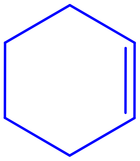
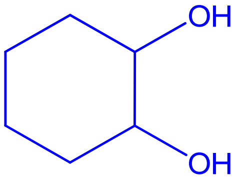
Molecular formula: C_6H_{10} **M44**

- Br_2(aq) decolourised, so C = C present
- Cold alkaline MnO_4^- oxidises C=C to C(OH) – C(OH)/1,2-diol
- Only two O atoms in molecular formula of **Y**, so only one C =C bond.
- So **FA 9** is $C_6H_{12}O_2 - 2 \times OH = C_6H_{10}$

M45 any 2 points mentioned

(ii) Draw the structural formulae for **FA 9** and compound **Y**.

Explain how you deduced the structure of **FA 9**.

Structure of **FA 9**	Structure of **Y**
	

				M46 for both structure correctly drawn
			Explanation…………………………………………………………………… …………………………………………………………………………………… …………………………………………………………………………………… …………………………………………………………………………………… …………………………………………………………………………………… [2]	
			Explanation along the lines of • C_6H_{10} has two double bond equivalents • There is only one C=C bond in the molecule So the compound must be cyclic. **M47(idea along this line)**	

M46	
M47	

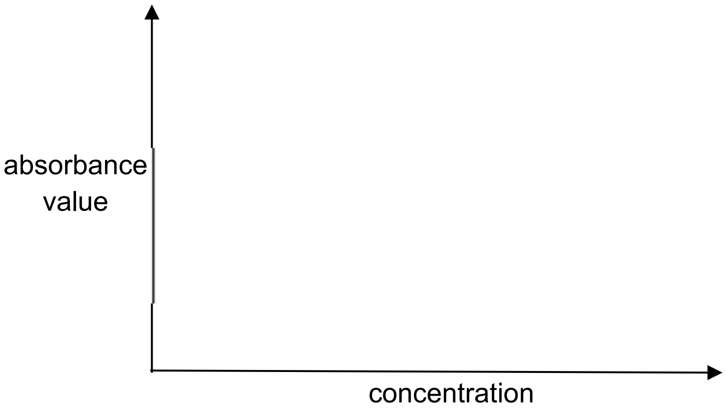
(f) **Planning**

Many transition metal complex ions are coloured. It is possible to use this property to determine the concentration of a solution of a coloured complex ion. A few cm^3 of the solution is placed inside a machine, known as a spectrometer. This machine measures the amount of light that is absorbed when a specific wavelength of visible light is shone through a coloured solution. It does this by comparing the amount of light passing through the sample with the amount of light passing through the pure solvent. The amount of light absorbed is expressed as an *absorbance value.* The more concentrated the solution, the higher the absorbance value, i.e., the absorbance value is directly proportional to the concentration of the solution.

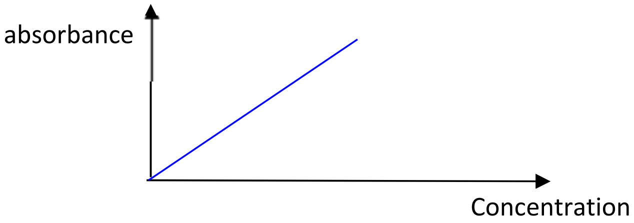
This technique can be used to determine the concentration of a solution of aqueous $\mathbf{W}O_4^-$. A series of known, but different, concentration of solution containing $\mathbf{W}O_4^-$ is prepared. A spectrometer is used to measure the absorbance of each solution. A graph of absorbance against concentration is then plotted. This graph is known as a calibration line.

The experiment is then repeated using a solution of unknown concentration. By comparing the absorbance of this solution with the calibration line, the concentration of $\mathbf{W}O_4^-$ in the unknown solution can be determined.

(i) Sketch the calibration line for the graph of absorbance against concentration that you would expect to obtain.



[1] **M48**



Correct graph **M48**

(ii) Using the information given above, you are required to write a plan to determine the concentration of **W**O_4^- in a solution of **Z**.

You may assume that you are provided with:
- solution **Z**, of unknown **W**O_4^- concentration less than 2 mol dm^{-3};
- a standard solution containing 5.00 mol dm^{-3} of **W**O_4^-;
- access to a spectrometer and instructions for its use;
- graph paper;
- the apparatus and chemicals normally found in a school or college laboratory.

Your plan should include details of:
- the preparation of 100.0 cm^3 of 2.00 mol dm^{-3} aqueous **W**O_4^-;
- the preparation of a suitable range of diluted solutions of accurate concentrations;
- an outline of how the results would be obtained;
- how the calibration line would be used to determine the concentration of **W**O_4^- in solution **Z**.

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.... [7]

M49	
M50	
M51	
M52	
M53	
M54	
M55	

Preparation of 100.0 cm^3 of 2.00 mol dm^{-3} of aqueous **WO_4^-**

Amount of **WO_4^-** in 100cm^3 of 2.00 mol dm^{-3} **WO_4^-** solution
= (100/1000) x 2.00
= 0.200 mol

Volume of 5.00 mol dm^{-3} standard solution required
= 0.2 / 5.00 = 0.04 dm^3 = 40 cm^3

1. Fill the burette with a standard solution containing 5.00 mol dm^{-3} of **WO_4^-**.
2. Run 40.00 cm^3 of the solution into a 100cm^3 volumetric flask.
3. Make up to the mark with deionised water.
4. Stopper, invert and shake the volumetric flask to obtain a homogeneous solution. Label this solution **Q**.

Preparation of a suitable range of diluted solutions

No	Volume of solution Y/ cm^3	Volume of distilled water / cm^3	Concentration of **WO_4^-** prepared/ mol dm^{-3}	Absorban A
1	20	0	2.00	
2	15	5	1.50	
3	10	10	1.00	
4	5	15	0.50	
5	0	20		

Table 2

5. To prepare 1.50 mol dm^{-3} solution, using a burette, measure out 15.00 cm^3 of solution **Q** into a 50 cm^3 beaker.
6. Using another burette, measure out 5.00 cm^3 of deionised water into the same beaker. Stir/ swirl the beaker to obtain a homogeneous solution.
7. Repeat step 5 and 6 with different volumes of solution Y and distilled water to prepare the stated concentrations of dilute solution.

Outline of how results would be obtained

8. Use the spectrometer to measure the absorbance of each of the diluted solutions prepared and record the absorbance in Table 2.
9. Plot a graph of the absorbance against concentration.
10. Draw the calibration line. (Best fit- linear line going through the origin)

Use of calibration line to determine unknown concentration

11. Using the spectrometer, measure and record absorbance of **WO_4^-** from solution **Z**.
12. Using the graph drawn in step 10, read off the corresponding concentration of **WO_4^-** from the calibration line.

Correct volume (40 cm^3) of 5.00 mol dm^{-3} solution used (BOD if student did not show pre-calculation) **M49**

- **40cm^3 if it is 100cm^3 volumetric flask**
- **100cm^3 if it is 250cm^3 volumetric flask(student must mention in the procedure that they will pour out 100cm^3)**

			Correct procedure for preparing 2.00 mol dm^{-3} solution using a volumetric flask (top up to the mark; stopper; invert and shake) **M50** Use of suitable apparatus with stated capacity **M51** - Burette for measuring out $40cm^3$ - Volumetric flask - Mention of appropriate apparatus for dilution Correct dilution concept for preparing diluted solutions (ignore use of less accurate apparatus; allow logical, scientifically – sound preparation of concentrations) **M52** - Using solution of known concentration Suitable concentration of diluted solutions (at least 3 more solutions apart from the 2.00 mol dm^{-3} solution prepared, need not prepare 0 mol dm^{-3}; table not required) Students need to calculate out the concentration in their planning. **M53** Measurement of absorbance of various diluted solutions using spectrometer, and plotting of graph of absorbance against concentration. **M54** Measurement of absorbance of solution **Z** and use of the absorbance value to read off the corresponding concentration in the calibration graph (award if students convey the idea in a graphical diagram) **M55**
			[Total: 21]

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 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 A*l* foil
nitrite, NO_2^- (aq)	NH_3 liberated on heating with OH^-(aq) and A*l* 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

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Please detach the insert from the question paper for use in **Question 2**.

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