TEMASEK JUNIOR COLLEGE
2019 JC2 PRELIMINARY EXAMINATION
Higher 2

CHEMISTRY 9729/01

18th September 2019
1 hour

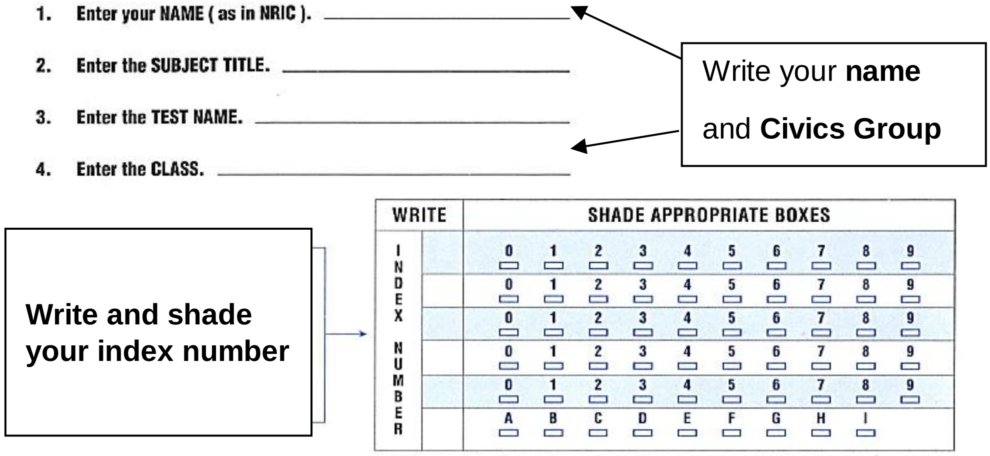
Additional Materials: Multiple Choice Answer Sheet (OMS)
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write in soft pencil.

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

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



1. Enter your NAME (as in NRIC). ____________
2. Enter the SUBJECT TITLE. ____________
3. Enter the TEST NAME. ____________
4. Enter the CLASS. ____________

Write your **name** and **Civics Group**

Write and shade your index number

	WRITE	SHADE APPROPRIATE BOXES									
INDEX NUMBER		0 ▭	1 ▭	2 ▭	3 ▭	4 ▭	5 ▭	6 ▭	7 ▭	8 ▭	9 ▭
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		A ▭	B ▭	C ▭	D ▭	E ▭	F ▭	G ▭	H ▭	I ▭	

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

Read the instructions on the Answer Sheet very carefully.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer.
Any rough working should be done in this booklet.
The use of an approved scientific calculator is expected, where appropriate.

This document consists of **16** printed pages including the cover page.

1 The number of neutrons and nucleons for five particles are shown below. The letters of the particles do not correspond to the identity of the elements in the Periodic Table.

Particle	Neutrons	Nucleons
U	16	33
V^-	18	35
S^{2-}	16	32
T^{2+}	17	34
Q^{3-}	16	31

Which of the following sets consists of particles that are isoelectronic?

A U, S^{2-}, T^{2+}

B U, S^{2-}, Q^{3-}

C V^-, S^{2-}, Q^{3-}

D V^-, T^{2+}, Q^{3-}

2 Methane was burned in an incorrectly adjusted burner. The methane was converted into a mixture of carbon dioxide and carbon monoxide in the ratio of 95 : 5, together with water vapour.

What will be the volume of oxygen consumed when x dm^3 of methane is burned?

A $(x - \frac{0.05x}{2})$ dm^3

B $(x - 0.05x)$ dm^3

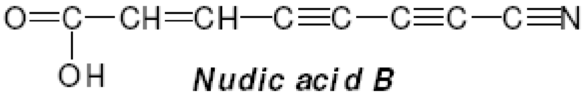
C $(2x - \frac{0.05x}{2})$ dm^3

D $(2x - 0.05x)$ dm^3

3 Which of the following particles contains the most number of unpaired electrons?

A	Na	**B**	P^{3-}
C	V	**D**	Mn^{2+}

4 *Nudic acid B* is an acidic antibiotic isolated from the culture medium of the basidiomycete *Tricholoma nudum* (Bull.) Fr.



$\mathrm{O{=}\underset{\underset{OH}{|}}{C}{-}CH{=}CH{-}C{\equiv}C{-}C{\equiv}C{-}C{\equiv}N}$

Nudic acid B

What is the number of σ and π bonds present in the molecule?

	σ	π
A	16	5
B	13	8
C	13	5
D	10	8

5 A pair of compounds have the following properties as described below.

(i) The first compound has a larger bond angle about the central atom than the second compound.

(ii) The second compound is more polar than the first compound.

Which pair of compounds fit the description above?

A $\mathrm{BC}l_3$, $\mathrm{C}l\mathrm{O_2}^{-}$

B $\mathrm{IC}l_2^{-}$, CO_2

C HCN, XeF_4

D $\mathrm{C}l\mathrm{O_2}^{-}$, CO_2

6 In which of the following pairs is the melting point of the first member lower than that of the second member?

I diamond, silicon
II H_2O, NH_3
III $SiCl_4$, Al_2O_3
IV Br_2, ICl

A I, II, III, IV

B I, III, IV

C III, IV

D I only

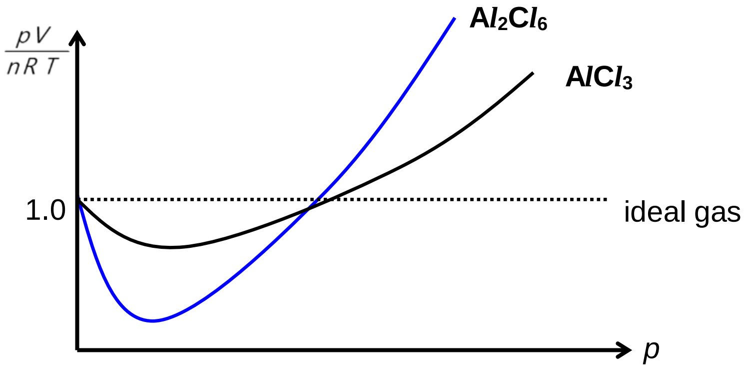
7 Gaseous Al_2Cl_6 decomposes into gaseous $AlCl_3$ in a 250 cm^3 closed reaction vessel maintained at a temperature of 500 K. The system reaches equilibrium with a total pressure of 1.16×10^5 Pa.

$$Al_2Cl_6(g) \rightleftharpoons 2AlCl_3(g)$$

The average M_r of the equilibrium gas mixture in the vessel is found to be 214.9.

Which of the following statements are correct?

1 The bond angle in both molecules is 120°.
2 The mass of the gaseous mixture inside the reaction vessel is 1.50 g.
3 The following graphs depicts the correct behaviour of the two gases under standard conditions.



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

8 The following information is given.

$2Cr(s) + \frac{3}{2}O_2(g) \longrightarrow Cr_2O_3(s)$ $\Delta H = -1120$ kJ mol^{-1}

$3C(s) + Cr_2O_3(s) \longrightarrow 2Cr(s) + 3CO(g)$ $\Delta H = +790$ kJ mol^{-1}

What is the standard enthalpy change of the following reaction, in kJ mol^{-1}?

$$2C(s) + O_2(g) \longrightarrow 2CO(g)$$

A −110

B −220

C −637

D −1273

9 In this question, the symbol ‘<’ means ‘less positive than’ or ‘more negative than’.

Both mercury(I) sulfate, Hg_2SO_4, and cadmium(I) sulfate, Cd_2SO_4, are odourless white crystalline solids. Hg_2SO_4 is sparingly soluble while Cd_2SO_4 is very soluble in water. Both sulfates are used in industry for electrochemical and electrolytic processes.

The following data is provided:
$\Delta H_{latt}^{\ominus}$ (Hg_2SO_4) = –2127 kJ mol^{-1}
$\Delta H_{hyd}^{\ominus}$ (Hg^+) = –625 kJ mol^{-1}
$\Delta H_{hyd}^{\ominus}$ (SO_4^{2-}) = –1160 kJ mol^{-1}

Which of the following statements are correct?

1 $\Delta H_{soln}^{\ominus}$ of Hg_2SO_4 equals to a magnitude of 283 kJ mol^{-1}.
2 $\Delta H_{latt}^{\ominus}$ of Hg_2SO_4 is less exothermic than that of Cd_2SO_4.
3 $\Delta G_{soln}^{\ominus}$ of Hg_2SO_4 is < $\Delta G_{soln}^{\ominus}$ of Cd_2SO_4

A 1 only

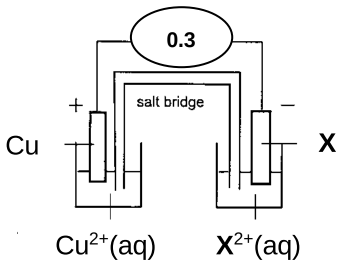
B 1 and 2 only

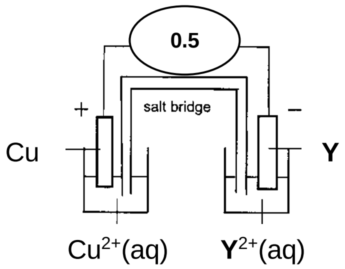
C 2 and 3 only

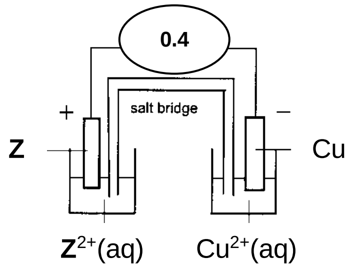
D 1,2 and 3 only

10 Three electrochemical cells are set up as shown below. The *e.m.f* in volts at standard conditions is shown on each voltmeter. The concentration of all the solutions are

1 mol dm^{-3}. **X**, **Y** and **Z** are metal electrodes.







The *e.m.f* indicates the order of reactivity of the metals.

The order of the strongest to the weakest oxidising agent is :

A Z^{2+}, Cu^{2+}, X^{2+}, Y^{2+}

B Y^{2+}, X^{2+}, Cu^{2+}, Z^{2+}

C Cu^{2+}, Z^{2+}, Y^{2+}, X^{2+}

D Z, Cu, X, Y

11 The standard reduction potentials, $E^{\ominus}$, for the electrode reactions NO_3^-/NH_4^+ and NO_3^-/NO_2 are +0.87 V and +0.81 V respectively.

Dilute HC*l* was added to separate beakers containing 1 mol dm^{-3} NO_3^-/NH_4^+ and 1 mol dm^{-3} NO_3^-/NO_2 until a pH of 5 was achieved.

Which of the following statements are correct for the two beakers?

1 The reducing abilities of NH_4^+ and NO_2 decreases.

2 NO_2 is a weaker reducing agent than NH_4^+ at pH 5.

3 The oxidising ability of NO_3^- decreases.

A 1 only

B 3 only

C 1 and 2 only

D 1,2 and 3 only

12 Excess marble chips are added to 30 cm^3 of 1 mol dm^{-3} of nitric acid at room temperature until no further reaction occurs.

How would the experiment be different if it is now repeated with 50 cm^3 of 0.5 mol dm^{-3} of nitric acid at the same temperature?

	Rate of reaction	Amount of products
A	Faster	Lesser
B	Faster	More
C	Slower	More
D	Slower	Lesser

13 CO and H_2 were placed in a reactor fitted with a movable piston and the following equilibrium is established.

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$

Which of the following best explains what happens when some argon gas is added to the mixture at constant volume and temperature?

A The position of equilibrium will not shift as the partial pressure of all gaseous reactants and products remain constant.

B The position of equilibrium will not shift as argon does not react with any substance in the mixture.

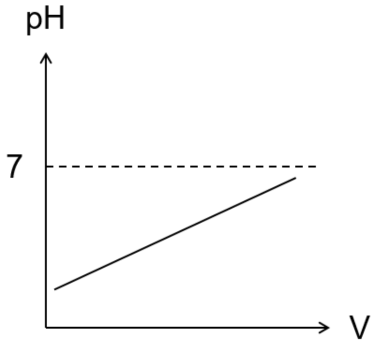
C The position of equilibrium will shift to the right to decrease total pressure.

D The position of equilibrium will shift to the left to increase total pressure.

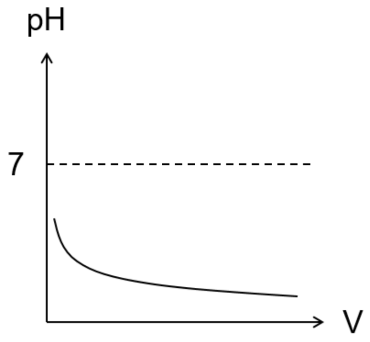
14 A solution of 1 mol dm^{-3} of weak acid is diluted with large excess of water at 25 ^{o}C.

Which of the following graph correctly shows how the pH of the solution varies with volume of mixture, V?

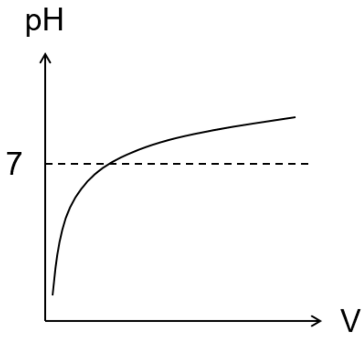
A



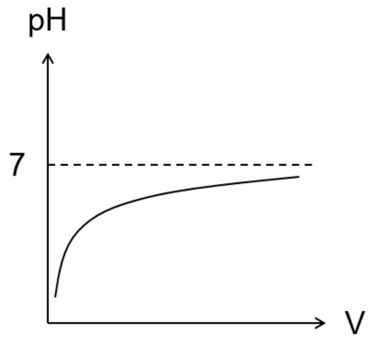
B



C



D



15 Zn^{2+} ions combine with hexacyanoferrate(III), $[Fe(CN)_6]^{3-}$, to produce a sparingly soluble salt, $Zn_3[Fe(CN)_6]_2$.

Given than the K$_{sp}$ value for the salt is **W**, what is the concentration of the anion at equilibrium?

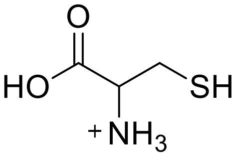
A $\sqrt[3]{\frac{\mathbf{W}}{108}}$

B $\sqrt[5]{\frac{\mathbf{W}}{108}}$

C $\sqrt[3]{\frac{8\mathbf{W}}{27}}$

D $\sqrt[5]{\frac{8\mathbf{W}}{27}}$

16 A solution of cysteine in its *fully protonated* form is titrated against a standard solution of potassium hydroxide. The structure of *fully protonated* cysteine is shown below and its 3 pK_a values are 1.9, 8.1 and 10.3.



Which of the following indicator(s) can be used to detect the isoelectric point of the cysteine?

	Indicator	Working range
1	Bromocresol Green	3.7 – 5.7
2	Methyl Red	4.1 – 6.1
3	Bromothymol Blue	6.0 – 8.0
4	Phenol Red	6.9 – 8.9

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

17 **X**, **Y** and **Z** are elements in Period 3 of the Periodic Table.

The results of some experiments carried out on respective chlorides and oxides of these elements are shown in the table below.

Element	Addition of $H_2O(l)$ to the oxides	Colour of universal indicator upon addition of $H_2O(l)$ to chlorides	Addition of HC*l* to the oxides
X	no reaction	orange	forms chloride salt
Y	forms hydroxide	green	forms chloride salt
Z	no reaction	red	no reaction

Which of the following is correct?

A **X** is A*l* and **Y** is Na.

B **X** is Si and **Y** is Mg

C **Y** is A*l* and **Z** is P.

D **Y** is Na and **Z** is A*l*.

18 $CaCO_3$ decomposes at 825°C to produce CO_2 and the metal oxide.

$BaSO_4$ decomposes at 1580 °C to produce SO_2 and the metal oxide.

Which one of the following statements correctly explains the greater thermal stability of $BaSO_4$?

1 The CO_2 molecule is smaller than SO_2.

2 The CO_3^{2-} ions are more easily polarised than SO_4^{2-}.

3 The charge density of Ca^{2+} is greater than that of Ba^{2+}.

4 The lattice energy of $CaCO_3$ is more exothermic than $CaSO_4$.

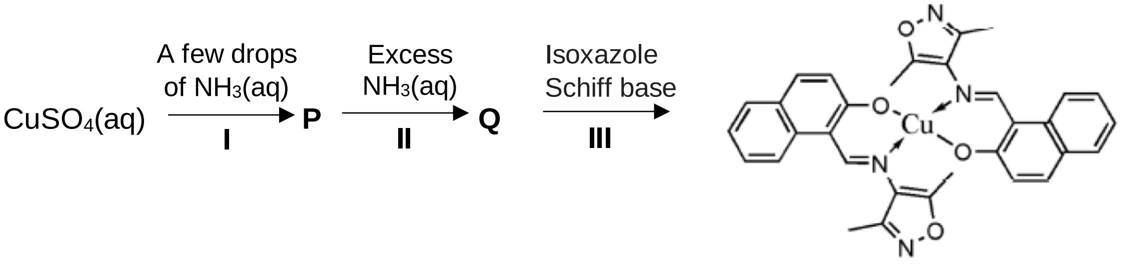
A 2 only

B 3 only

C 1 and 3 are correct.

D 2 and 4 are correct.

19 A reaction scheme starting from aqueous copper(II) sulfate solution is shown below. Both **P** and **Q** are copper-containing species.



Copper complex with Isoxazole Schiff base

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

A The copper complex with isoxazole schiff base has a coordination number of 4.

B The copper centre in the complex with isoxazole schiff base has an oxidation state of +2.

C **Q** is a deep blue solution containing $[Cu(NH_3)_4(H_2O)_2]SO_4$.

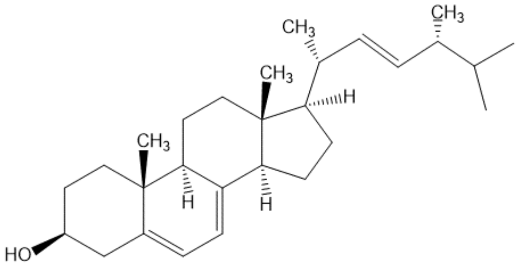
D **Q** undergoes reduction in reaction **III**.

20 An alkane **X** with the molecular formula C_4H_{10} reacts with chlorine gas in the presence of light to form two monochlorinated alkanes **Y** and **Z** in the molar ratio of 9:1.

What are the structures of **X** and **Z**?

	X	**Z**
A	$CH_3CH_2CH_2CH_3$	$CH_3CH_2CH_2CH_2Cl$
B	$CH_3CH_2CH_2CH_3$	$CH_3CH_2CHClCH_3$
C	$CH_3CH(CH_3)CH_3$	$CH_3CCl(CH_3)CH_3$
D	$CH_3CH(CH_3)CH_3$	$CH_3CH(CH_3)CH_2Cl$

21 Ergosterol is a compound present in ergot and many other fungi. A steroid alcohol, it is converted to vitamin D_2 when irradiated with ultraviolet light.



Ergosterol

How many possible stereoisomers exist for Ergosterol?

A 2^8 **B** 2^9 **C** 2^{10} **D** 2^{11}

22 A mixture of propyne and propadiene is produced as side products during the cracking of propane. Propyne exists in equilibrium with propadiene.

$$\underset{\text{Propyne}}{H\text{–}C{\equiv}C\text{–}CH_3} \rightleftharpoons \underset{\text{Propadiene}}{H_2C{=}C{=}CH_2}$$

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

A Propyne contains a σ bond formed by 1s-2sp overlap.

B Propadiene contains a π bond formed by 2p-2p overlap.

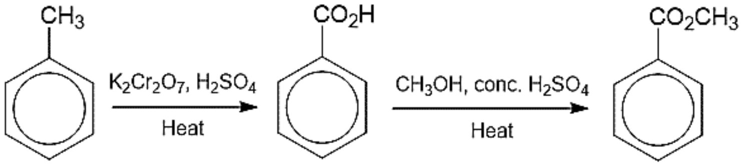
C Both propyne and propadiene contain sp hydridised carbons.

D Propyne has a longer C-C single bond compared to propane.

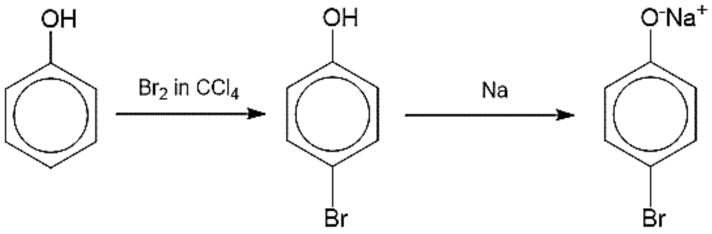
23 The reaction conditions for four different transformations are given below.

Which transformation will give the desired product?

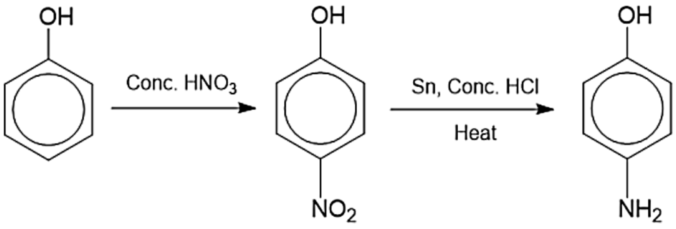
A



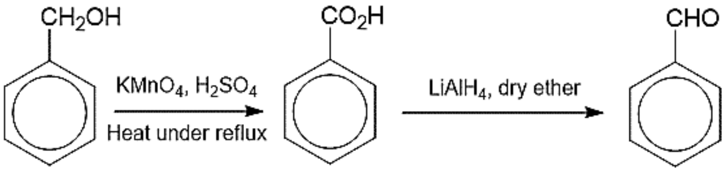
B



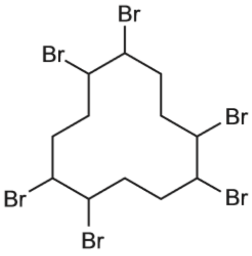
C



D



24 The primary application of hexabromocyclododecane (HBCD) is in polystyrene foam used as thermal insulation in the building industry. Usage of HBCD is under concern due to its toxicity. As HBCD has a number of possible stereoisomers, the substance poses a difficult problem for manufacture and regulation.



HBCD

Which statements about HBCD are correct?

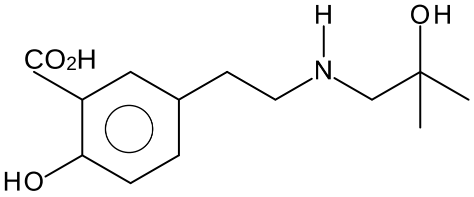
1 The stereoisomers of HBCD have similar chemical and biological properties.

2 The empirical formula of HBCD is C_2H_3Br.

3 The molecule is planar.

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

25 Compound **G** has the following structure.



Which of the statement is correct about the following reactions with 1 mole of compound **G**?

	Reagent	**Result**
A	excess sodium metal	3 moles of H_2 produced
B	hot acidified potassium dichromate(VI)	green solution was obtained
C	aqueous sodium hydroxide	anion in the product has a charge of 2-.
D	excess propanoyl chloride	2 moles of HC*l* produced

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

Reduction of **Y** with lithium aluminum hydride produces **Z** with a relative molecular mass 12 less than **Y**, i.e. M_r(**Z**) = M_r(**Y**) - 12.

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

1 $CH_2{=}CHCO_2H$

2 $CH_3CH_2COCO_2H$

3 $CH_3CH_2CONH_2$

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

27 Which of the following will **not** yield a final organic product containing deuterium? (D = ^{2}H)

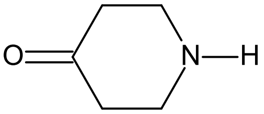
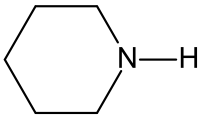
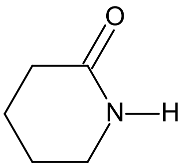
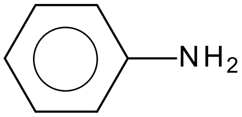
A $CH_3CH_2CH_2CHO \xrightarrow[\text{amount of NaCN}]{\text{DCN, trace}}$

B $CH_3CH_2CH_2COCl \xrightarrow{D_2O}$

C $CH_3CH_2CH_2CON(CH_3)_2 \xrightarrow[\text{heat}]{\text{DC}l\text{, } D_2O}$

D $CH_3CH_2CH_2CN \xrightarrow[\text{heat}]{\text{NaOD, } D_2O}$

28 Consider the following four compounds:

1	2	3	4
			

Which of the following shows the compounds arranged in order of increasing pK_b value?

A 3, 4, 1, 2

B 2, 1, 4, 3

C 2, 1, 3, 4

D 1, 2, 4, 3

29 A peptide contains seven amino acid residues. When it is partially hydrolysed, the following dipeptide and tripeptide fragments are produced.

gly-ser, ala-met, gly-ala-gly, ser-lys, met-gly-ala

What could be the structure of this peptide?

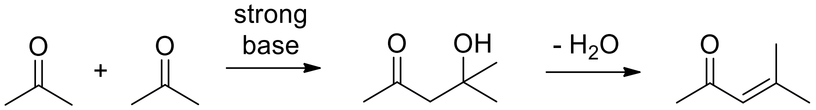
A ala-met-gly-ala-gly-ser-lys

B gly-ser-lys-ala-met-gly-ala

C gly-ala-gly-ser-lys-ala-met

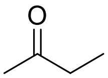
D met-gly-ala-gly-ser-lys-ala

30 The aldol condensation reaction is commonly used in synthetic organic chemistry to obtain a carbonyl compound. In the first step, a carbonyl compound reacts with a strong base at the α carbon to form a nucleophile.

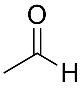


unsaturated carbonyl compound

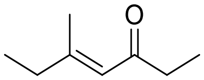
Which of the following is **not** a possible product when butanone and ethanal reacts with a strong base?

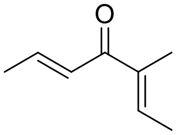


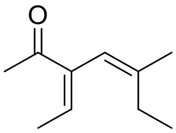
butanone

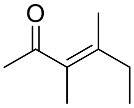


ethanal

A 

B 

C 

D 

2019 TJC JC2 H2 Chemistry Prelim MCQ Worked Solutions

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

Question 1 **Answer: C**

Particle	Neutron	Nucleon	Proton	Electron
U	16	33	17	17
V^-	18	35	17	18
S^{2-}	16	32	16	18
T^{2+}	17	34	17	15
Q^{3-}	16	31	15	18

Question 2 **Answer: C**

$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$
x 0.95x
$CH_4 + 3/2\ O_2 \longrightarrow CO + 2H_2O$
0.05x

If combustion is complete, x dm^3 CH_4 will require 2x dm^3 O_2.
Combustion of 1 mol CH_4 to form CO, requires 3/2 mol O_2 ie ½ mol O_2 less than complete combustion.
To obtain 0.05x mol CO will need 0.05x/2 mol less O_2.
Amt of O_2 needed for incomplete combustion = 2x – 0.05x/2

Or
Volume of methane burnt = y dm^3
5% of methane is burnt to give CO and the remaining 95% is burnt to give CO_2
Vol of methane burnt to give CO = 0.05y
Vol of methane burnt to give CO_2 = (1-0.05)y

	CH_4	+	$2O_2$	→	CO_2	+	$2H_2O$
Volume used	(1-0.05)y		2(1-0.05)y				

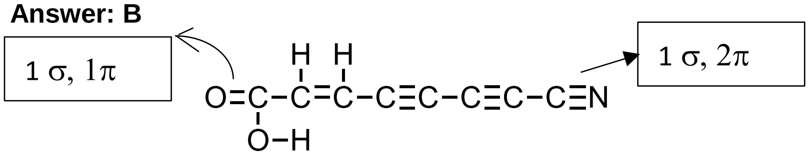
	CH_4	+	$3/2O_2$	→	CO	+	$2H_2O$
Volume used	0.05y		3/2(0.05y)				

Vol of O_2 used = 2(1-0.05)y + 3/2(0.05y)
= 2y – 2(0.05)y + 3/2(0.05y)
= 2y – ½ (0.05y)

Question 3 **Answer: D**

Na : $[Ne]3s^1$ (1 unpaired electron)
P^{3-} : [Ar] (0 unpaired electron)
V : $[Ar]3d^34s^2$ (3 unpaired electron)
Mn^{2+}: $[Ar]3d^5$ (5 unpaired electron)

Question 4 **Answer: B**



Question 5 **Answer: A**

ICl_2^- : 2BP + 3 LP, shape linear, Bond angle 180^0, non-polar
CO_2 : 2 BP, shape linear, Bond angle 180^0 , non-polar
BCl_3 : 3 BP shape trigonal planar, Bond angle 120^0 , non-polar
ClO_2^- : 2 BP + 2 LP, shape bent, Bond angle <109.5^0 , polar
HCN : 2 BP, shape linear, Bond angle 180^0, polar
XeF_4 : 4 BP + 2 LP, shape square planar, Bond angle 90^0, non-polar

Question 6 **Answer: C**

I Both diamond and silicon have giant molecular structures. The atomic radius of C is smaller than Si. C-C bond length is shorter than Si-Si bond. Diamond has a higher mp than silicon as more energy is needed to break the stronger C-C bonds.

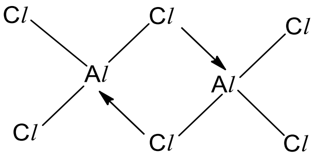
II H_2O is able to form more hydrogen bonds on average compared to NH_3 as it has 2 lone pair of electrons on O.

III $SiCl_4$ has a simple molecular structure and Al_2O_3 has a giant ionic structure. The id-id attractions between $SiCl_4$ molecules is weaker than the strong ionic bonds in Al_2O_3.

IV Both Br_2 and ICl have similar M_r. The id-id attractions between Br_2 molecules is weaker than the pd-pd attractions between ICl molecules.

Question 7 **Answer: C**

1 Structure of dimer Al_2Cl_6



Shape of $AlCl_3$ = Trigonal planar hence bond angle is 120^o.

Shape of Al_2Cl_6 = Tetrahedral about each Al atom hence bond angle is not 120^o.

2 Using ideal gas equation, pV = nRT
pV = (m/M) RT where M = molar mass
$(1.16 \times 10^5)(250 \times 10^{-6}) = (x / 214.9)(8.31)(500)$
X = 1.50 g

3 Size of electron cloud for : Al_2Cl_6 > $AlCl_3$
Extent of distortion of electron cloud for: Al_2Cl_6 > $AlCl_3$
Strength of intermolecular id-id : Al_2Cl_6 > $AlCl_3$
Deviation from ideality for: Al_2Cl_6 > $AlCl_3$

Question 8 **Answer: B**

$3C(s) + Cr_2O_3(s) \longrightarrow 2Cr(s) + 3CO(g)$ $\Delta H = +790$ kJ mol^{-1}

$\Delta H_{rxn} = \sum\Delta H_f(\text{products}) - \sum\Delta H_f(\text{reactants})$

$+790 = 3\,\Delta H_f(CO) - \Delta H_f\,(Cr_2O_3)$

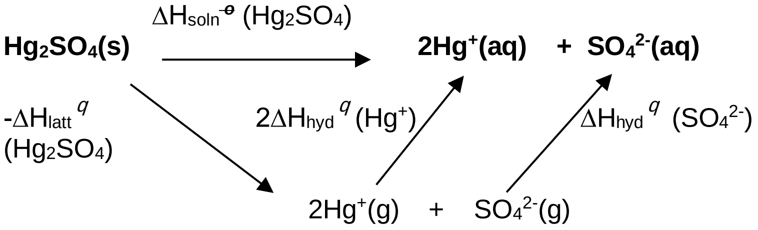
$+790 = 3\,\Delta H_f(CO) - (-1120)$

$\Delta H_f(CO) = (+790 - 1120) / 3 =$ **–110 kJ mol^{-1}**

By definition, $C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g)$ $\Delta H_f(CO) = -110$ kJ mol^{-1}
Hence, $2C(s) + O_2(g) \longrightarrow 2CO(g)$ $2\,\Delta H_f(CO) = -220$ kJ mol^{-1}

Question 9 **Answer: B**

Energy cycle for $\Delta H_{soln}{}^{q}$ Hg_2SO_4



By Hess' law:

$$\Delta H_{soln}{}^{q}\ (Hg_2SO_4) = -\Delta H_{latt}{}^{q}\ (Hg_2SO_4) + 2\Delta H_{hyd}{}^{q}\ (Hg^+) + \Delta H_{hyd}{}^{q}\ (SO_4^{2-})$$
$$= -(-2127) + 2(-625) + (-1160)$$
$$= \underline{\mathbf{-\ 283\ kJ\ mol^{-1}}}$$

Since the calculated value of $\Delta H_{soln}{}^{q}$ (Hg_2SO_4) is a negative value at r.t.p., it means that:

1. **Correct.** Magnitude is 283 kJ mol^{-1}
2. **Correct.** $\Delta H_{latt}{}^{q} \propto \frac{q_+ q_-}{r_+ + r_-}$, since <u>Hg^+ has a bigger ionic radius as compared to Cd^+</u> (q^+, q^-, r^- same), $\Delta H_{latt}{}^{q}$ of Hg_2SO_4 is less exothermic than that of Cd_2SO_4.
3. **Incorrect.** <u>$\Delta G_{soln}{}^{\ominus}$ of Hg_2SO_4 is less negative than $\Delta G_{soln}{}^{\ominus}$ of Cd_2SO_4</u> since Hg_2SO_4 is less soluble than Cd_2SO_4.

Question 10 **Answer: A**

$E^{q}{}_{cell} = E^{q}{}_{red} - E^{q}{}_{oxi}$
$0.3\ V = E^{\ominus}{}_{Cu^{2+}/Cu} - E^{\ominus}{}_{X^{2+}/X}$
$0.5\ V = E^{\ominus}{}_{Cu^{2+}/Cu}{}^{q} - E^{\ominus}{}_{Y^{2+}/Y}$
$0.4\ V = E^{\ominus}{}_{Z^{2+}/Z} - E^{\ominus}{}_{Cu^{2+}/Cu}{}^{q}$

From the data in the terms of increasing positive value: $E^{\ominus}{}_{Z^{2+}/Z} > E^{\ominus}{}_{Cu^{2+}/Cu} > E^{\ominus}{}_{X^{2+}/X} > E^{\ominus}{}_{Y^{2+}/Y}$
Tendency to be reduced for : $\mathbf{Z^{2+}}$, Cu^{2+}, $\mathbf{X^{2+}}$, $\mathbf{Y^{2+}}$
Thus, the strongest to the weakest oxidising agents is $\mathbf{Z^{2+}}$, Cu^{2+}, $\mathbf{X^{2+}}$, $\mathbf{Y^{2+}}$

Question 11 **Answer: C**

$NO_3^- + 10H^+\ 8e \rightleftharpoons \mathbf{NH_4^+} + 3H_2O$ $E^{q} = 0.87$ V -- (1)
$NO_3^- + 2H^+ + e \rightleftharpoons \mathbf{NO_2} + H_2O$ $E^{q} = 0.81$ V --(2)

As $[H^+]$ increases. By *Le Chatelier's Principle*, the <u>position of both equilibria shifts to the right to decrease $[H^+]$, favouring reduction</u>

Oxidising ability of NO_3^- <u>increases</u> while <u>reducing abilities of NO_2 and NH_4^+ decreases</u>.

Since for eqm (2), <u>a lesser number of moles of H^+ is required for one mole of NO_3^- to be reduced, there is greater tendency for equilibrium (2) to shift to the right hence backward reaction is less favoured. Hence, NO_2 is a weaker reducing agent</u> where $[H^+] = 10^{-5}$ mol dm^{-3} < standard condition of 1 mol dm^{-3}).

Question 12 **Answer: D**

Rate would be slower as concentration of nitric acid is lower. Amount of products would be lesser as nitric acid is the limiting agent and there are less amount of nitric acid used in the 2nd scenario (0.025 mol vs 0.030 mol)

Question 13 **Answer: A**

Total pressure increases at constant volume but *partial pressure* of individual product and reactant remains constant. So position of equilibrium will NOT shift at all.

Question 14 **Answer: D**

$[H^+] = \sqrt{K_a C}$
When the acid is diluted, the conc of acid drops, so $[H^+]$ will drop too → pH increases, following a logarithm function since pH = $-\lg[H^+]$.

However at infinitely dilute condition, $[H^+]_{overall} = [H^+]_{acid} + [H^+]_{water}$, where $[H^+]_{acid} << [H^+]_{water}$, so $[H^+]_{overall} \approx [H^+]_{water} = 10^{-7}$ mol dm^{-3} at 25 °C. So the pH at infinitely dilute condition will reach a constant value of 7.

Question 15 **Answer: D**

$Zn_3[Fe(CN)_6]_2 \rightleftharpoons 3Zn^{2+} + 2[Fe(CN)_6]^{3-}$

At eqm, there are 3y mol of Zn^{2+} and 2y mol of $[Fe(CN)_6]^{3-}$.

$K_{sp} = [Zn^{2+}]^3 [Fe(CN)_6{}^{3-}]^2$

$= (3y)^3(2y)^2 = 108y^5 = \mathbf{W}$

$y = \sqrt[5]{\frac{\mathbf{W}}{108}}$

$[Fe(CN)_6{}^{3-}] = 2 \times \sqrt[5]{\frac{\mathbf{W}}{108}} = \sqrt[5]{\frac{8\mathbf{W}}{27}}$

Question 16 **Answer: A**

pK_a value of –COOH = 1.9, –SH = 8.1 and $-NH_3^+$ = 10.3.
At isoelectric point, only $-COO^-$ and $-NH_3^+$ exist, so pI = ½ (1.9+8.1) = 5.0

Hence only Bromocresol Green and Methyl Red can detect the isoelectric point of cysteine as the pI is within the working range of both indicators.

Question 17 **Answer: A**

X is A*l*:
- Al_2O_3 has no reaction with water due to high lattice energy.
- $AlCl_3$ undergoes hydrolysis with water to give an acidic solution of pH 3
- Al_2O_3, an amphoteric oxide, reacts with HC*l* to form $AlCl_3$ (chloride salt) and water.

Y is Na
- Na_2O reacts with water to forms NaOH (formation of hydroxide).
- NaC*l* undergoes only hydration with water to form a solution with pH = 7
- Na_2O, a basic oxide, reacts with HC*l* to form NaC*l* and H_2O.

Z is Si
- SiO_2 does not react with water due to its giant covalent structure
- $SiCl_4$ reacts with water to give an acidic solution pH 1
- SiO_2 does not react with HC*l*.

Question 18 **Answer: B**

Thermal stability is increased by (a) lower polarising power of the cation and (b) lower polarisability of the anion.

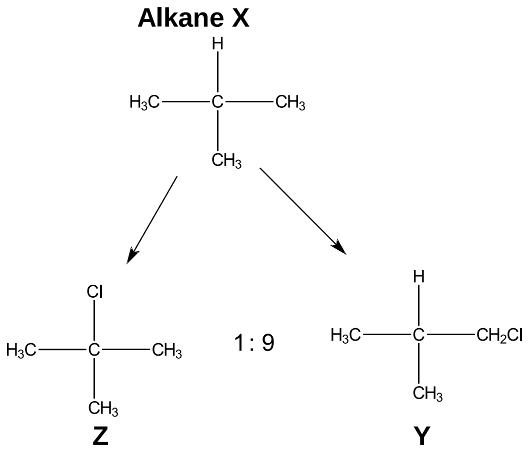
Ba^{2+} has a lower polarising power than Ca^{2+} due to its larger ionic radius. As $BaSO_4$ requires a higher temperature for decomposition, it is thermally more stable due to the lower polarising power of Ba^{2+}. It is not due to the polarisability of the SO_4^{2-} anion because the SO_4^{2-} anion is larger and more polarisable than CO_3^{2-}.

Statement 1 and 4 are incorrect as it does not help to explain thermal stability. Statement 2 is incorrect because SO_4^{2-} is more easily polarised than CO_3^{2-} ions.

Question 19 **Answer: D**

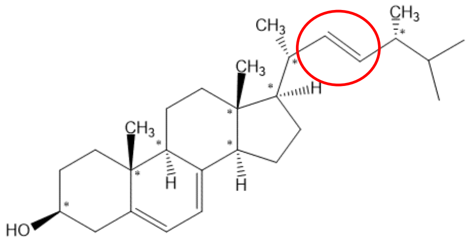
Option **A** is correct as there are 4 dative bonds formed in the complex to the central copper ion, hence coordination number is 4.
Option **B** is correct as these are ligand exchange reactions with no change in oxidation state. Copper (**II**) complexes are formed in this reaction scheme.
Option **C** is correct as **Q** is formed in presence of excess ammonia and the complex $[Cu(NH_3)_4(H_2O)_2]^{2+}$ is formed.
Option **D** is incorrect as reduction reaction does not occur during a ligand exchange reaction (Reaction **III**).

Question 20 **Answer: C**

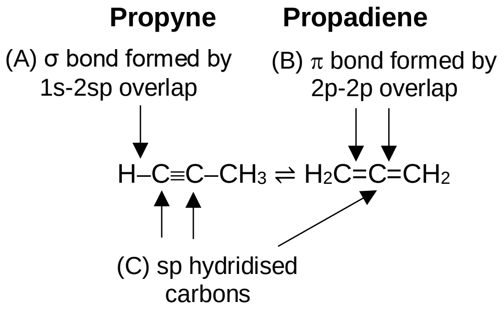


Question 21 **Answer: B**

Max number of stereoisomers = $2^{8+1} = 2^9$ [Note: C=C in ring does not exhibit cis-trans isomerism]



Question 22 **Answer: D**



D is incorrect as the C-C single bond in propyne is sp-sp^3 overlap, while that in propane ($CH_3–CH_2–CH_3$) is sp^3-sp^3 overlap. The bond length in propyne is shorter as sp orbital has more s character, resulting in more effective overlap.

Question 23 **Answer: B**

A is incorrect as oxidation of methylbenzene to benzoic acid requires $KMnO_4/H_2SO_4$, heat.
C is incorrect as aqueous NaOH needs to be added to liberate the free phenylamine and concentrated HNO_3 will result in substitution at 2, 4 position.
D is incorrect as $LiAlH_4$ will reduce carboxylic acid back to primary alcohol.

Question 24 **Answer: A**

Option 1 is incorrect as stereoisomers have different biological properties.
Option 2 is correct. Molecular formula = $C_{12}H_{18}Br_6$, Empirical formula = C_2H_3Br
Option 3 is incorrect as the carbon atoms are tetrahedral.

Question 25 **Answer: C**

A 1 mole of compound **G** reacts with Na (alcohol, phenol, carboxylic acid) to produce 1.5 mole of H_2.
B Tertiary alcohol cannot be oxidised so no green solution obtained.
C 1 mole of compound **G** reacts with 2 moles of NaOH (carboxylic acid and phenol) so product has a charge of 2-.
D 1 mole of compound **G** reacts with 3 moles of CH_3COCl (alcohol, phenol, amine) to produce 3 moles of HCl.

Question 26 **Answer: B**

1 $CH_2{=}CHCO_2H$ gives $CH_2{=}CHCH_2OH$ (gains 2 H and loses 1 O). Alkene is not reduced.
→ net change in $M_r = +2 - 16 = -14$

2 $CH_3CH_2COCO_2H$ gives $CH_3CH_2CH(OH)CH_2OH$ (gains 4H and lose 1 O)
→ net change in $M_r = +4 - 16 = -12$

3 $CH_3CH_2CONH_2$ gives $CH_3CH_2CH_2NH_2$ (gains 2H and lose 1 O)
→ net change in $M_r = +2 -16 = -14$

Question 27 **Answer: D**

A Product is $CH_3CH_2CH_2CHCN(OD)$
B Product is $CH_3CH_2CH_2CO_2D$
C Product is $CH_3CH_2CH_2CO_2D$ and $^{+}ND_2(CH_3)_2$
D Product is $CH_3CH_2CH_2CO_2^-$ which does not contain deuterium.

Question 28 **Answer: B**

Increasing pK_b: arrange from most basic to least basic.
1 and 2 are both secondary amines. However, 1 has an electron-withdrawing group (C=O) attached to it which reduces the electron density on the nitrogen and hence it is less basic than 2.
3 is neutral.
4 is less basic than 1 and 2 since the lone pair of electrons on the nitrogen is delocalised into the benzene ring and hence less available for dative bonding with a proton.

Question 29 **Answer: A**

ala-met
    met-gly-ala
        gly-ala-gly
            gly-ser
                ser-lys

Therefore, the structure of the polypeptide is ala-met-gly-ala-gly-ser-lys

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Question 30 **Answer: C**

Working backwards via pattern recognition: "break C=C bond and place back O at C=C bond" to get first carbonyl compound and the remaining fragment belongs to the second carbonyl compound.

A & D: forms from 2 molecules of butanone

B: forms from 1 molecule of butanone and 2 molecules of ethanal

C: C=C on the right is NOT at C2 and C3 from C=O group

TEMASEK JUNIOR COLLEGE

PRELIMINARY EXAMINATIONS
HIGHER 2

CANDIDATE NAME

CIVICS GROUP /

CENTER NUMBER S

INDEX NUMBER

CHEMISTRY **9729/02**

Paper 2 Structured Questions **28 August 2019**

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your Civics Group, centre number, index number and name on all the work you hand in.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.
The use of an approved scientific calculator is expected, where appropriate.
A Data Booklet is provided.

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

For Examiner's Use	
1	**/7**
2	**/10**
3	**/10**
4	**/14**
5	**/20**
6	**/14**
Total	**/ 75**

This document consists of **20** printed pages

[Turn over

1 **(a)** The table below shows the first, second and third ionisation energies of some elements in the Periodic Table.

Element	**First Ionisation energy ($kJ\ mol^{-1}$)**	**Second Ionisation energy ($kJ\ mol^{-1}$)**	**Third Ionisation energy ($kJ\ mol^{-1}$)**
Ca	590	1150	4940
Mn	716	1510	3250
Fe	762	1560	2960
Co	757	1640	3230
Ni	736	1750	3390

(i) Explain why the first and second ionisation energies of the transition metals are relatively invariant.

[2]

(ii) Write the electronic configurations of Ca and Fe atoms at ground state. Explain the differences in the values of the third ionisation energies between iron and calcium.

[2]

(b) Calcium cyanamide, $CaCN_2$, is used as a fertiliser in agriculture. Through hydrolysis in the presence of carbon dioxide, calcium cyanamide produces cyanamide, NH_2CN. Cyanamide can be extracted by organic solvents.

(i) Draw the dot–and–cross diagram for the cyanamide molecule, NH_2CN.

[1]

(ii) With reference to structure and bonding, deduce whether $CaCN_2$ has a higher or lower melting point as compared to NH_2CN.

[2]

[Total: 7]

2 A saturated solution of magnesium methanoate, $Mg(HCO_2)_2$, has a solubility of approximately 143 g dm^{-3} at room temperature. The exact solubility can be determined by titrating magnesium methanoate solution against a standard potassium manganate(VII) solution.

During the titration, the methanoate ion, HCO_2^-, is oxidised to carbon dioxide while the manganate(VII) ion, MnO_4^-, is reduced to Mn^{2+}.

(a) **(i)** Write the overall equation for the reaction between HCO_2^- and MnO_4^- under acidic conditions.

[1]

[Turn over

(ii) Calculate the approximate concentration of HCO_2^- ions present in the saturated solution. [1]

(iii) The titre value from titrating 25.0 cm^3 of saturated magnesium methanoate solution against 0.0500 mol dm^{-3} potassium manganate(VII) solution is found to be too high.

Describe the steps to prepare a suitable solution of magnesium methanoate from the saturated solution. Your plan should include details of quantities measured and apparatus used.

[3]

(b) An industrial chemist introduced 2 atm of carbon dioxide and 2 atm of hydrogen gas into a 1 dm^3 container at 300 K. The temperature is then raised to 900 K, at which the K_p is 0.641.

$$CO_2(g) + H_2(g) \rightleftharpoons H_2O(g) + CO(g) \qquad \Delta H < 0$$

(i) Calculate the partial pressure of H_2 present at equilibrium at 900 K.

[3]

(ii) Explain if the K_p value at 300 K is higher or lower than 0.641.

[2]

[Total: 10]

[Turn over

3 **(a)** Sulfur tetrachloride decomposes to sulfur dichloride and a gas that bleaches litmus.

(i) Using the VSEPR theory, deduce and draw the shape of SCl_2. Give a value for the bond angle. [3]

Shape : ____________________

Bond angle : ________________

(ii) State whether the bond angle of SCl_2 is expected to be larger or smaller than SF_2. Explain your answer.

[1]

(b) **(i)** There are two possible molecular arrangements for SCl_4 with different relative stabilities.

Draw these two molecular arrangements in the boxes below, showing clearly the shape around the central atom.

[2]

(I) (II)

(ii) Apply the principles of the VSEPR theory to discuss the relative stabilities of molecular arrangements (I) and (II).

[1]

(c) SCl_4 combines with BCl_3 to give **X** with the composition by mass: S, 11.0% ; B, 3.7%.

(i) Derive the empirical formula of **X**.

[1]

(ii) Draw a likely structure of **X**, showing clearly the shape around the central atom(s). State the type of bond formed when SCl_4 and BCl_3 combine to form **X**.

[2]

Type of bond : ____________________

[Total: 10]

4 **(a)** Hydrogen halides are acids resulting from the chemical reaction of hydrogen with one of the halogens.

(i) Briefly explain the trend in the boiling point for hydrogen chloride, hydrogen bromide and hydrogen iodide.

[2]

(ii) By quoting appropriate data from the *Data Booklet*, explain the trend in the thermal stability of the hydrogen halides.

[2]

(b) The chlorides of aluminium and silicon react differently with water to produce acidic solutions.

(i) A sample of aluminum chloride is dissolved in water.

State and explain the pH and the colour observed when universal indicator is added to the resulting solution. Write equations where appropriate.

[3]

(ii) Explain why $SiCl_4$ can be hydrolysed by water.

[1]

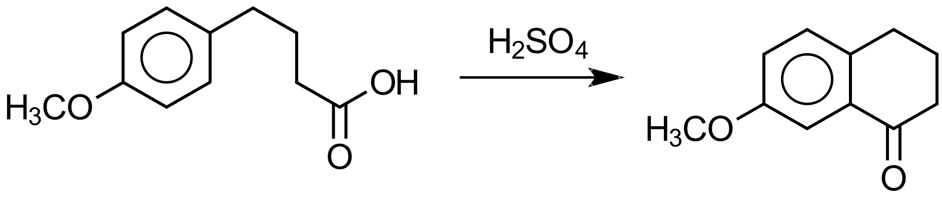
(c) In electrophilic substitution reactions, $AlCl_3$ can function as a Lewis acid catalyst to generate the electrophile.

Deduce whether Al_2Cl_6 can also function in the same manner.

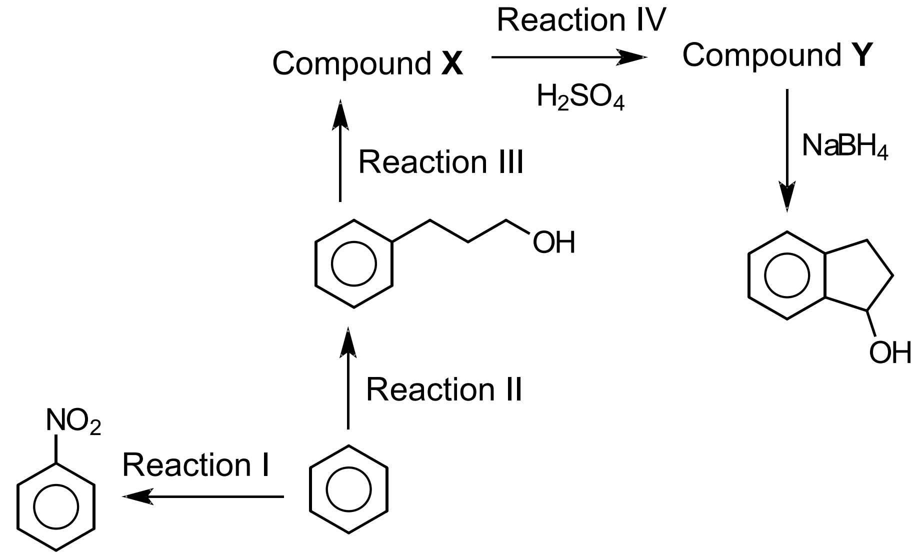
[1]

(d) French scientist Charles Friedel and American scientist James Crafts, first discovered Friedel-Crafts Acylation in 1877.

Intramolecular Friedel-Crafts reaction could also work for some carboxylic acids, as seen from the example below.



The synthesis of compound **Y** involves the intramolecular Friedel-Crafts reaction in Reaction **IV**.



Suggest reagents and conditions for Reaction **I** to Reaction **III** and give the structural formula for compounds **X** and **Y**.

[5]

Reaction **I**: ____

Reaction **II**: ____

Reaction **III**: ____

Compound **X**

Compound **Y**

[Total: 14]

5 This question is about the use of catalytic reagents in green chemistry.

Green chemistry is the study and design of chemical processes and products to reduce the use and generation of hazardous chemicals. One principle of green chemistry proposes the use of catalytic reagents over stoichiometric reagents to reduce the amount of by-products and to increase efficiency.

In 1997, Roger Sheldon proposed E factor and Atom Utilisation as indicators of the amount of waste generated in a chemical reaction.

The E factor is defined as the mass of by-products produced per kg of product in chemical industry. The table below shows the typical product mass and E factor for the different industries.

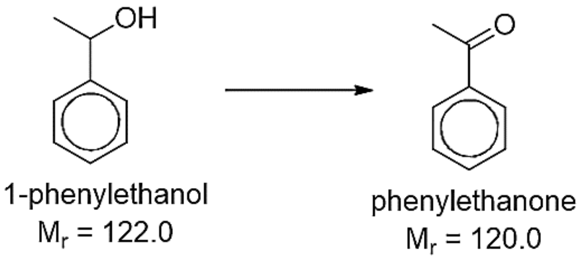
Industry	Typical product mass / 10^3 kg	Typical E factor
Bulk chemicals	10,000	2
Pharmaceuticals	100	50

The Atom Utilisation is defined as

$$\frac{\text{molar mass of the desired product}}{\sum \text{molar mass of all materials produced}} \times 100\%$$

In general, a reaction with a low E factor and a high Atom Utilisation value indicates that less waste is generated.

(a) 1-phenylethanol can be oxidised to phenylethanone via a stoichiometric reaction or via a catalytic reaction.



Details of each reaction are given in the table below.

Type of reaction	Reagents used	By-product(s)	Atom Utilisation
Stoichiometric reaction	CrO_3 and H_2SO_4	$Cr_2(SO_4)_3$ and H_2O	44%
Catalytic reaction	O_2 and Ruthenium	H_2O	x

(i) Calculate the Atom Utilisation, x, for the oxidation of 1-phenylethanol via catalytic reaction. Hence explain which type of reaction is more efficient for producing phenylethanone.

[2]

The environmental friendliness of a process can be represented by the overall environmental quotient, EQ, of the by-products which is given by

$$\sum_{\text{by-products}} \text{E} \times \text{Q}$$

where E is the E factor and Q is the unfriendliness quotient.

The higher the EQ value, the more toxic the by-product is to the environment. Q values for several substances are given below.

Substance	Q value
$Cr_2(SO_4)_3$	1000
CrO_3	1000
Ru	100
H_2SO_4	100
H_2O	1
O_2	1

(ii) 1-phenylethanol is oxidised to phenylethanone in both bulk chemical and pharmaceutical industry using the stoichiometric reaction.

Determine which industry is more environment-friendly in producing phenylethanone, showing clearly all workings.

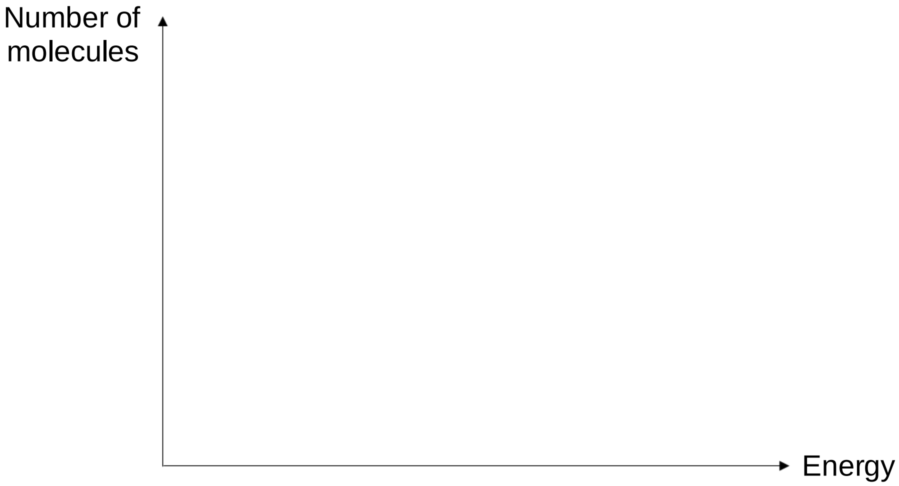
[2]

(b) Catalysts such as ruthenium are known as *heterogeneous* catalysts.

(i) Outline briefly how this type of catalyst speeds up the reaction between oxygen and 1-phenylethanol. [2]

(ii) Sketch a suitable Boltzmann distribution curve below and hence explain the effect of ruthenium on the rate constant of the reaction.

[3]



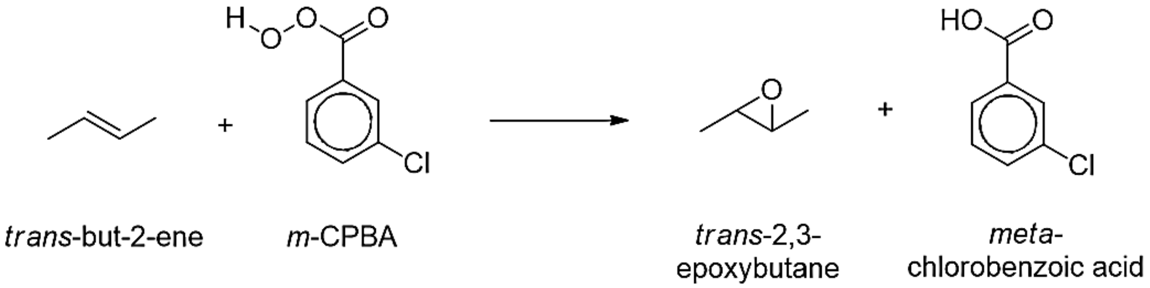
(iii) The reaction rate between oxygen and 1-phenylethanol can be increased by pumping more oxygen gas into a constant-volume reaction vessel.

On the same graph in **(b)(ii)**, sketch a new curve to represent energy distribution of reactants when more oxygen gas is added. Label the graph clearly as **(b)(iii)**.

[1]

(c) Epoxidation is a reaction to synthesise epoxides from alkenes.

Trans-2,3-epoxybutane, an epoxide, is synthesised by reacting trans-but-2-ene with m-CPBA.



To study the kinetics between trans-but-2-ene and m-CPBA, several experiments were conducted using different volumes of m-CPBA and trans-but-2-ene, topped up with suitable volumes of hexane solvent. The set-up is placed on a piece of paper with an “X” mark.

The product, meta-chlorobenzoic acid, has low solubility in hexane and is precipitated out as soon as it is formed and the reaction is monitored by measuring the time taken for the “X” to disappear.

Experiment	Volume of trans-but-2-ene / cm^3	Volume of m-CPBA / cm^3	Volume of hexane / cm^3	Time taken for “X” to disappear / s
1	20	10	15	10.0
2	20	15	10	6.7
3	10	5	30	40.0
4	40	20	30	y

(i) Briefly explain the low solubility of the product meta-chlorobenzoic acid in hexane. [2]

(ii) Determine the order of reaction with respect to trans-but-2-ene and m-CPBA. Showing your workings clearly.

[2]

(iii) Hence, construct a rate equation for the reaction between trans-but-2-ene and m-CPBA.

[1]

(iv) State the value of y in experiment 4.

[1]

(d) A thermal experiment was conducted to determine the enthalpy change of combustion of trans-2,3-epoxybutane.

8.26 g of trans-2,3-epoxybutane was burnt in excess oxygen and the temperature of water in the bomb calorimeter was measured. The following data was collected.

Heat capacity of calorimeter: 154 J K^{-1}

Volume of water: 400 cm^3

Temperature rise: 32 ^oC

The experiment was only 20% efficient.

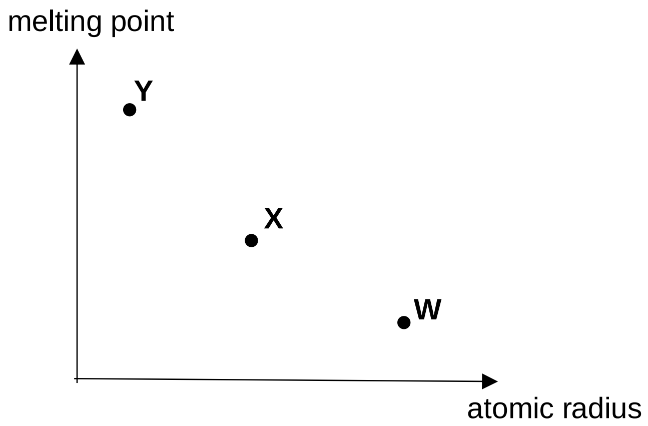
(i) Calculate the enthalpy change of combustion of trans-2,3-epoxybutane.

[3]

(ii) Suggest one modification to the set-up so that the experiment can be made more efficient. [1]

[Total: 20]

6 **(a)** **W**, **X** and **Y** represent consecutive elements in Period 3. The following shows a graph of their melting points plotted against the atomic radius (not drawn to scale).



The oxide of **Y** is insoluble in water but dissolves when the oxide of **W** is subsequently added.

(i) Suggest the identities of **Y** and **W**. [1]

(ii) Explain the above observations and write equations for all the reactions that has occurred. [3]

(b) An experiment was conducted to investigate the thermal decomposition of Group 2 carbonates.

Equal amounts of carbonates of magnesium, strontium and barium were heated for two minutes. The gas produced was bubbled through calcium hydroxide and the time taken for the white ppt to be formed was recorded as follows:

Group 2 Carbonate	$MgCO_3$	$SrCO_3$	$BaCO_3$
Time taken for white ppt to be formed / s	40	240	never

(i) Using relevant data from the *Data Booklet*, explain the results obtained.

[3]

(ii) If the experiment was repeated with calcium carbonate under the same conditions, suggest a value for the time needed for the white ppt to be observed.

[1]

(c) Inorganic reducing agents such as lithium aluminium hydride and sodium borohydrides are commonly used in organic chemistry.

A student attempted to synthesise propanal by reducing propanoic acid. He found that there was no reaction when sodium borohydride was used and the product formed with lithium aluminium hydride was not propanal.

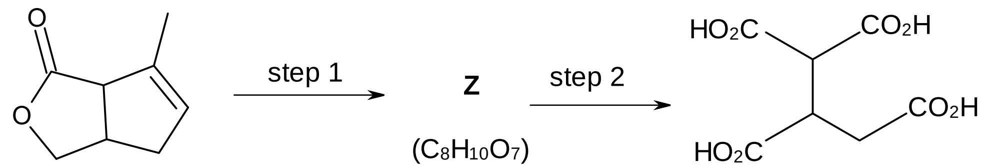
(i) Explain why lithium aluminium hydride can be used to reduce propanoic acid but not sodium borohydride.

[1]

(ii) Draw the displayed formula of the organic product formed instead of propanal.

[1]

(d) Carboxylic acids can be made from a variety of other compounds. In the following reaction scheme, identify the intermediate compound **Z** and suggest reagents and conditions for the two steps.



[3]

Step 1: ____

Step 2: ____

Compound **Z**

(e) Carboxylic acids are also useful compounds to synthesise esters such as propyl ethanoate which is responsible for the smell of pears and is used as a flavor additive.

In the synthesis of propyl ethanoate, the oxygen atom in a suitable alcohol is labelled with the oxygen isotope, ^{18}O.

Write an equation for this reaction, indicating clearly where the ^{18}O atom(s) are.

[1]

[Total: 14]

1 **(a)** The table below shows the first, second and third ionisation energies of some elements in the Periodic Table.

Element	**First Ionisation energy ($kJ\ mol^{-1}$)**	**Second Ionisation energy ($kJ\ mol^{-1}$)**	**Third Ionisation energy ($kJ\ mol^{-1}$)**
Ca	590	1150	4940
Mn	716	1510	3250
Fe	762	1560	2960
Co	757	1640	3230
Ni	736	1750	3390

(i) Explain why the first and second ionisation energies of the transition metals are relatively invariant.

[2]

The first and second I.E of the transition elements involves the removal of 4s electrons. Across the period, • nuclear charge increases due to increasing number of protons. Screening effect increases as electrons are added to the penultimate 3d subshell, providing a shield between nucleus and outer 4s electrons. • Increase in nuclear charge is only *slightly* more significant than the increase in screening effect. Hence, small increase in both the first and second I.E.

(ii) Write the electronic configurations of Ca and Fe atoms at ground state. Explain the differences in the values of the third ionisation energies between iron and calcium.

[2]

• Electronic Configuration of Fe: **$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6\ 4s^2$**

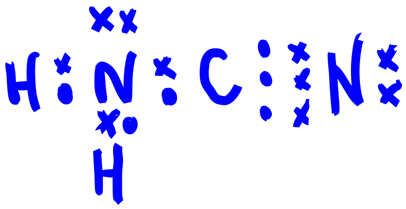
Electronic Configuration of Ca: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$

• The third ionisation energy of calcium is more than that of iron because an electron is removed from a 3p orbital of Ca^{2+} whereas an electron is removed from a 3d orbital of the Fe^{2+}. The 3p electron is nearer to the nucleus compared to the 3d electron and hence required more energy to remove.

(b) Calcium cyanamide, $CaCN_2$, is used as a fertiliser in agriculture. Through hydrolysis in the presence of carbon dioxide, calcium cyanamide produces cyanamide, NH_2CN. Cyanamide can be extracted by organic solvents.

(i) Draw the dot–and–cross diagram for the cyanamide molecule, NH_2CN.

[1]



(ii) With reference to structure and bonding, deduce whether $CaCN_2$ has a higher or lower melting point as compared to NH_2CN.

[2]

- **NH_2CN has simple molecular structure with hydrogen bonds between its molecules.**

$CaCN_2$ has a giant ionic lattice structure held by strong electrostatic forces of attraction/ionic bonds between the oppositely charged ions.

- **Melting involves the breaking of the stronger electrostatic forces of attraction between the oppositely charges ions (Ca^{2+} and CN_2^{2-}) as compared to the (or) weaker hydrogen bonds between NH_2CN molecules. Hence more energy is required to melt $CaCN_2$, hence higher melting point.**

[Total: 7]

2 A saturated solution of magnesium methanoate, $Mg(HCO_2)_2$, has a solubility of approximately 143 g dm^{-3} at room temperature. The exact solubility can be determined by titrating magnesium methanoate solution against a standard potassium manganate(VII) solution.

During the titration, the methanoate ion, HCO_2^-, is oxidised to carbon dioxide while the manganate(VII) ion, MnO_4^-, is reduced to Mn^{2+}.

(a) **(i)** Write the overall equation for the reaction between HCO_2^- and MnO_4^- under acidic conditions.

[1]

Oxidation :$HCO_2^- \rightarrow CO_2 + H^+ + 2e^-$ (x5)

Reduction : $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$ (x2)

- **$2MnO_4^- + 11H^+ + 5HCO_2^- \rightarrow 2Mn^{2+} + 8H_2O + 5CO_2$**

(ii) Calculate the approximate concentration of HCO_2^- ions present in the saturated solution.

[1]

- **$[HCO_2^-]$ in saturated solution = $\frac{143}{24.3+2(1+12+2\times16)} \times 2$**
$= 2.50$ mol dm^{-3}

(iii) The titre value from titrating 25.0 cm^3 of saturated magnesium methanoate solution against 0.0500 mol dm^{-3} potassium manganate(VII) solution is found to be too high.

Describe the steps to prepare a suitable solution of magnesium methanoate from the saturated solution. Your plan should include details of quantities measured and apparatus used.

[3]

Assuming the titre volume of potassium manganate(VII) solution to be 25.00 cm^3 (accept 20.00 to 25.00 cm^3),

No. of moles of HCO_2^- in 25.0 cm^3 of diluted solution
$= \frac{25}{1000} \times 0.05 \times \frac{5}{2} = 3.125 \times 10^{-3}$ mol
No. of moles of HCO_2^- in 250 cm^3 of diluted solution = 3.125×10^{-2} mol

- **Volume of saturated HCO_2^- solution needed for dilution**
  $= \frac{3.125 \times 10^{-2}}{2.5} \times 1000 = 12.50$ cm^3

●●
Using a burette, transfer 12.50 cm^3 of saturated magnesium methanoate solution into a 250 cm^3 standard flask. Make up to the mark with water and shake well.

(b) An industrial chemist introduced 2 atm of carbon dioxide and 2 atm of hydrogen gas into a 1 dm^3 container at 300 K. The temperature is then raised to 900 K, at which the K_p is 0.641.

$$CO_2(g) + H_2(g) \rightleftharpoons H_2O(g) + CO(g) \qquad \Delta H < 0$$

(i) Calculate the partial pressure of H_2 present at equilibrium at 900 K.

[3]

Since P ∝ T,

- **$P_{CO_2} = P_{H_2} = 6$ atm at 900K**

	$CO_2(g)$ +	$H_2(g)$ ⇌	$H_2O(g)$ +	$CO(g)$
Initial partial pressure /atm	6	6	0	0
Change in partial pressure /atm	-x	-x	+x	+x
Equilibrium partial pressure /atm	6-x	6-x	x	x

$K_p = \frac{P_{H_2O} \times P_{CO}}{P_{CO_2} \times P_{H_2}}$

- **$0.641 = \frac{x^2}{(6-x)^2}$**
  x = 2.67 atm
- **$P_{H_2} = 6 - 2.67 = 3.33$ atm**

(ii) Explain if the K_p value at 300 K is higher or lower than 0.641.

[2]

• The value of K_p at 300 K is higher than 0.641.
• By Le Chatelier's Principle, at the lower temperature of 300 K, the system will favour the exothermic forward reaction to produce more heat. Thus position of equilibrium shifts to the right and K_p increases.

[Total: 10]

3 **(a)** Sulfur tetrachloride decomposes to sulfur dichloride and a gas that bleaches litmus.

[3]

(i) Using the VSEPR theory, deduce and draw the shape of SCl_2. Give a value for the bond angle.

There are <u>2 bond pairs and 2 lone pairs of electrons around S</u>. To <u>minimize repulsion and maximize stability</u>, the <u>4 electron pairs are directed to the corners of a tetrahedron</u>. The shape is <u>bent</u>.

√ 2 bond pairs and 2 lone pairs around S.

√ 4 electrons pairs arranged tetrahedrally to

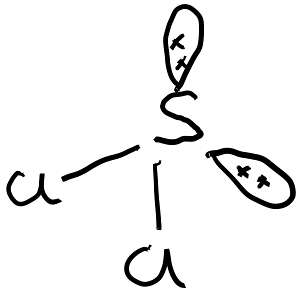
√ minimize repulsion and maximize stability.

√ bent

√ diagram

√ bond angle : any angle between 90^0 & 109.5^0.

2 √ : 1m



(ii) State whether the bond angle of SCl_2 is expected to be larger or smaller than SF_2. Explain your answer.

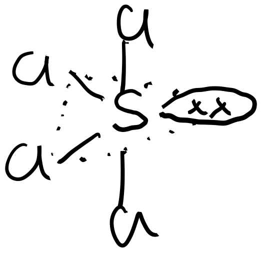
[1]

<u>C*l* is less electronegative than F. The bond pair of electrons is closer to S for SCl_2 resulting in a greater bond pair-bond pair repulsion</u>. Hence the bond angle of SCl_2 is <u>larger</u>.

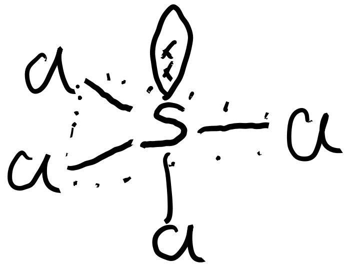
(b) **(i)** There are two possible molecular arrangements for SCl_4 with different relative stabilities. Draw these two molecular arrangements in the boxes below, showing clearly the shape around the central atom.

[2]

(I)



(II)



(ii) Apply the principles of the VSEPR theory to discuss the relative stabilities of molecular arrangements (I) and (II).

[1]

- **Since electron pairs exert repulsion on one another in the following order:**

lone pair – lone pair repulsion > lone pair – bond pair repulsion > bond pair – bond pair repulsion

[Turn over

<u>Arrangement I</u> gives the more stable molecule when the lone pair is placed in the equatorial positions (120^0 apart).

(c) SCl_4 combines with BCl_3 to give **X** with the composition by mass: S, 11.0% ; B, 3.7%.

(i) Derive the empirical formula of **X**.

[1]

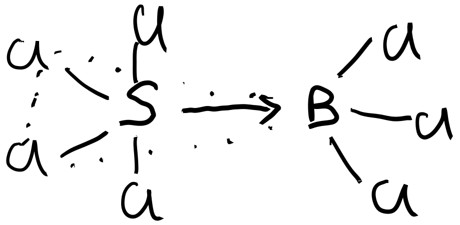
	S	**B**	**C*l***
Mole ratio	**11/32.1**	**3.7/10.8**	**85.3/35.5**
	0.343	**0.343**	**2.40**
Simplest ratio	**1**	**1**	**7**

Empirical formula : $SBCl_7$

(ii) Draw a likely structure of **X**, showing clearly the shape around the central atom(s). State the type of bond formed when SCl_4 and BCl_3 combine to form **X**.

[2]

●



●Type of bond : Dative/co-ordinate

[Total: 10]

4 **(a)** Hydrogen halides are acids resulting from the chemical reaction of hydrogen with one of the halogens.

(i) Briefly explain the trend in the boiling point for hydrogen chloride, hydrogen bromide and hydrogen iodide.

[2]

● Order of boiling point : HI > HBr > HC*l*
● Down the group, <u>size of electron cloud of HX increases</u>, leading to <u>greater distortion of electron cloud</u>. Extent of <u>instantaneous dipole-induced dipole interactions becomes stronger</u> and more extensive. Larger amount of energy required to break these intermolecular forces of attraction between the molecules.

(ii) By quoting appropriate data from the *Data Booklet*, explain the trend in the thermal stability of the hydrogen halides.

[2]

● Bond energy of H-C*l*, H-Br and H-I are <u>431, 366 and 299 kJ mol^{-1}</u> respectively.
● As seen from the data, the <u>H-X bond energy decreases down the group</u> resulting in <u>a decrease in the strength of the H-X bond</u>. Hence, <u>thermal stability of the hydrogen halides decreases</u> down the group. *OR*
● Radius of Cl, Br, I are <u>0.099, 0.114, 0.133 nm</u> respectively.
● <u>H-X bond length increases down the group</u>, <u>extent of effective orbital overlap decreases</u> and the <u>H-X bond strength decreases</u>. Hence, <u>thermal stability of the hydrogen halides decreases</u> down the group.

(b) The chlorides of aluminium and silicon react differently with water to produce acidic solutions.

(i) A sample of aluminum chloride is dissolved in water.

State and explain the pH and the colour observed when universal indicator is added to the resulting solution. Write equations where appropriate.

[3]

● Orange & pH = 3 to 4
● $AlCl_3$ undergoes both hydration and hydrolysis as Al^{3+} has a high charge density, hence a high polarising power. It draws electrons away from its surrounding water molecules and weakens the O-H bond.
Hydration: $AlCl_3(s) + 6H_2O(l) \rightarrow [Al(H_2O)_6]^{3+}(aq) + 3Cl^-(aq)$
Hydrolysis: $[Al(H_2O)_6]^{3+}(aq) \rightleftharpoons [Al(H_2O)_5OH]^{2+}(aq) + H^+(aq)$
1m for both equation

(ii) Explain why $SiCl_4$ can be hydrolysed by water.

[1]

● $SiCl_4$ is a covalent chloride that undergoes hydrolysis in water. Hydrolysis occurs due to energetically accessible & vacant 3d-orbitals available for dative bonding with water/accept lone pair electron from water.

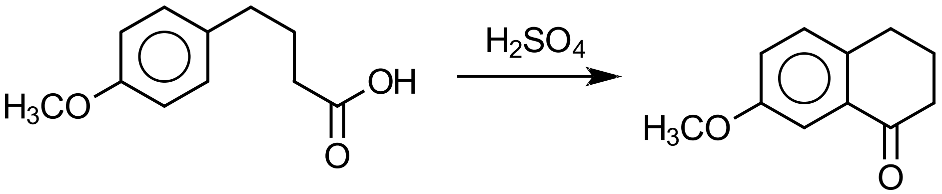
(c) In electrophilic substitution reactions, $AlCl_3$ can function as a Lewis acid catalyst to generate the electrophile.
Deduce whether Al_2Cl_6 can also function in the same manner.

[1]

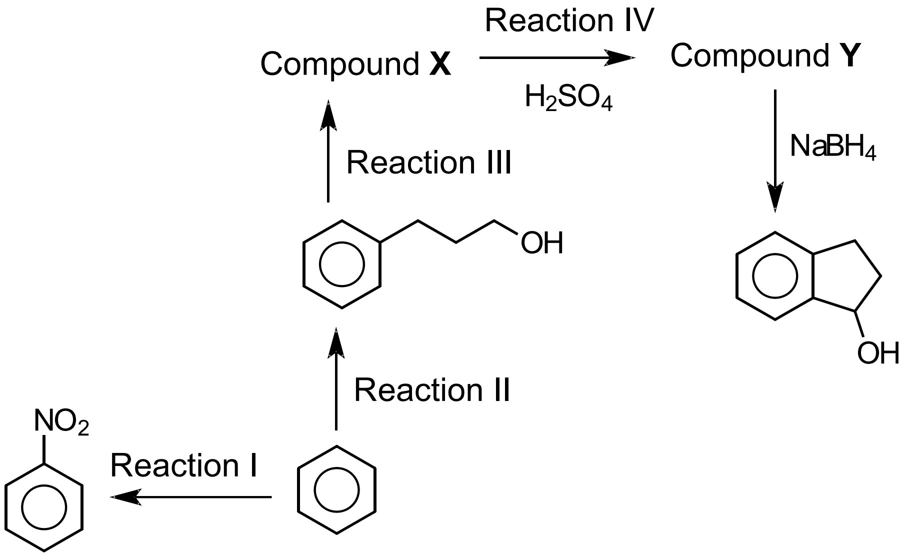
● No, because Al_2Cl_6 is not electron-deficient/has achieved octet structure and is less likely to accept a lone pair of electrons to form a dative bond.

(d) French scientist Charles Friedel and American scientist James Crafts, first discovered Friedel-Crafts Acylation in 1877.

Intramolecular Friedel-Crafts reaction could also work for some carboxylic acids, as seen from the example below.



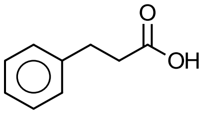
The synthesis of compound **Y** involves the intramolecular Friedel-Crafts reaction in Reaction **IV**.



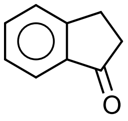
Suggest reagents and conditions for Reaction **I** to Reaction **III** and give the structural formula for compounds **X** and **Y**.

[5]

- **Reaction I: concentrated nitric acid, concentrated sulfuric acid, heat < 60°C**
- **Reaction II: $ClCH_2CH_2CH_2OH$, anhydrous $AlCl_3$ as catalyst, rtp**
- **Reaction III: acidified $K_2Cr_2O_7$, heat under reflux (cannot use $KMnO_4$)**
- **X:**



- **Y:**



[Total: 14]

5 This question is about the use of catalytic reagents in green chemistry.

Green chemistry is the study and design of chemical processes and products to reduce the use and generation of hazardous chemicals. One principle of green chemistry proposes the use of catalytic reagents over stoichiometric reagents to reduce the amount of by-products and to increase efficiency.

In 1997, Roger Sheldon proposed E factor and Atom Utilisation as indicators of the amount of waste generated in a chemical reaction.

The E factor is defined as the mass of by-products produced per kg of product in chemical industry. The table below shows the typical product mass and E factor for the different industries.

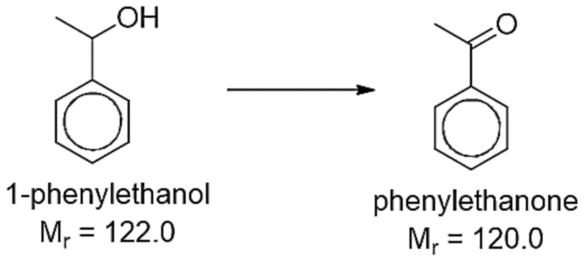
Industry	Typical product mass / 10^3 kg	Typical E factor
Bulk chemicals	10,000	2
Pharmaceuticals	100	50

The Atom Utilisation is defined as

$$\frac{\text{molar mass of the desired product}}{\sum \text{molar mass of all materials produced}} \times 100\%$$

In general, a reaction with a low E factor and a high Atom Utilisation value indicates that less waste is generated.

(a) 1-phenylethanol can be oxidised to phenylethanone via a stoichiometric reaction using chromium(VI) oxide in acidic medium or via a catalytic reaction using oxygen in the presence of ruthenium metal catalyst.



Details of each reaction are given in the table below.

Type of reaction	Reagents used	By-product(s)	Atom Utilisation
Stoichiometric reaction	CrO_3 and H_2SO_4	$Cr_2(SO_4)_3$ and H_2O	44%
Catalytic reaction	O_2 and Ruthenium	H_2O	x

(i) Calculate the Atom Utilisation, x, for the oxidation of 1-phenylethanol via catalytic reaction. Hence explain which type of reaction is more efficient for producing phenylethanone. [2]

- **Atom Utilisation for the catalytic reaction**
  = M_r of phenylethanone / (M_r of phenylethanone + M_r of water)
  = 120/(120+18) = 87.0%

- **Catalytic reaction is more efficient as the Atom Utilisation value is higher implying less waste is produced from the reaction.**

The environmental friendliness of a process can be represented by the overall environmental quotient, EQ, of the by-products which is given by

$$\sum_{\text{by-products}} E \times Q$$

where E is the E factor and Q is the unfriendliness quotient.

The higher the EQ value, the more toxic the by-product is to the environment. Q values for several substances are given below.

Substance	Q value
$Cr_2(SO_4)_3$	1000
CrO_3	1000
Ru	100
H_2SO_4	100
H_2O	1
O_2	1

(ii) 1-phenylethanol is oxidised to phenylethanone in both bulk chemical and pharmaceutical industry using the stoichiometric reaction.

Determine which industry is more environment-friendly in producing phenylethanone, showing clearly all workings.

[2]

- **Bulk chemical industry: 1000x2 + 1x2 = 2002**
  Pharmaceutical industry: 1000x50 + 1x50 = 50,050
- **Hence, the bulk chemical industry is more environmental friendly as the EQ value is lower, implying less amount of toxic waste is generated.**

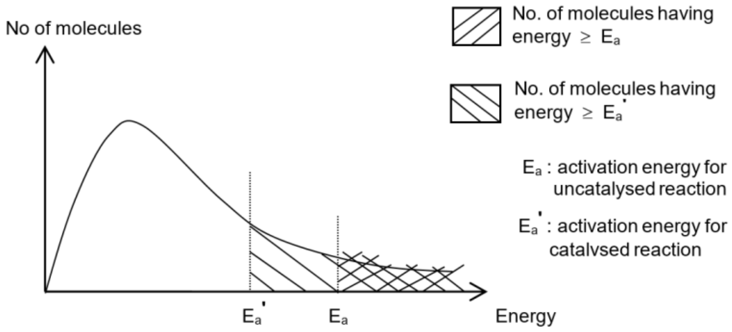
(b) Catalysts such as ruthenium are known as *heterogeneous* catalysts.

(i) Outline briefly how this type of catalyst speeds up the reaction between oxygen and 1-phenylethanol. [2]

- **Ruthenium provides the surface in which adsorption of reactant molecules and desorption of product molecules take place.**
- **The activation energy is lower than that of the uncatalysed reaction because the effective surface concentration of oxygen and 1-phenylethanol on the catalyst is higher and the intramolecular bonds of reactants are weakened by the adsorption effect.**

(ii) With a sketch of a suitable Boltzmann distribution curve below, explain the effect of ruthenium on the rate constant of the reaction.

[3]



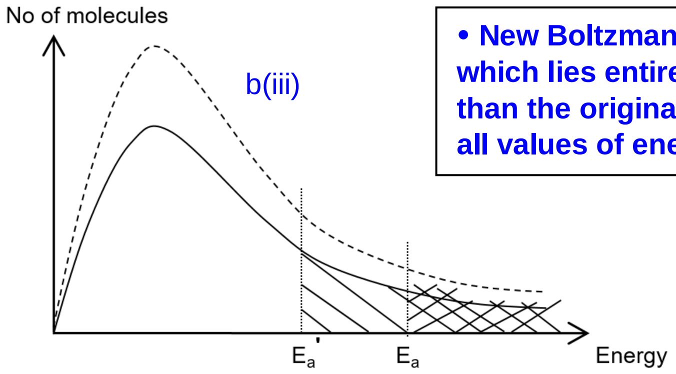
- **Correct Boltzmann curve with legends and correct Ea and Ea' shown**

- **The ruthenium catalyst provides an alternative pathway which involves a lower activation energy, E_a'. The number of reactant molecules having energy greater than or equal to Ea' increases significantly.**
- **Frequency of effective collisions increases and rate constant increases, hence rate increases.**

(iii) The reaction rate between oxygen and 1-phenylethanol can be increased by pumping more oxygen gas into a constant-volume reaction vessel.

On the same graph in **(b)(ii)**, sketch a new curve to represent energy distribution of reactants when more oxygen gas is added. Label the graph clearly as **(b)(iii)**.

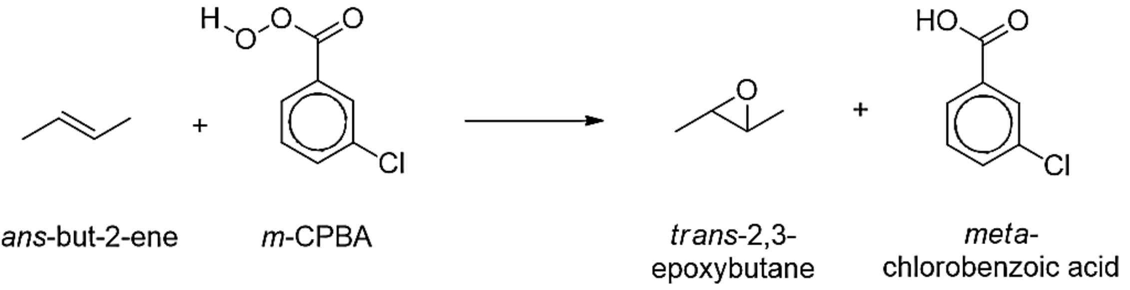
[1]



- **New Boltzmann curve which lies entirely higher than the original curve at all values of energy**

(c) Epoxidation is a reaction to synthesise epoxides from alkenes.

Trans-2,3-epoxybutane, an epoxide, is synthesised by reacting trans-but-2-ene with m-CPBA.



To study the kinetics between trans-but-2-ene and m-CPBA, several experiments were conducted using different volumes of m-CPBA and trans-but-2-ene, topped up with suitable volumes of hexane solvent. The set-up is placed on a piece of paper with an "X" mark.

The product, meta-chlorobenzoic acid, has low solubility in hexane and is precipitated out as soon as it is formed and the reaction is monitored by measuring the time taken for the "X" to disappear.

Experiment	Volume of trans-but-2-ene / cm^3	Volume of m-CPBA / cm^3	Volume of hexane / cm^3	Time taken for "X" to disappear / s
1	20	10	15	10.0
2	20	15	10	6.7
3	10	5	30	40.0
4	40	20	30	y

(i) Briefly explain the low solubility of the product meta-chlorobenzoic acid in hexane. [2]

Formation of • id-id interaction between meta-chlorobenzoic acid and hexane release insufficient energy to overcome the • hydrogen-bonding interactions between molecules of meta-chlorobenzoic acid and id-id interactions between hexane molecules.

(ii) Determine the order of reaction with respect to trans-but-2-ene and m-CPBA. Showing your workings clearly. [2]

Total volume is constant at 45 cm^3, so the volume $\propto$ concentration. Rate of reaction $\propto$ 1/t.

Relative rate for expt 1 = 1/10 = 0.100

Relative rate for expt 2 = 1/6.7 = 0.149

Relative rate for expt 3 = 1/40 = 0.025

• Comparing expt 1 and 2, keeping conc of trans-but-2-ene constant, when conc of m-CPBA increases by 1.5 times, rate increases by 1.5 times → 1st order reaction wrt m-CPBA.

• Comparing expt 1 and 3, when conc of m-CPBA and trans-but-2-ene each halves, rate decreases by 4 times → 1st order reaction wrt trans-but-2-ene.

(iii) Hence, construct a rate equation for the reaction between trans-but-2-ene and m-CPBA.

[1]

• Rate = k[trans-but-2-ene][m-CPBA]

(iv) State the value of *y* in experiment 4.

[1]

• 10s

(d) A thermal experiment was conducted to determine the enthalpy change of combustion of trans-2,3-epoxybutane.

8.26 g of trans-2,3-epoxybutane was burnt in excess oxygen and the temperature of water in the bomb calorimeter was measured. The following data are collected.

Heat capacity of calorimeter: 154 J K^{-1}

Volume of water: 400 cm^3

Temperature rise: 32 ^{o}C

The experiment was only 20% efficient.

(i) Calculate the enthalpy change of combustion of trans-2,3-epoxybutane.

[3]

• Total heat gained by water & calorimeter = 400x4.18x32 + 154x32 = 58432 J

• Total heat given out by burning 10cm^3 of trans-2,3-epoxybutane = 58432 x 100/20 = 292160 J

Amount of trans-2,3-epoxybutane burnt = 8.26/(4x12+8+16) = 0.1147 mol

• Enthalpy change of combustion = -292 160 / 0.1147 = -2550 kJ mol^{-1}

(ii) Suggest one modification to the set-up so that the experiment can be made more efficient.

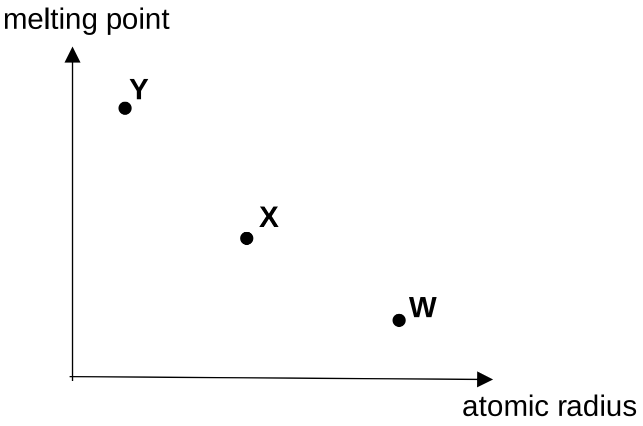
[1]

Install windshield / conduct the experiment in a draught-free room / insulate the copper calorimeter

[Total: 20]

[Turn over

6 (a) **W**, **X** and **Y** represent consecutive elements in Period 3. The following shows a graph of their melting points plotted against the atomic radius (not drawn to scale).



The oxide of **Y** is insoluble in water but dissolves when the oxide of **W** is subsequently added.

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

- **Y is <u>aluminum</u> and W is <u>Sodium</u> (X: Magnesium)**

(ii) Explain the above observations and write equations for all the reactions that has occurred. [3]

- **Al_2O_3 is insoluble in water due to its <u>high lattice energy</u>.**

  When Na_2O dissolves in water, it forms NaOH(aq).

- **$Na_2O(s) + H_2O(l) \rightarrow 2NaOH(aq)$**

  Since Al_2O_3 is an amphoteric oxide, it can react with NaOH(aq) and hence dissolves.

- **$Al_2O_3(s) + 2NaOH(aq) + 3H_2O(l) \rightarrow 2NaAl(OH)_4(aq)$**

Note: Y is not Si because SiO_2 does not dissolve in weakly alkaline solution.

(b) An experiment was conducted to investigate the thermal decomposition of Group 2 carbonates.

Equal amounts of carbonates of magnesium, strontium and barium were heated for two minutes. The gas produced was bubbled through calcium hydroxide and the time taken for the white ppt to be formed was recorded as follows:

Group 2 carbonate	$MgCO_3$	$SrCO_3$	$BaCO_3$
Time taken for white ppt to be formed / s	40	240	never

(i) Using relevant data from the *Data Booklet*, explain the results obtained. [3]

- **The ionic radius of Mg^{2+}, Sr^{2+} and Ba^{2+} are 0.065 nm, 0.113 nm and 0.135 nm respectively.**

Down Group 2, the ionic charge of the cation remains the same while the ionic radius increases, hence √ charge density decreases down the group.

Hence, Mg^{2+} has the greatest polarising power and can √ distort the electron cloud of CO_3^{2-}/polarise the C-O bond to the greatest extent, √ weakening the C–O bond the most.

As a result, $MgCO_3$ √ decomposes most readily/is least stable to heat than $SrCO_3$ and $BaCO_3$ and requires the least amount of time to for the white ppt to be formed with calcium hydroxide.

•• Every 2√ 1 mark

(ii) If the experiment was repeated with calcium carbonate under the same conditions, suggest a value for the time needed for the white ppt to be observed.

[1]

The time needed for the white ppt to be observed is 70 s (accept any value between 40 – 240).

(c) Inorganic reducing agents such as lithium aluminium hydride and sodium borohydrides are commonly used in organic chemistry.

A student attempted to synthesise propanal by reducing propanoic acid. He found that there was no reaction when sodium borohydride was used and the product formed with lithium aluminium hydride was not propanal.

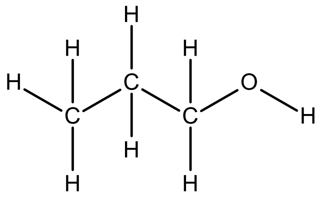
(i) Explain why lithium aluminium hydride can be used to reduce propanoic acid but not sodium borohydride.

[1]

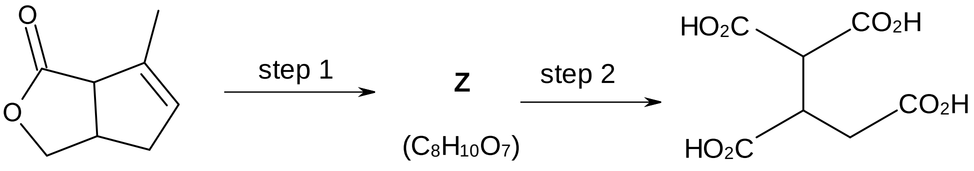
$LiAlH_4$ is a stronger reducing agent than $NaBH_4$ as the H in the *Al*-H bond is more electron rich. This is due to the greater electronegativity difference between *Al* and H in the *Al*-H bond (electronegativity difference is 2.1-1.5).

(ii) Draw the displayed formula of the organic product formed instead of propanal.

[1]

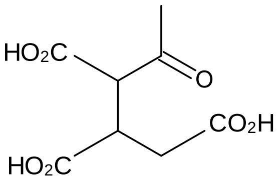


(d) Carboxylic acids can be made from a variety of other compounds. In the following reaction scheme, identify the intermediate compound **Z** and suggest reagents and conditions for the two steps.



[3]

- **Step 1: $KMnO_4$, H_2SO_4, heat**

- **Z:** 

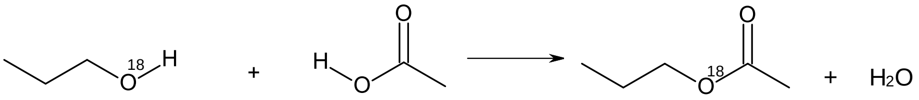
- **Step 2: alkaline I_2(aq), heat, followed by acidification using H_2SO_4(aq) or HC*l*(aq)**

(e) Carboxylic acids are also useful compounds to synthesise esters such as propyl ethanoate which is responsible for the smell of pears and is used as a flavor additive.

In the synthesis of propyl ethanoate, the oxygen atom in a suitable alcohol is labelled with the oxygen isotope, ^{18}O.

Write an equation for this reaction, indicating clearly where the ^{18}O atom(s) are.

[1]

- 

[Total: 14]

TEMASEK
JUNIOR COLLEGE

PRELIMINARY EXAMINATIONS

HIGHER 2

CHEMISTRY 9729/03

Paper 3 Free Response 16 September 2019

2 hours

Candidates answer on separate booklet.

Additional Materials: 12-Page Answer Booklet
Data Booklet

READ THESE INSTRUCTIONS FIRST

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

Section A
Answer **all** questions.

Section B
Answer **one** question.

A Data Booklet is provided.
The use of an approved scientific calculator is expected, where appropriate.

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

This document consists of **14** printed pages and **2** blank pages.

Section A

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

1 The term *chelates*, originates from the Greek word *chele* for “claw”. It refers to compounds containing ligands bonded to a central metal atom or ion at two or more points.

Ligand exchange occurs when ammonia and ethylenediamine (en), $H_2NCH_2CH_2NH_2$, are added separately to copper sulfate solution.

(a) **(i)** Explain all the changes observed when aqueous ammonia is added dropwise to $Cu^{2+}(aq)$ till in excess. Suggest the formulae of all relevant copper compounds formed and write equations for all reactions. [4]

(ii) Suggest why ethylenediamine can function as a *chelating ligand*. [1]

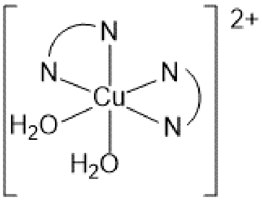
(iii) When ethylenediamine is added to $Cu^{2+}(aq)$, the following occurs.

$$[Cu(H_2O)_6]^{2+} + 2en \rightarrow [Cu(en)_2(H_2O)_2]^{2+} + 4H_2O$$

Predict whether ethylenediamine or ammonia gives a more positive entropy change when added to $Cu^{2+}(aq)$. [2]

(iv) Suggest the coordination number and shape of $[Cu(en)_2(H_2O)_2]^{2+}$. [1]

(v) The complex ion $[Cu(en)_2(H_2O)_2]^{2+}$ can exist as three stereoisomers, **A**, **B** and **C**. Isomers **A** and **B** rotate plane-polarised light but **C** does not. The structure of **A** is represented below.



Isomer **A**

where  represents ethylenediamine (en)

Draw the structure of **C**. [1]

(b) Photochromic glass used for sunglasses contains Ag*Cl* crystals which are added while the glass is in molten state. The glass darkens when exposed to bright light and the following reaction is involved.

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

(i) Suggest why the glass darkens when exposed to bright light. [1]

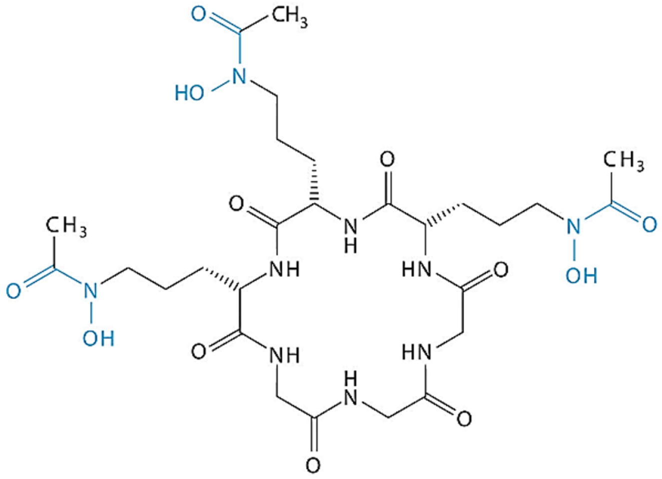
The glass darkens significantly within about a minute of exposure to bright light but takes a longer time to clear when there is less light. Small amount of Cu*Cl* crystals are often added to the glass to speed up the reverse process. No elemental copper is involved in the process.

$$Ag + Cl \rightarrow Ag^+ + Cl^-$$

(ii) Explain why the copper(I) ions can be described as a *homogeneous catalyst*. [2]

(iii) State the property, typical of transition metals, which allows copper(I) ions to behave as a homogenous catalyst in the reverse reaction. Include relevant chemical equations to support your answer. [3]

(c) Microorganisms synthesise and secrete organic molecules called siderophores to increase the total concentration of available iron in the surrounding medium. Ferrichrome is a siderophore produced by fungi.



Ferrichrome

(i) Ferrichrome binds to iron(III) ions via its oxygen atoms. This process facilitates the transportation of iron(III) ions into the interior of a cell.

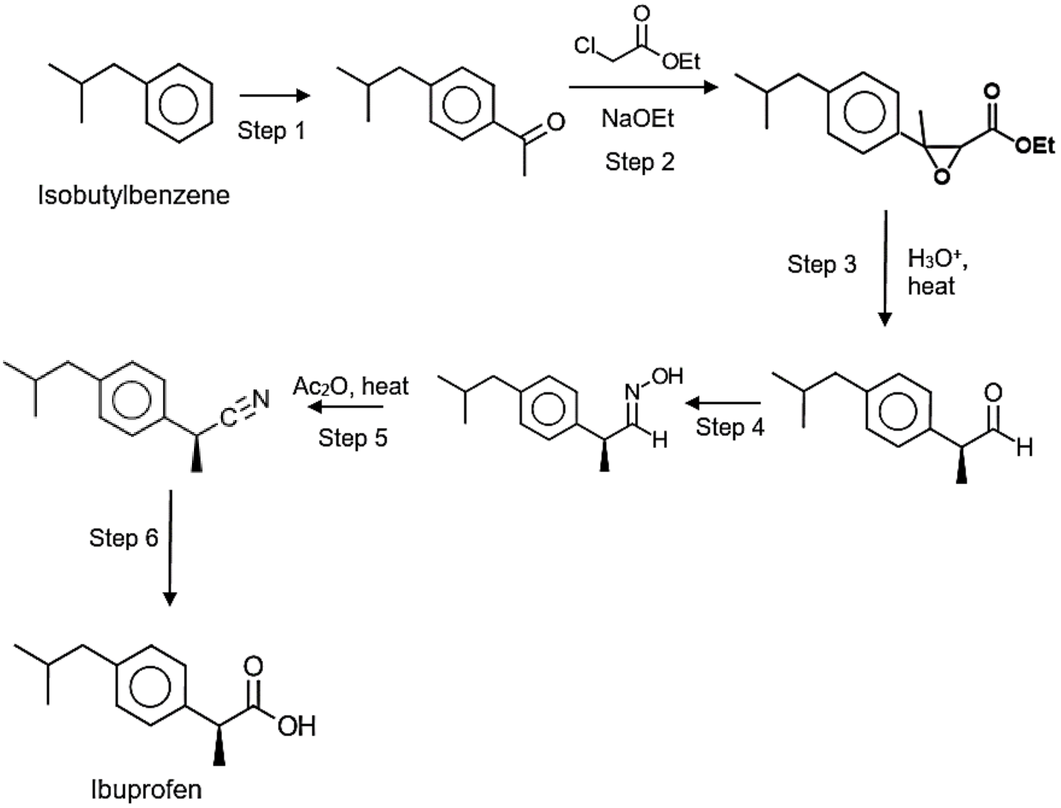
Suggest what bonds are formed during this process and why iron(III) does not bind to nitrogen atoms in ferrichrome. [2]

(ii) Draw the structures of the products formed when ferrichrome is heated with aqueous sodium hydroxide. [3]

[Total: 20]

2 Ibuprofen is a nonsteroidal anti-inflammatory drug. It works by reducing hormones that cause inflammation and pain in the body. Ibuprofen is used to reduce fever and treat pain or inflammation.

The conventional synthesis of ibuprofen from isobutylbenzene is shown below. Step 4 of the synthesis resembles the reaction between a carbonyl compound and Brady's reagent.

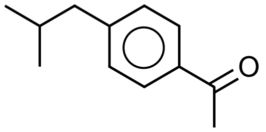


(a) Name the types of reaction that are occurring during steps 4 and 5. [2]

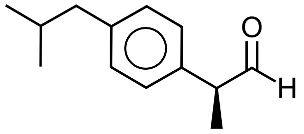
(b) Suggest the reagents and conditions for steps 1, 4 and 6. [3]

(c) Draw the structures of the stereoisomers of the product formed from step 4 and state the type of stereoisomerism exhibited. [2]

(d) Describe a simple chemical test to distinguish between the two compounds, **X** and **Y** obtained from synthesis above. [2]



Compound **X**



Compound **Y**

(e) Potassium chloride and potassium iodide can be distinguished by treating the compounds separately with concentrated sulfuric acid.

(i) Potassium chloride and concentrated sulfuric acid reacts in an equimolar ratio to produce white fumes of hydrogen chloride.

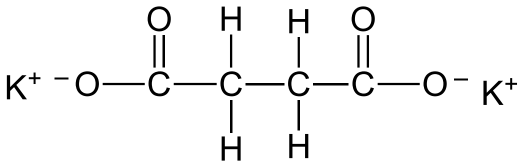
Write an equation for the reaction of potassium chloride with concentrated sulfuric acid. [1]

(ii) Potassium iodide reacts with concentrated sulfuric acid in a similar manner. However, the white fumes of hydrogen iodide would further react with concentrated sulfuric acid to produce violet fumes and hydrogen sulfide gas.

Suggest an explanation for the difference in reactions, and write equations for the above observations. [2]

(f) When aqueous potassium salts of a dicarboxylic acid are electrolysed using inert platinum electrodes, alkenes are formed at the anode.

(i) The electrolysis of aqueous potassium succinate gives ethene at the anode.



$K^{+}\ {}^{-}O-C(=O)-CH_2-CH_2-C(=O)-O^{-}\ K^{+}$

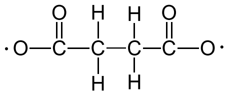
Potassium Succinate

Write an ion-electron half equation for the oxidation of succinate at the anode. [1]

(ii) Write an equation for the reaction at the cathode and for the overall reaction. [2]

(iii) The mechanism of the reaction at the anode involves three steps:

Step 1: There is an initial loss of 2 electrons on succinate ion to form

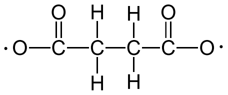


$\cdot O-C(=O)-CH_2-CH_2-C(=O)-O\cdot$

Step 2: This is followed by decarboxylation which involves the homolytic breaking of two C–C bonds, giving a radical intermediate $\cdot CH_2CH_2\cdot$

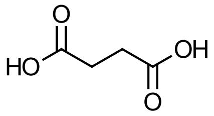
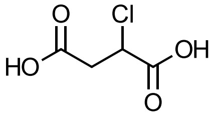
Step 3: The third step involves forming a covalent bond, producing ethene as the product.

Use the information given above to draw the mechanism for Steps 2 and 3.

You are advised to use structural formulae for all species, such as  $\cdot O-C(=O)-CH_2-CH_2-C(=O)-O\cdot$, so that it is clear which bonds are broken and which are formed.

Represent with a half arrow () for movement of a single unpaired electron and indicate any unpaired electrons by a dot (•). [2]

(g) The strength of a carboxylic acid depends on its structure. An example of this is the comparison of succinic acid and its derivatives.

Acid	pK_{a1}
	4.21
	-

Explain if pK_a of chlorosuccinic acid is lower or higher than the pK_a of succinic acid. [1]

[Total: 18]

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3 On 28 November 2018, an explosion erupted near the Hebei Shenghua Chemical Industrial plant, killing at least 23 people and injuring many more. It was reported that the explosion originated from a truck transporting ethyne gas, C_2H_2, which then set off a chain reaction that engulfed at least 50 other vehicles.

When mixed appropriately with air, C_2H_2 explodes upon ignition as follows.

$$C_2H_2\,(g) + \frac{5}{2}O_2\,(g) \longrightarrow 2CO_2\,(g) + H_2O\,(g)$$

This explosion may have generated an estimated 20.8 million kilojoules of energy.

(a) Describe the hybridisation of the orbitals in, and the bonds between, the carbon atoms within an ethyne molecule. [3]

(b) **(i)** Using the bond energies in the *Data Booklet*, calculate the enthalpy change of combustion of ethyne. [2]

(ii) Using your answer in **(b)(i)**, calculate the volume of ethyne gas transported by the truck at 28°C and 1 bar. [2]

(c) One of the ways that ethyne gas can be produced is via the reaction of calcium carbide, CaC_2, with water, producing solid calcium hydroxide as a by-product.

(i) Using the following information and relevant data from the *Data Booklet*, construct an energy cycle to calculate the lattice energy of solid calcium hydroxide. [3]

$$Ca^{2+}(g) + 2OH^{-}(g) \longrightarrow Ca(OH)_2\,(s)$$

standard enthalpy change of atomisation of Ca (s) = + 178 kJ mol^{-1}

standard enthalpy change of formation of OH^{-} (g) = − 230 kJ mol^{-1}

standard enthalpy change of formation of $Ca(OH)_2$ (s) = − 985 kJ mol^{-1}

(ii) Suggest, with reasoning, how the magnitude of the lattice energy of $Ca(OH)_2$ compares with that of calcium carbide, CaC_2, given the following data. [2]

Ion	Radius (pm)
OH^{-}	133
C_2^{2-}	118

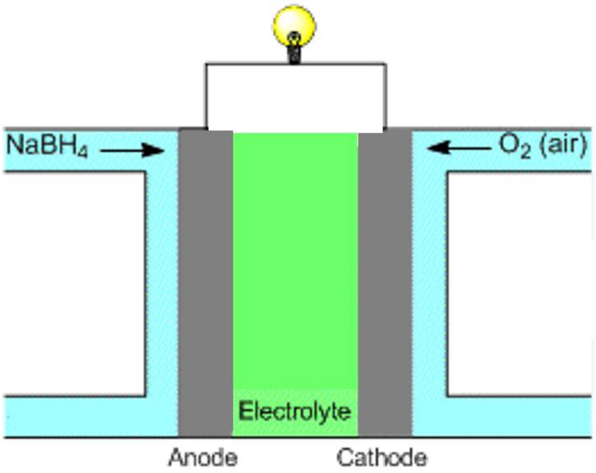
(iii) The value of $\Delta G^{\ominus}$ for the reaction of calcium carbide with water is -148 kJ mol^{-1}.

$$CaC_2\,(s) + 2H_2O\,(l) \longrightarrow Ca(OH)_2\,(s) + C_2H_2\,(g) \qquad \Delta H = -128 \text{ kJ mol}^{-1}$$

Calculate $\Delta S^{\ominus}$ in J mol^{-1} K^{-1} to one decimal place for the reaction. Explain the significance of its sign with reference to the equation. [2]

(d) Similar to calcium carbide, sodium borohydride, $NaBH_4$, can be used in fuel cells.

Direct borohydride fuel cells (DBFCs), are fuel cells which are directly fed by $NaBH_4$ as the fuel and oxygen as the oxidant. The electrolyte used is potassium hydroxide. Sodium metaborate, $NaBO_2$, and water are formed as the only products during the discharging process.



(i) Deduce the ion-electron half–equations for the anode and cathode and hence write the overall cell reaction during discharging. [2]

(ii) A typical DBFC fuel cell generates about 1.64 V. Using the *Data Booklet*, calculate the E^θ involving the $NaBO_2/NaBH_4$ half-cell. [1]

(iii) Use the half–equations you have written in **(d)(i)** to calculate the value of $\Delta G^\ominus$ and comment on the significance of $\Delta G^\ominus$. [1]

(iv) Explain qualitatively what happens to the cell potential, E_{cell} when a small amount of propanal contaminant is accidently added to the anode half-cell.

The contaminant does not take part in the cell reaction. [2]

(v) In a particular DBFC, a current of 1.35×10^{-2} A cm^{-3} was passed through the circuit for 95 minutes.

Calculate the mass of $NaBO_2$ that was produced per 25 cm^3 of solution. [2]

[Total: 22]

Section B

Answer **one** question from this section.

4 Chlorine-containing compounds have many useful applications. One such example is the use of chloric(I) acid, $HClO$, to disinfect water in swimming pools.

$HClO$ dissociates in water as shown below.

$$HClO + H_2O \rightleftharpoons H_3O^+ + ClO^-$$

(a) **(i)** Write an expression for K_a of $HClO$. [1]

(ii) A disinfectant solution was prepared by dissolving 10 g of $HClO$ and x g of $NaClO$ in 100 cm^3 of water.

For effective disinfection, a pH of 7.35 was needed to reach the optimal $[ClO^-]:[HClO]$ ratio.

Given that the pK_a of $HClO$ is 7.55, determine the optimal $[ClO^-]:[HClO]$ ratio and hence the mass of $NaClO$, x. [2]

(iii) A worker accidentally poured some alkaline solution into the disinfectant solution formed in **(a)(ii)** but found that the pH was still about 7.35.

Write an equation to explain this. [1]

(b) Hydrogen chloride is another chlorine-containing compound.

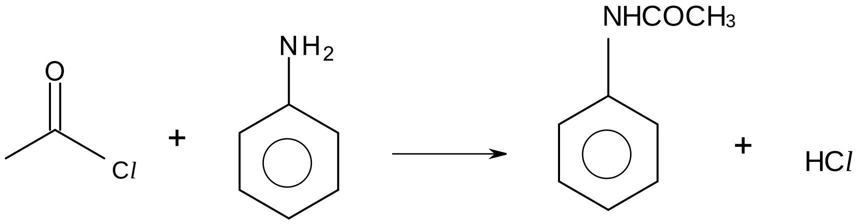
Alkyl chlorides can be synthesised from alcohols using hydrogen chloride. However, acyl chlorides **cannot** be prepared from carboxylic acids in the same way. One key factor is due to the stronger C-O bond present in carboxylic acids.

$$ROH \xrightarrow{HCl} RCl$$

$$RCO_2H \; \cancel{\xrightarrow{HCl}} \; RCOCl$$

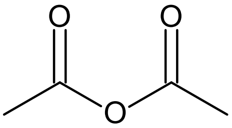
Suggest an explanation for the stronger C-O bond in carboxylic acids. [1]

(c) Acetanilide is an analgesic and can be formed from ethanoyl chloride and phenylamine.



acetanilide

Instead of ethanoyl chloride, ethanoic anhydride is more commonly used in the laboratory to form acetanilide in a similar manner.



ethanoic anhydride

(i) Suggest the other organic product that is produced together with acetanilide. [1]

The experimental procedure for the laboratory synthesis of acetanilide using ethanoic anhydride is given below.

1. Mix phenylamine and hydrochloric acid in a beaker.
2. Stir the mixture until a clear solution is obtained.
3. To the clear solution, add ethanoic anhydride and immediately add a solution of sodium ethanoate.
4. Stir the mixture vigorously.
5. Cool the solution in an ice water bath.
6. Filter the acetanilide formed. Wash with cold water and crystallise using a mixture of water and methanol.

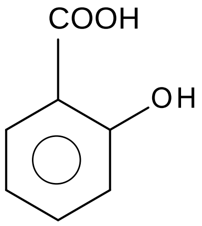
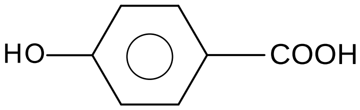
(ii) In step 1, HC*l* was added to increase the solubility of phenylamine in water. Explain. [1]

(iii) Sodium ethanoate is essential to ensure phenylamine is present in step 3 to react with ethanoic anhydride.

Suggest the role of sodium ethanoate. [1]

(iv) Suggest how you could check that the acetanilide obtained in step 6 is pure. [1]

(d) Aspirin is another analgesic and it can be synthesised from salicylic acid. The pK_a values of salicylic acid and its isomer are given below:

Acid	pK_{a1}	pK_{a2}
 Salicylic acid	3.0	13.4
 4-hydroxybenzoic acid	4.1	9.7

Explain the following:

(i) pK_{a1} of salicylic acid is smaller than pK_{a1} of 4-hydroxybenzoic acid. [1]

(ii) pK_{a2} is larger than pK_{a1} of 4-hydroxybenzoic acid. [1]

(e) When compound **A**, $C_{10}H_{11}NO$, is oxidised with acidified manganate(VII) ions, $[C_7H_8NO_2]^+$ and compound **B**, $C_3H_4O_3$, are formed. Compound **B** produces effervescence when Na_2CO_3 is added to it and gives an orange precipitate with 2,4-dinitrophenylhydrazine reagent.

Compound **A** reacts readily with 4 moles of Br_2(aq) to give compound **C**, $C_{10}H_9NO_2Br_4$.

Compound **A** also gives an orange precipitate with 2,4-dinitrophenylhydrazine reagent and reacts with hot alkaline aqueous iodine to give compound **D**, $C_9H_8NO_2Na$.

Suggest the structures of compounds **A**, **B**, **C** and **D**. Explain the reactions that occur. [9]

[Total: 20]

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[**Turn Over**

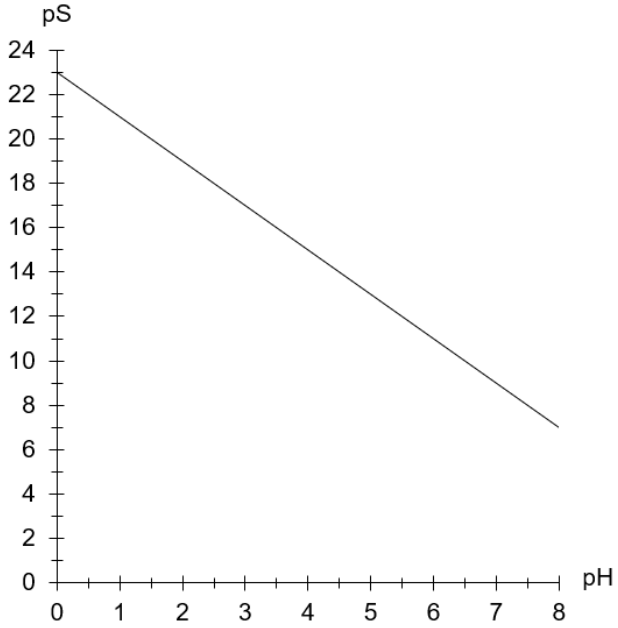
5 **(a)** Hydrogen sulfide gas, H_2S, is a reagent used in qualitative analysis. When H_2S is passed into a solution containing metal cations, metal sulfides are precipitated.

In aqueous medium, H_2S dissociates partially in a step-wise manner to give two equilibrium reactions:

$$H_2S \rightleftharpoons H^+ + HS^-$$

$$HS^- \rightleftharpoons H^+ + S^{2-}$$

The relationship between the H^+ ion concentration and S^{2-} ion concentration, as a result of H_2S dissociation, is shown in the graph below, where $pS = -\log_{10}[S^{2-}]$.



Solution **X** contains 0.1 mol dm^{-3} $CuSO_4$ and 0.05 mol dm^{-3} $MnSO_4$. Hydrogen sulfide gas is bubbled into **X** until saturation and the pH is maintained at 2.0.

The value of the solubility product of CuS and MnS are 1.0×10^{-44} and 1.4×10^{-15}, respectively.

(i) With reference to CuS, define the term *solubility product*. [1]

(ii) Calculate the minimum concentration of sulfide ions needed to precipitate CuS. [1]

(iii) The minimum concentration of sulfide ions needed to precipitate MnS is 2.80×10^{-14} mol dm^{-3}.

Using the graph above and your answer in **(a)(ii)**, explain whether it is possible to separate copper and manganese ions in **X** at pH = 2. [2]

(iv) Determine the maximum pH for solution **X** before separation of copper and manganese ions is no longer possible. [1]

(b) When water ligands in a hydrated metal ion are substituted by other ligands, the equilibrium constant for the reaction is referred to as the stability constant, K_{stab}, of the new complex. The higher the value of K_{stab}, the more likely the complex will be formed.

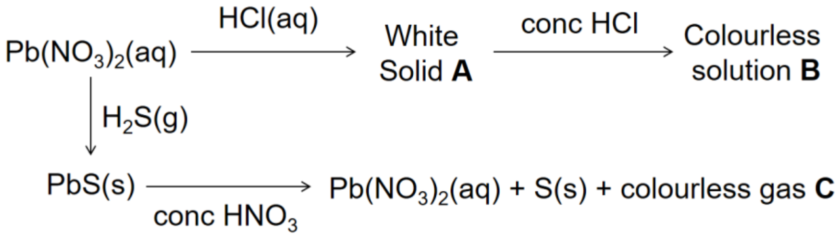
The stability constants for 3 reactions are given below.

Reaction	Colour of complex formed	Value of $\log_{10}(K_{stab})$
$Fe^{3+}(aq) + 6CN^{-}(aq) \rightleftharpoons [Fe(CN)_6]^{3-}(aq)$	Yellow	31.0
$Fe^{3+}(aq) + EDTA^{4-}(aq) \rightleftharpoons [Fe(EDTA)]^{-}(aq)$	Brown	25.1
$Fe^{3+}(aq) + SCN^{-}(aq) \rightleftharpoons [Fe(SCN)]^{2+}(aq)$	Red	2.1

Describe the colour change(s) of the solution when excess NaSCN is added to $[Fe(EDTA)]^{-}$, followed by an excess of KCN(aq).

Explain the observation, with reference to the table above. [2]

(c) A solution of $Pb(NO_3)_2$ is subjected to the following reactions.



(i) Suggest the identity of white solid **A** and complex anion present in colourless solution **B**. [2]

(ii) Colourless gas **C** is obtained from the reaction of solid PbS and concentrated HNO_3, which is readily oxidised in air to form a brown acidic gas.

Suggest the identity of **C**. [1]

(d) Thiols are sulfur-containing compounds that can be prepared from alkyl halides and the hydrosulfide nucleophile, ^{-}SH.

Ethanethiol is prepared from chloroethane using NaSH as shown below.

$$CH_3CH_2Cl \xrightarrow{NaSH} CH_3CH_2SH$$

Ethanethiol

(i) Suggest a synthesis of propanethiol starting from propylethanoate.

You should state the reagents and conditions for each step, and show clearly the structure of any intermediate compounds. [3]

CH_3CH_2SH can react with a base, NaH, to give $CH_3CH_2S^-$.

$CH_3CH_2SH + NaH \rightarrow CH_3CH_2S^-Na^+ + H_2$ ----- Reaction 1

$CH_3CH_2S^-$ further reacts with chloroethane, to yield diethyl sulfide

$CH_3CH_2S^-Na^+ + CH_3CH_2Cl \rightarrow CH_3CH_2SCH_2CH_3 + NaCl$ ----- Reaction 2

Diethyl sulfide

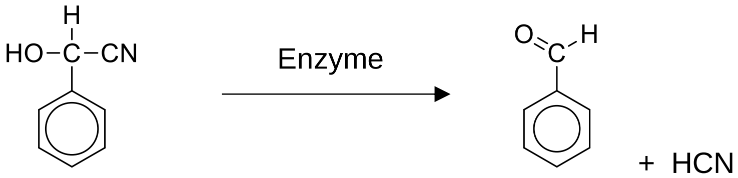
(ii) Suggest why $CH_3CH_2S^-$, is a better nucleophile than $CH_3CH_2O^-$. [1]

(iii) Diethyl sulfide is a good nucleophile.

In Reaction 2, a side product, $C_6H_{15}SCl$, is formed when chloroethane is used in excess. $C_6H_{15}SCl$ gives a white precipitate with aqueous silver nitrate.

Suggest the structural formula of the side product $C_6H_{15}SCl$. [1]

(e) The millipede *Apheeloria corrugate* protects itself by secreting the cyanohydrin mandelonitrile and an enzyme that decompose mandelonitrile into benzaldehyde and HCN.



Mandelonitrile

(i) State the type of reaction for the formation of Mandelonitrile from benzaldehyde. [1]

(ii) Suggest a chemical test that will give a positive test for Mandelonitrile but not for benzaldehyde. [2]

(iii) A student made the following statement, "benzaldehyde can be directly synthesized from phenylmethanol, $C_6H_5CH_2OH$, but not from benzoic acid."

Based on your knowledge of the reagents and conditions for each reaction, deduce if the statement is true. [2]

[Total: 20]

PRELIMINARY EXAMINATIONS

HIGHER 2

TEMASEK
JUNIOR COLLEGE

CHEMISTRY 9729/03

Paper 3 Free Response

16 September 2019

2 hours

Candidates answer on separate booklet.

Additional Materials: 12-Page Answer Booklet
Data Booklet

READ THESE INSTRUCTIONS FIRST

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

Section A
Answer **all** questions.

Section B
Answer **one** question.

A Data Booklet is provided.
The use of an approved scientific calculator is expected, where appropriate.

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

This document consists of **14** printed pages and **2** blank pages.

[Turn Over

Section A

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

1 The term *chelates*, originates from the Greek word *chele* for “claw”. It refers to compounds containing ligands bonded to a central metal atom or ion at two or more points.

Ligand exchange occurs when ammonia and ethylenediamine (en), $H_2NCH_2CH_2NH_2$, are added separately to copper sulfate solution.

(a) **(i)** Explain all the changes observed when aqueous ammonia is added dropwise to $Cu^{2+}(aq)$ till in excess. Suggest the formulae of all relevant copper compounds formed and write equations for all reactions. [4]

When aqueous ammonia is added dropwise to blue $Cu^{2+}(aq)$ solution, a blue precipitate of $Cu(OH)_2$ is formed. Ammonia acts as a base.

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

$$[Cu(H_2O)_6]^{2+}(aq) + 2OH^-(aq) \rightleftharpoons [Cu(OH)_2(H_2O)_4](s) + 2H_2O(l) \quad \text{— (1)}$$

Blue ppt

$$\text{OR } Cu^{2+}(aq) + 2OH^-(aq) \rightleftharpoons Cu(OH)_2(s)$$

In excess ammonia, blue precipitate $Cu(OH)_2(s)$ dissolves to give a dark blue solution due to the formation of the complex ion, $[Cu(NH_3)_4(H_2O)_2]^{2+}(aq)$.

Ammonia acts as a ligand (or ligand exchange has taken place).

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

Dark blue solution

Formation of the complex shifts the equilibrium in equation (1) to the left, thus, the blue precipitate dissolves.

(ii) Suggest why ethylenediamine can function as a *chelating ligand*. [1]

- **Ethylenediamine molecule has two lone pair of electrons on the nitrogen atoms to form two dative bonds with the Cu^{2+} ion.**

(iii) When ethylenediamine is added to $Cu^{2+}(aq)$, the following occurs.

$$[Cu(H_2O)_6]^{2+} + 2en \rightarrow [Cu(en)_2(H_2O)_2]^{2+} + 4H_2O$$

Predict whether ethylenediamine or ammonia gives a more positive entropy change when added to $Cu^{2+}(aq)$. [2]

$$Cu(H_2O)_6]^{2+} + 2en \rightarrow [Cu(en)_2(H_2O)_2]^{2+} + 4H_2O$$

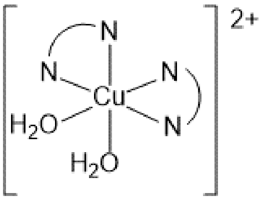
$$[Cu(H_2O)_6]^{2+}(aq) + 4NH_3(aq) \rightarrow [Cu(NH_3)_4(H_2O)_2]^{2+}(aq) + 4H_2O(l)$$

- **Ethylenediamine (a bidentate ligand) gives a more positive change in entropy when added to $Cu^{2+}(aq)$ as**
- **there is an increase in number of particles (from 3 to 5) and thus more way of arranging the particles.**

(iv) Suggest the coordination number and shape of $[Cu(en)_2(H_2O)_2]^{2+}$. [1]

- **Coordination number = 6, Shape = Octahedral**

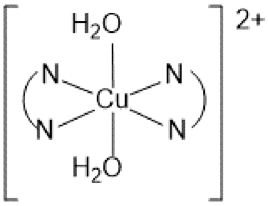
(v) The complex ion $[Cu(en)_2(H_2O)_2]^{2+}$ can exist as three stereoisomers, **A**, **B** and **C**. Isomers **A** and **B** rotate plane-polarised light but **C** does not. The structure of **A** is represented below.



Isomer **A**

where  represents ethylenediamine (en)

Draw the structure of **C**. [1]



- **Isomer C**

(b) Photochromic glass used for sunglasses contains AgC*l* crystals which are added while the glass is in molten state. The glass darkens when exposed to bright light and the following reaction is involved.

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

(i) Suggest why the glass darkens when exposed to bright light. [1]

- **In presence of UV light, colorless Ag^+ cations form elemental Ag and the glass appear darker.**

The glass darkens significantly within about a minute of exposure to bright light but takes a longer time to clear when there is less light. Small amount of CuC*l* crystals are often added to the glass to speed up the reverse process. No elemental copper is involved in the process.

$$Ag + Cl \rightarrow Ag^+ + Cl^-$$

(ii) Explain why the copper(I) ions can be described as a *homogeneous catalyst*. [2]

The copper(I) ions are in the •same phase as the reactants, and is •not consumed/used up by the reaction.

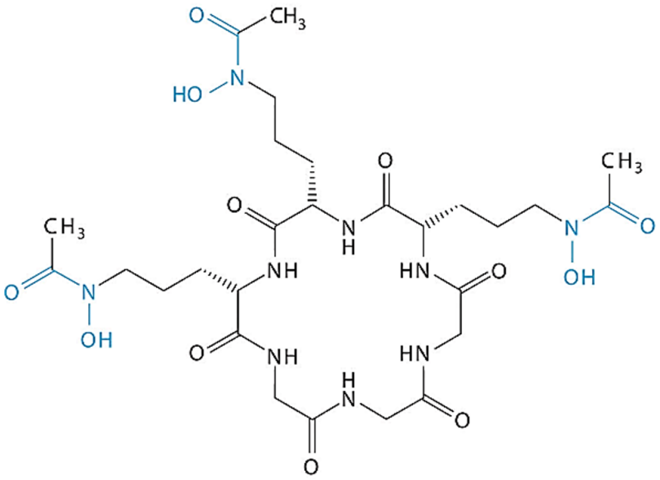
(iii) State the property, typical of transition metals, which allows copper(I) ions to behave as a homogenous catalyst in the reverse reaction. Include relevant chemical equations to support your answer. [3]

- **The catalytic activity of transition metals in homogenous catalysis depends on their ability to exist in variable oxidation states.**

The catalysed pathway for the reverse reaction.

- **$Cu^+ + Cl \rightarrow Cu^{2+} + Cl^-$**
- **$Cu^{2+} + Ag \rightarrow Cu^+ + Ag^+$**

(c) Microorganisms synthesise and secrete organic molecules called siderophores to increase the total concentration of available iron in the surrounding medium. Ferrichrome is a siderophore produced by fungi.



Ferrichrome

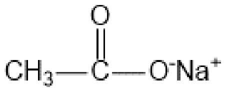
(i) Ferrichrome binds to iron(III) ions via its oxygen atoms. This process facilitates the transportation of iron(III) ions into the interior of a cell.

Suggest what bonds are formed during this process and why iron(III) does not bind to nitrogen atoms in ferrichrome. [2]

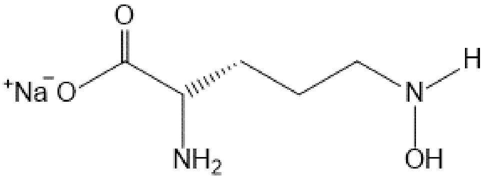
- **Ferrichrome binds to iron(III) ions through the formation of dative bonds between oxygen atoms and iron(III) ions.**
- **Lone pair of electrons on the nitrogen atoms are delocalised over the C=O group and are not available for dative bonding to iron(III) ions.**

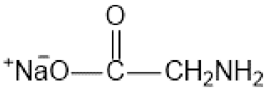
(ii) Draw the structures of the products formed when ferrichrome is heated with aqueous sodium hydroxide. [3]

●●● 1 mark for each structure



$CH_3-\overset{\overset{O}{\|}}{C}-O^-Na^+$



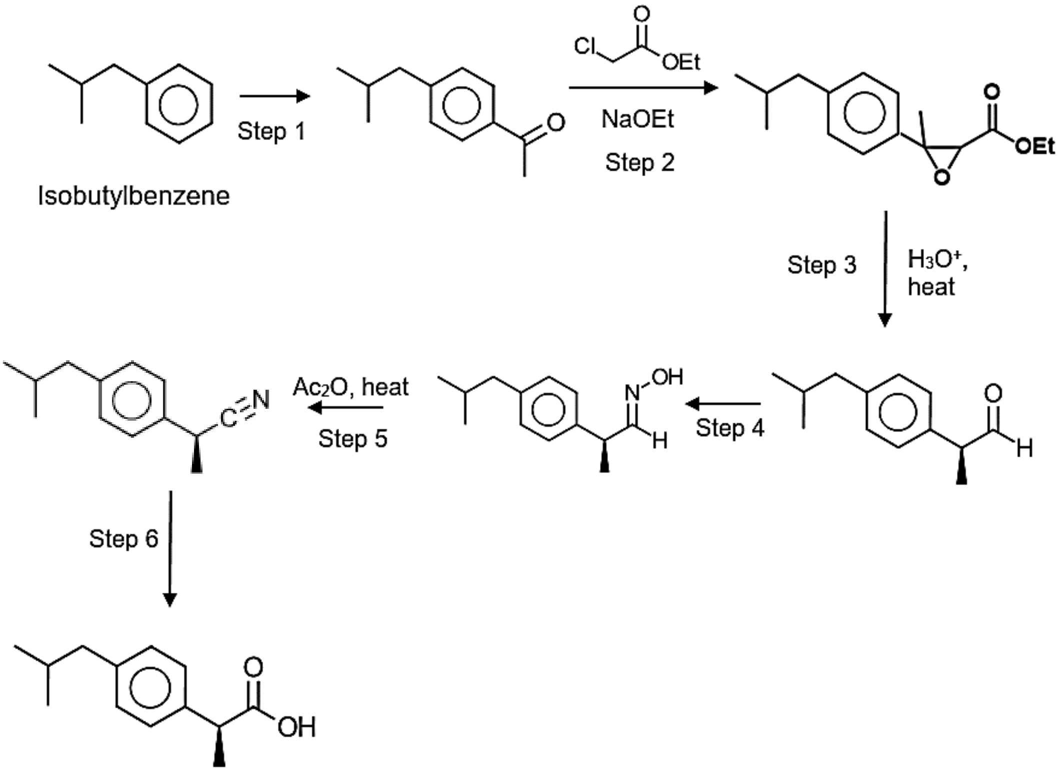


$^+Na^-O-\overset{\overset{O}{\|}}{C}-CH_2NH_2$

[Total: 20]

2 Ibuprofen is a nonsteroidal anti-inflammatory drug. It works by reducing hormones that cause inflammation and pain in the body. Ibuprofen is used to reduce fever and treat pain or inflammation.

The conventional synthesis of ibuprofen from isobutylbenzene is shown below. Step 4 of the synthesis resembles the reaction between a carbonyl compound and Brady's reagent.



Isobutylbenzene

Ibuprofen

(a) Name the types of reaction that are occurring during steps 4 and 5. [2]

•Step 4 : condensation reaction

•Step 5 : elimination

(b) Suggest the reagents and conditions for steps 1, 4 and 6. [3]

•Step 1 : CH_3COCl , anhydrous $AlCl_3$, r.t.p

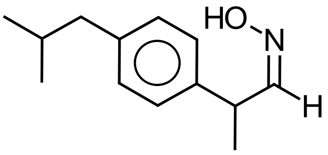
•Step 4 : NH_2OH, r.t.p

•Step 6 : dilute HCl, heat

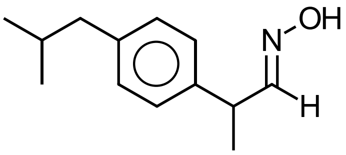
(c) Draw the structures of the stereoisomers of the product formed from step 4 and state the type of stereoisomerism exhibited. [2]

•Type : cis-trans isomerism

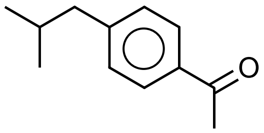
•



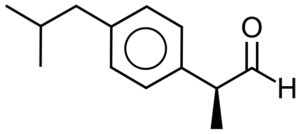
and



(d) Describe a simple chemical test to distinguish between the two compounds, **X** and **Y** obtained from synthesis above. [2]



Compound **X**



Compound **Y**

•Add Tollens reagent (diammine silver(I) complex), **HEAT** to separate samples.

•Silver mirror observed for compound Y. No silver mirror for compound X.

Alternative tests :

*** Alkaline aq. Iodine and warm. Yellow ppt observed for compound X and no yellow ppt for compound Y.**

*** Fehling's reagent, heat. Brick-red observed for compound Y and no brick-red ppt for compound X**

*** Acidified $K_2Cr_2O_7$, heat. Orange dichromate turned green when added to compound Y. No colour change for compound X.**

(e) Potassium chloride and potassium iodide can be distinguished by treating the compounds separately with concentrated sulfuric acid.

(i) Potassium chloride and concentrated sulfuric acid reacts in an equimolar ratio to produce white fumes of hydrogen chloride.

Write an equation for the reaction of potassium chloride with concentrated sulfuric acid. [1]

Reaction of KCl and H_2SO_4

•$KCl + H_2SO_4 \longrightarrow KHSO_4 + HCl$

(ii) Potassium iodide reacts with concentrated sulfuric acid in a similar manner. However, the white fumes of hydrogen iodide would further react with concentrated sulfuric acid to produce violet fumes and hydrogen sulfide gas.

Suggest an explanation for the difference in reactions, and write equations for the above observations. [2]

Reaction of KI and H_2SO_4

$KI + H_2SO_4 \longrightarrow HI + KHSO_4$

Half equations:

$2I^- \rightarrow I_2 + 2e^-$ (x4)

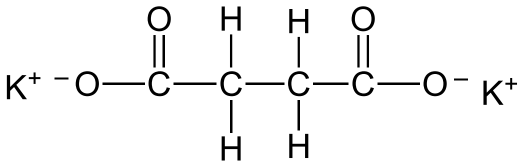
$H_2SO_4 + 8H^+ + 8e^- \rightarrow H_2S + 4H_2O$

• Overall: $8HI + H_2SO_4 \longrightarrow 4I_2 + H_2S + 4H_2O$

• I^- being a stronger reducing agent (than Cl^-) will reduce H_2SO_4 to H_2S and itself oxidised to I_2. OR • $E^{\ominus}_{I_2/I^-}$ is more negative than $E^{\ominus}_{Cl_2/Cl^-}$, thus more easily oxidized, stronger reducing agent than Cl^-. $E^{\ominus}_{I_2/I^-} = +0.54V$; $E^{\ominus}_{Cl_2/Cl^-} = +1.36V$.

(f) When aqueous potassium salts of a dicarboxylic acid are electrolysed using inert platinum electrodes, alkenes are formed at the anode.

(i) The electrolysis of aqueous potassium succinate gives ethene at the anode.

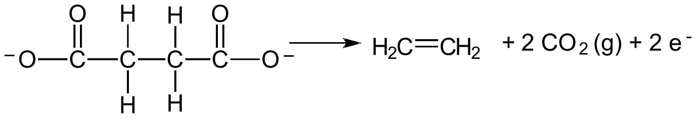


$K^{+}\ {}^{-}O_2CCH_2CH_2CO_2^{-}\ K^{+}$

Potassium Succinate

Write an ion-electron half equation for the oxidation of succinate at the anode. [1]

●



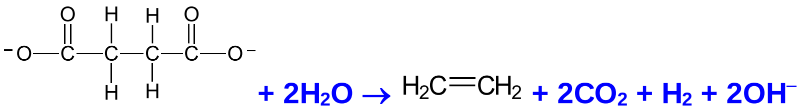
$^{-}O_2CCH_2CH_2CO_2^{-} \rightarrow H_2C{=}CH_2 + 2\,CO_2(g) + 2\,e^{-}$

(ii) Write an equation for the reaction at the cathode and for the overall reaction. [2]

●At the cathode: $2H_2O + 2e^{-} \rightarrow H_2 + 2OH^{-}$

[Explanation: Since $E^{\ominus}_{H_2O/H_2}$ *is more positive than* $E^{\ominus}_{K^+/K}$*,* H_2O *is preferentially reduced at the cathode, liberating* H_2*.]*

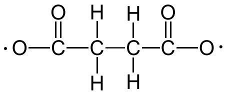
●Overall reaction:



$^{-}O_2CCH_2CH_2CO_2^{-} + 2H_2O \rightarrow H_2C{=}CH_2 + 2CO_2 + H_2 + 2OH^{-}$

(iii) The mechanism of the reaction at the anode involves three steps:

Step 1: There is an initial loss of 2 electrons on succinate ion to form



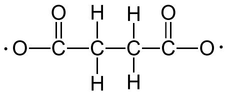
$\cdot O_2CCH_2CH_2CO_2\cdot$

Step 2: This is followed by decarboxylation which involves the homolytic breaking of two C–C bonds, giving a radical intermediate •CH_2CH_2•

Step 3: The third step involves forming a covalent bond, producing ethene as the product.

Use the information given above to draw the mechanism for Steps 2 and 3.

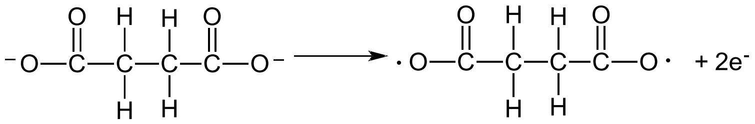
You are advised to use structural formulae for all species, such as



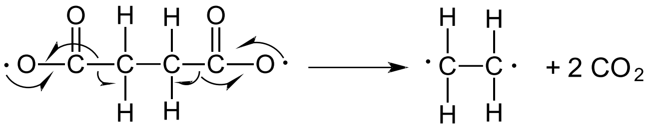
$\cdot O_2CCH_2CH_2CO_2\cdot$,

so that it is clear which bonds are broken and which are formed.

Represent with a half arrow () for movement of a single unpaired electron and indicate any unpaired electrons by a dot (•). [2]



$^{-}O_2CCH_2CH_2CO_2^{-} \rightarrow \cdot O_2CCH_2CH_2CO_2\cdot + 2e^{-}$



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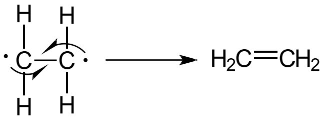
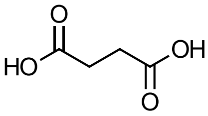
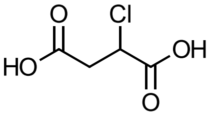


●

(g) The strength of a carboxylic acid depends on its structure. An example of this is the comparison of succinic acid and its derivatives.

Acid	pK_{a1}
	4.21
	-

Explain if pK_a of chlorosuccinic acid is lower or higher than the pK_a of succinic acid. [1]

●pK_a of chlorosuccinic acid is lower (a stronger acid)

Reason: presence of electron-withdrawing Cl-atom disperse the negative charge on anion more, better stabilising the anion more, so chlorosuccinic acid is a stronger acid (lower pK_a).

[Total: 18]

3 On 28 November 2018, an explosion erupted near the Hebei Shenghua Chemical Industrial plant, killing at least 23 people and injuring many more. It was reported that the explosion originated from a truck transporting ethyne gas, C_2H_2, which then set off a chain reaction that engulfed at least 50 other vehicles.

When mixed appropriately with air, C_2H_2 explodes upon ignition as follows.

$$C_2H_2\,(g) + \frac{5}{2}O_2\,(g) \longrightarrow 2CO_2\,(g) + H_2O\,(g)$$

This explosion may have generated an estimated 20.8 million kilojoules of energy.

(a) Describe the hybridisation of the orbitals in, and the bonds between, the carbon atoms within an ethyne molecule. [3]

- One of the 2s electrons in each C atom is promoted to the vacant 2p orbital, and **the s and one p orbital then hybridise/mix to give two sp hybrid orbitals** which contain one electron each.
- One **σ bond** between adjacent C atoms formed through / bonded by **head –on overlap of** one **sp hybrid orbital of each C atom**.

- Two π **bonds** are formed through **sideway overlap of the** two unhybridised **p orbitals of each C atom.**

(b) **(i)** Using the bond energies in the *Data Booklet*, calculate the enthalpy change of combustion of ethyne. [2]

$$H–C{\equiv}C–H + \frac{5}{2}O{=}O \longrightarrow 2\ O{=}C{=}O + H–O–H$$

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

$$\mathbf{\Delta H_c^\ominus = [2(410) + (840) + \frac{5}{2}(496)] – [4(805) + 2(460)]}$$

- = –**1240 kJ mol^{-1}**

(ii) Using your answer in **(b)(i)**, calculate the volume of ethyne gas transported by the truck at 28°C and 1 bar. [2]

- Amount of ethyne gas used for combustion = $\frac{20.8\times10^6}{1240}$ = 16774 mol

Using pV=nRT

- Vol. of ethyne gas produced = $\frac{16774\times8.31\times(273+28)}{1.00\times10^5}$ = 420 m^3

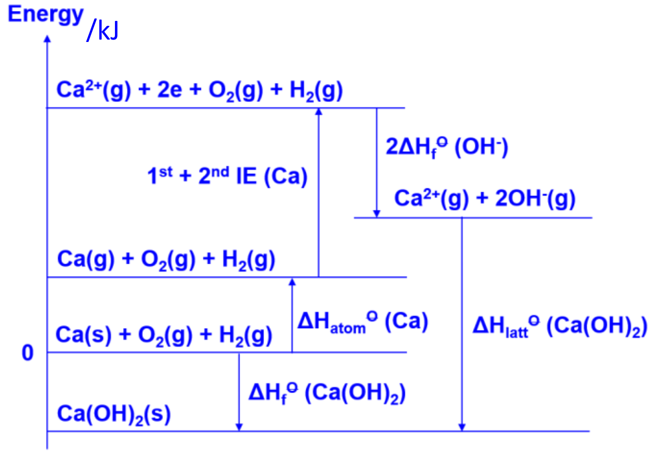
(c) One of the ways that ethyne gas can be produced is via the reaction of calcium carbide, CaC_2, with water, producing solid calcium hydroxide as a by-product.

(i) Using the following information and relevant data from the *Data Booklet*, construct an energy cycle to calculate the lattice energy of solid calcium hydroxide. [3]

$$Ca^{2+}(g) + 2OH^-(g) \longrightarrow Ca(OH)_2(s)$$

standard enthalpy change of atomisation of Ca (s)	= + 178 kJ mol^{-1}
standard enthalpy change of formation of OH^- (g)	= − 230 kJ mol^{-1}
standard enthalpy change of formation of $Ca(OH)_2$ (s)	= − 985 kJ mol^{-1}

Energy Level Diagram

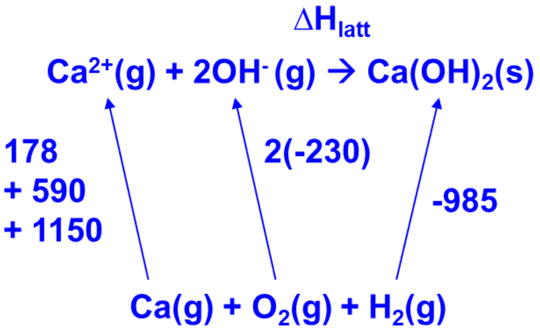


By Hess' Law,

$\Delta H_f^\ominus (Ca(OH)_2)$ = $\Delta H_{at}^\ominus$ (Ca) + 1st IE (Ca) + 2nd IE (Ca) + $2\Delta H_f^\ominus(OH^-)$ + $\Delta H_{latt} (Ca(OH)_2)$

– 985 = 178 + 590 + 1150 + 2(– 230) + $\Delta H_{latt} (Ca(OH)_2)$

• $\Delta H_{latt} (Ca(OH)_2)$ = – 2443 kJ mol^{-1}



(ii) Suggest, with reasoning, how the magnitude of the lattice energy of $Ca(OH)_2$ compares with that of calcium carbide, CaC_2, given the following data. [2]

Ion	Radius (pm)
OH^-	133
C_2^{2-}	118

$|\Delta H_{latt}| \propto \frac{q_+ q_-}{r_+ + r_-}$ for ionic compound

Ionic radius or r^- : OH^- **>** C_2^{2-} q_+ , r_+ constants

Ionic charge or r^- : OH^- **<** C_2^{2-}

•

Magnitude/value of the lattice energy CaC_2 is larger than that of $Ca(OH)_2$

(iii) The value of $\Delta G^\ominus$ for the reaction of calcium carbide with water is -148 kJ mol^{-1}.

$CaC_2(s) + 2H_2O(l) \longrightarrow Ca(OH)_2(s) + C_2H_2(g)$ $\quad \Delta H = -128$ kJ mol^{-1}

Calculate $\Delta S^\ominus$ in J mol^{-1} K^{-1} to one decimal place for the reaction. Explain the significance of its sign with reference to the equation. [2]

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

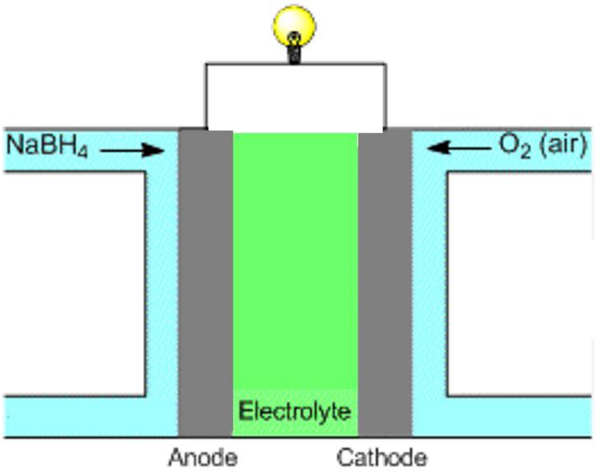
$-148 = -128 - (298)\Delta S^\ominus$

• **$\Delta S^\ominus$ = +67.1 J mol^{-1} K^{-1} (to 1 dp)**

• $\Delta S^\ominus$ is positive because there is **an increase in the number of moles of gaseous molecules** produced in the chemical reaction (from 0 in reactants to 1 in products) **and hence an increase in disorder** of the system.

(d) Similar to calcium carbide, sodium borohydride, $NaBH_4$, can be used in fuel cells.

Direct borohydride fuel cells (DBFCs), are fuel cells which are directly fed by $NaBH_4$ as the fuel and oxygen as the oxidant. The electrolyte used is potassium hydroxide. Sodium metaborate, $NaBO_2$, and water are formed as the only products during the discharging process.



(i) Deduce the ion-electron half–equations for the anode and cathode and hence write the overall cell reaction during discharging. [2]

- **Anode: $NaBH_4 + 8OH^- \rightarrow NaBO_2 + 6H_2O + 8e^-$**

  Cathode: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

- **Overall: $NaBH_4 + 2O_2 \rightarrow NaBO_2 + 2H_2O$**

(ii) A typical DBFC fuel cell generates about 1.64 V. Using the *Data Booklet*, calculate the E^θ involving the $NaBO_2/NaBH_4$ half-cell. [1]

$E^\theta_{cell} = E^\theta_{red} - E^\theta_{oxid}$

$1.64 = 0.40 - E^\theta_{oxid}$

• **E^θ = -1.24 V**

(iii) Use the half–equations you have written in **(d)(i)** to calculate the value of $\Delta G^{\ominus}$ and comment on the significance of $\Delta G^{\ominus}$. [1]

n = **8**

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

$\Delta G^{\ominus} = -(8 \times 1.64 \times 96500) =$ **-1266080 J mol^{-1}**

$\Delta G^{\ominus}$ is negative or G < 0 hence the **reaction is spontaneous** or energetically **feasible**

(iv) Explain qualitatively what happens to the cell potential, E_{cell} when a small amount of propanal contaminant is accidently added to the anode half-cell.

The contaminant does not take part in the cell reaction. [2]

$NaBO_2 + 6H_2O + 8e^- \rightleftharpoons NaBH_4 + 8OH^-$ -- (1) **E_{oxid}**

The **$NaBH_4$ is used to reduce the propanal** to propanol, causing the $[NaBH_4]$ to decrease.

By *Le Chatelier's Principle*, the **equilibrium position (1) will shift right to increase $NaBH_4$, favouring the reduction reaction.**

E_{oxid} or **$E_{NaBO2/NaBH4}$ will become more positive/less -ve**

Hence, producing a less positive E_{cell} or **a value less than 1.64 V** .

(v) In a particular DBFC, a current of 1.35×10^{-2} A cm^{-3} was passed through the circuit for 95 minutes.

Calculate the mass of $NaBO_2$ that was produced per 25 cm^3 of solution. [2]

• Quantity of charge, Q = It = $(1.35 \times 10^{-2}$ A cm$^{-3})(25) \times (95 \times 60) =$ **1923.8 C**

No of moles of electrons transferred $= \dfrac{1923.75}{96500} = 1.993 \times 10^{-2}$ mol

No of moles of $NaBO_2 = \dfrac{0.01993}{8} = 2.49 \times 10^{-3}$ mol

Mass of $NaBO_2 = 2.49 \times 10^{-3} \times (23.0 + 10.8 + 32) =$ **0.164 g** •

[Total: 22]

Section B

Answer **one** question from this section.

4 Chlorine-containing compounds have many useful applications. One such example is the use of chloric(I) acid, HC*l*O, to disinfect water in swimming pools.

HC*l*O dissociates in water as shown below.

$$HClO + H_2O \rightleftharpoons H_3O^+ + ClO^-$$

(a) **(i)** Write an expression for K_a of HC*l*O. [1]

- $K_a = \dfrac{[H_3O^+][ClO^-]}{[HClO]}$

(ii) A disinfectant solution was prepared by dissolving 10 g of HC*l*O and x g of NaC*l*O in 100 cm^3 of water.

For effective disinfection, a pH of 7.35 was needed to reach the optimal $[ClO^-]$:[HC*l*O] ratio.

Given that the pK_a of HC*l*O is 7.55, determine the optimal $[ClO^-]$:[HC*l*O] ratio and hence the mass of NaC*l*O, x. [2]

$pH = pK_a + \lg \dfrac{[ClO^-]}{[HClO]}$ **or**

$7.35 = 7.55 + \lg \dfrac{[ClO^-]}{[HClO]}$

$\dfrac{[ClO^-]}{[HClO]} =$ • 0.631

$[ClO^-] = 0.631 \times \dfrac{\left(\frac{10}{1+35.5+16}\right)}{\frac{100}{1000}}$

$= 1.20 \text{ mol dm}^{-3}$

$K_a = \dfrac{[H_3O^+][ClO^-]}{[HClO]}$

$10^{-7.35} = \dfrac{(10^{-7.35})[ClO^-]}{[HClO]}$

$\dfrac{[ClO^-]}{[HClO]} = 0.631$

Mass of ClO^- which needs to be added **$= \frac{100}{1000} \times 1.20 \times (23 + 35.5 + 16)$**

= • 8.95 g

(iii) A worker accidentally poured some alkaline solution into the disinfectant solution formed in **(a)(ii)** but found that the pH was still about 7.35.

Write an equation to explain this. [1]

- **$HClO + OH^- \rightarrow ClO^- + H_2O$**

Since OH^- is neutralised by the weak acid, there is negligible change in pH.

(b) Hydrogen chloride is another chlorine-containing compound.

Alkyl chlorides can be synthesised from alcohols using hydrogen chloride. However, acyl chlorides **cannot** be prepared from carboxylic acids in the same way. One key factor is due to the stronger C-O bond present in carboxylic acids.

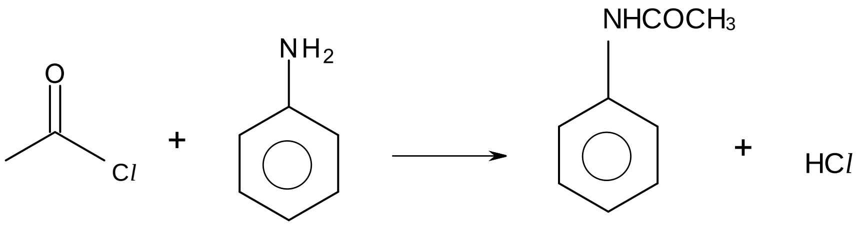
$$ROH \xrightarrow{HCl} RCl$$

$$RCO_2H \; \cancel{\xrightarrow{HCl}} \; RCOCl$$

Suggest an explanation for the stronger C-O bond in carboxylic acids. [1]

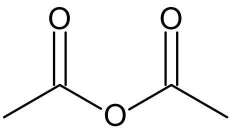
- **The strengthening of the C-O bond is due to the effective overlap/delocalisation of the lone pair of electrons on the O of the O-H into the C=O resulting in a partial double bond character.**

(c) Acetanilide is an analgesic and can be formed from ethanoyl chloride and phenylamine.



acetanilide

Instead of ethanoyl chloride, ethanoic anhydride is more commonly used in the laboratory to form acetanilide in a similar manner.



ethanoic anhydride

(i) Suggest the other organic product that is produced together with acetanilide. [1]

- **CH_3CO_2H**

The experimental procedure for the laboratory synthesis of acetanilide using ethanoic anhydride is given below.

1. Mix phenylamine and hydrochloric acid in a beaker.
2. Stir the mixture until a clear solution is obtained.
3. To the clear solution, add ethanoic anhydride and immediately add a solution of sodium ethanoate.
4. Stir the mixture vigorously.
5. Cool the solution in an ice water bath.
6. Filter the acetanilide formed. Wash with cold water and crystallise using a mixture of water and methanol.

(ii) In step 1, HC*l* was added to increase the solubility of phenylamine in water. Explain. [1]

- **$C_6H_5NH_3^+$ is formed which forms ion-dipole interactions with water and hence is more soluble than $C_6H_5NH_2$ which has a non-polar benzene ring.**

(iii) Sodium ethanoate is essential to ensure phenylamine is present in step 3 to react with ethanoic anhydride.

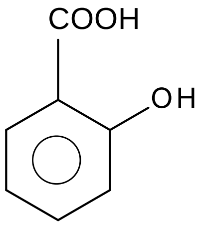
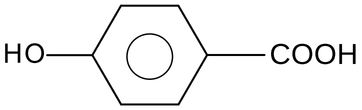
Suggest the role of sodium ethanoate. [1]

- **Sodium ethanoate acts as a base to react with $C_6H_5NH_3^+$ to regenerate the free amine so that it can act as a nucleophile.**

(iv) Suggest how you could check that the acetanilide obtained in step 6 is pure. [1]

- **Determine the melting point of the acetanilide obtained. If the melting point has a narrow range/fixed temperature, it is pure.**

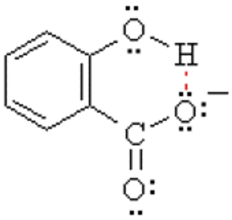
(d) Aspirin is another analgesic and it can be synthesised from salicylic acid. The pK_a values of salicylic acid and its isomer are given below:

Acid	pK_{a1}	pK_{a2}
 Salicylic acid	3.0	13.4
 4-hydroxybenzoic acid	4.1	9.7

Explain the following:

(i) pK_{a1} of salicylic acid is smaller than pK_{a1} of 4-hydroxybenzoic acid. [1]

- **This is because the 2-hydroxybenzoate ion is stabilised by intramolecular hydrogen bonding. In 4-hydroxybenzoate ion, the –OH group is too far away for hydrogen bonding to form.**



(ii) pK_{a2} is larger than pK_{a1} of 4-hydroxybenzoic acid. [1]

- **Electrostatically unfavourable / more difficult to remove H^+ from a negatively charged anion, conjugate base less likely to dissociate 2nd H^+.**

OR

- **Removal of 2nd H^+ would destabilise the anion as stabilisation by intramolecular H-bonding is no longer present.**

(e) When compound **A**, $C_{10}H_{11}NO$, is oxidised with acidified manganate(VII) ions, $[C_7H_8NO_2]^+$ and compound **B**, $C_3H_4O_3$, are formed. Compound **B** produces effervescence when Na_2CO_3 is added to it and gives an orange precipitate with 2,4-dinitrophenylhydrazine reagent.

Compound **A** reacts readily with 4 moles of Br_2(aq) to give compound **C**, $C_{10}H_9NO_2Br_4$.

Compound **A** also gives an orange precipitate with 2,4-dinitrophenylhydrazine reagent and reacts with hot alkaline aqueous iodine to give compound **D**, $C_9H_8NO_2Na$.

Suggest the structures of compounds **A**, **B**, **C** and **D**. Explain the reactions that occur. [9]

[✔] A has a high C:H ratio, hence a benzene ring is present.

[✔] B undergoes acid-carbonate/acid-base/neutralisation reaction with Na_2CO_3, it has $-CO_2H$ group or it is a carboxylic acid.

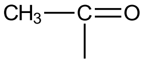
[✔] B undergoes condensation reaction with 2,4-dinitrophenylhydrazine. B is a product of strong oxidation, it is a ketone not aldehyde.

[✔] A undergoes condensation reaction with 2,4-dinitrophenylhydrazine. It can be a ketone or aldehyde/ carbonyl compound.

[✔]A undergoes electrophilic addition with aq Br_2, one Br atom and one OH atom are added at the carbon-carbon double bond of A (or confirm A has alkene group).

[✔] A undergoes electrophilic substitution with Br_2(aq). Since C has 4 Br atoms, the remaining 3 Br atoms are at the benzene ring, implying that A is a phenylamine/ has activating group like NH_2 bonded to benzene and the [✔] 2-, 4- and 6- positions with respect to NH_2 group are unsubstituted.

[✔] A is undergoes oxidation with by alkaline aq iodine, suggesting that it has

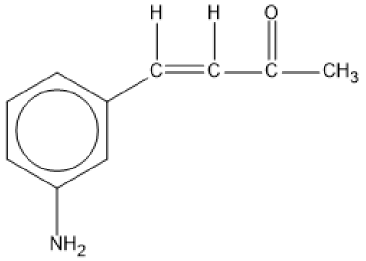


$CH_3-C=O$

group and it forms a salt of carboxylic acid E.

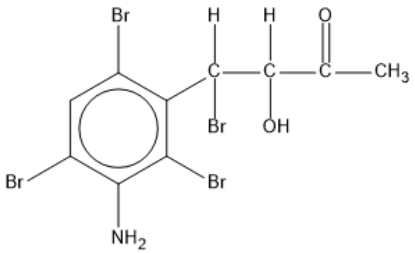
Every [✔]: 1 mark [Max: 5m]

A:

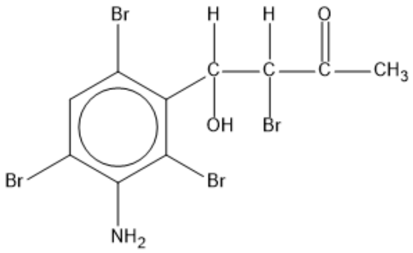


B: CH_3COCO_2H

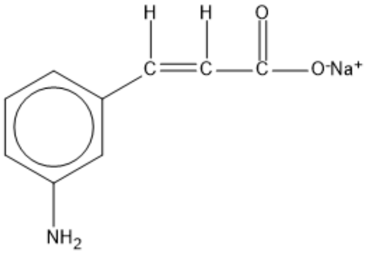
C:



or



D:



[Each structure 1m]

[Total: 20]

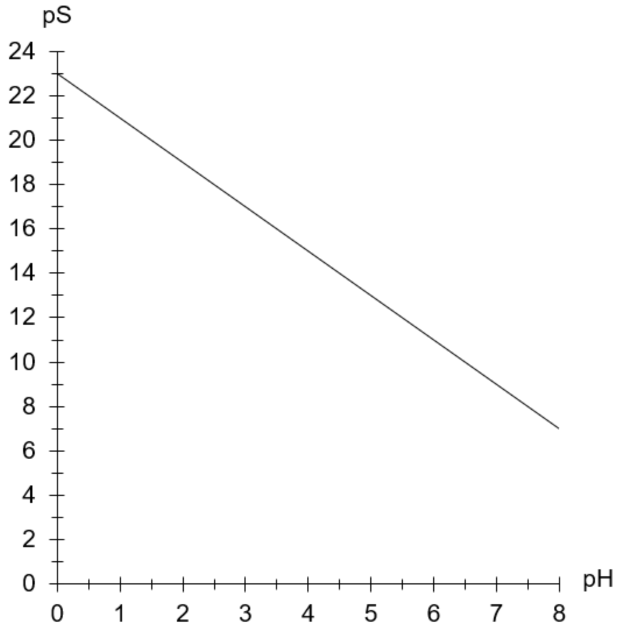
5 **(a)** Hydrogen sulfide gas, H_2S, is a reagent used in qualitative analysis. When H_2S is passed into a solution containing metal cations, metal sulfides are precipitated.

In aqueous medium, H_2S dissociates partially in a step-wise manner to give two equilibrium reactions:

$$H_2S \rightleftharpoons H^+ + HS^-$$

$$HS^- \rightleftharpoons H^+ + S^{2-}$$

The relationship between the H^+ ion concentration and S^{2-} ion concentration, as a result of H_2S dissociation, is shown in the graph below, where $pS = -\log_{10}[S^{2-}]$.



Solution **X** contains 0.1 mol dm^{-3} $CuSO_4$ and 0.05 mol dm^{-3} $MnSO_4$. Hydrogen sulfide gas is bubbled into **X** until saturation and the pH is maintained at 2.0.

The value of the solubility product of CuS and MnS are 1.0×10^{-44} and 1.4×10^{-15}, respectively.

(i) With reference to CuS, define the term *solubility product*. [1]

K_{sp} of CuS is the • <u>product of the concentrations of Cu^{2+} ions and S^{2-} ions</u> in a <u>saturated solution</u> at a <u>given temperature</u>.

(ii) Calculate the minimum concentration of sulfide ions needed to precipitate CuS. [1]

K_{sp} of CuS = $[Cu^{2+}][S^{2-}] = 1.0 \times 10^{-44}$ mol^2 dm^{-6}

• Min $[S^{2-}]$ for precipitation of CuS = $1.0 \times 10^{-44}/0.1 = 1.0 \times 10^{-43}$ mol dm^{-3}

(iii) The minimum concentration of sulfide ions needed to precipitate MnS is 2.80×10^{-14} mol dm^{-3}.

Using the graph above and your answer in **(a)(ii)**, explain whether it is possible to separate copper and manganese ions in **X** at pH = 2. [2]

• From graph, when pH = 2, pS = 19 → $[S^{2-}] = 10^{-19}$ mol dm^{-3}

• Since [S^{2-}] at pH = 2 is greater than min [S^{2-}] for precipitation of CuS but smaller than min [S^{2-}] for precipitation of MnS, ionic product of CuS exceeds its K_{sp}. Hence, only CuS will be precipitated and separation of the 2 ions is possible at pH = 2.

OR

• At pH = 2, pS = 19 → [S^{2-}] = 10^{-19} mol dm^{-3}

•

Ionic product of CuS = 0.1×10^{-19} = $1.00 \times 10^{-20} > K_{sp}$

Ionic product of MnS = 0.05×10^{-19} = $5.00 \times 10^{-21} < K_{sp}$

Only CuS is precipitated, so separation is possible.

(iv) Determine the maximum pH for solution **X** before separation of copper and manganese ions is no longer possible. [1]

Max [S^{2-}] before MnS is precipitated = 2.80×10^{-14} mol dm^{-3}

pS = -lg 2.80×10^{-14} ≈ 13.5 *[accept range 13 to 14]*

From graph, when pS = 13.5, • pH = 4.75 *[Accept 4.5 < pH < 5.0]*

(b) When water ligands in a hydrated metal ion are substituted by other ligands, the equilibrium constant for the reaction is referred to as the stability constant, K_{stab}, of the new complex. The higher the value of K_{stab}, the more likely the complex will be formed.

The stability constants for 3 reactions are given below.

Reaction	Colour of complex formed	Value of $\log_{10}(K_{stab})$
$Fe^{3+}(aq) + 6CN^{-}(aq) \rightleftharpoons [Fe(CN)_6]^{3-}(aq)$	Yellow	31.0
$Fe^{3+}(aq) + EDTA^{4-}(aq) \rightleftharpoons [Fe(EDTA)]^{-}(aq)$	Brown	25.1
$Fe^{3+}(aq) + SCN^{-}(aq) \rightleftharpoons [Fe(SCN)]^{2+}(aq)$	Red	2.1

Describe the colour change(s) of the solution when excess NaSCN is added to $[Fe(EDTA)]^{-}$, followed by an excess of KCN(aq).

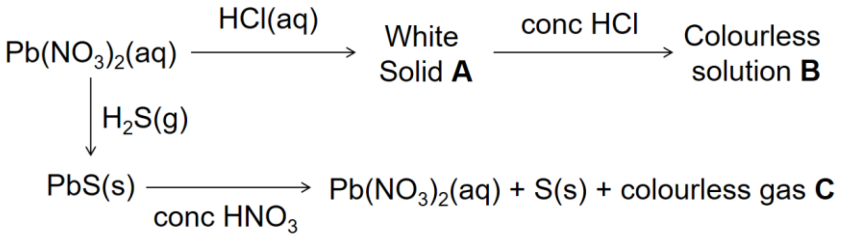
Explain the observation, with reference to the table above. [2]

Brown to yellow.

SCN^{-} cannot substitute $EDTA^{4-}$ as $[Fe(SCN)]^{2+}$ is less stable than $[Fe(EDTA)]^{-}$ from a lower K_{stab} value, so colour remains brown.

CN^{-} can substitute $EDTA^{4-}$ ligands as $[Fe(CN)_6]^{3-}$ is more stable than $[Fe(EDTA)]^{-}$ from a larger K_{stab} value, so colour changes from brown to yellow.

(c) A solution of $Pb(NO_3)_2$ is subjected to the following reactions.



(i) Suggest the identity of white solid **A** and complex anion present in colourless solution **B**. [2]

A is • $PbCl_2$

B is • $[PbCl_4]^{2-}$

(ii) Colourless gas **C** is obtained from the reaction of solid PbS and concentrated HNO_3, which is readily oxidised in air to form a brown acidic gas.

Suggest the identity of **C**. [1]

• NO

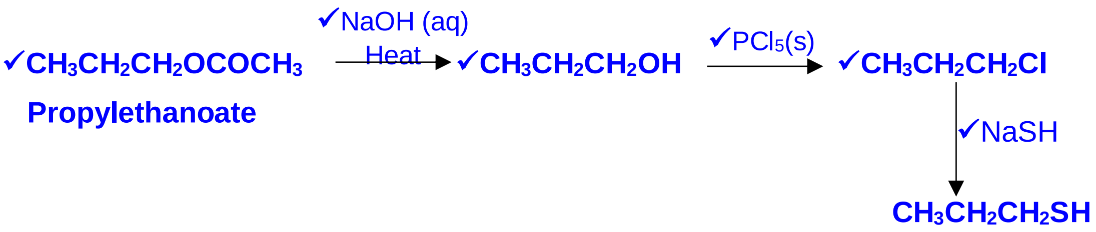
(d) Thiols are sulfur-containing compounds that can be prepared from alkyl halides and the hydrosulfide nucleophile, ^-SH.

Ethanethiol is prepared from chloroethane using NaSH as shown below.

$$CH_3CH_2Cl \xrightarrow{NaSH} \underset{\text{Ethanethiol}}{CH_3CH_2SH}$$

(i) Suggest a synthesis of propanethiol starting from propylethanoate.

You should state the reagents and conditions for each step, and show clearly the structure of any intermediate compounds. [3]



6 ✓ 3m 3-5 ✓ 2m 2✓ 1m

CH_3CH_2SH can react with a base, NaH, to give $CH_3CH_2S^-$.

$$CH_3CH_2SH + NaH \rightarrow CH_3CH_2S^-Na^+ + H_2 \quad \text{----- Reaction 1}$$

$CH_3CH_2S^-$ further reacts with chloroethane, to yield diethyl sulfide

$$CH_3CH_2S^-Na^+ + CH_3CH_2Cl \rightarrow \underset{\text{Diethyl sulphide}}{CH_3CH_2SCH_2CH_3} + NaCl \quad \text{----- Reaction 2}$$

(ii) Suggest why $CH_3CH_2S^-$, is a better nucleophile than $CH_3CH_2O^-$. [1]

• The valence electron (3p) on S are further away and less tightly held, hence they are stronger nucleophiles.

[Alternative answers: Oxygen is more electronegative than Sulfur and hence less likely to donate the lone pair of electrons. Hence, $CH_3CH_2O^-$ is a weaker nucleophile.

or Oxygen is smaller than sulfur and the electrons are closer and more strongly held than that in sulfur. Hence, $CH_3CH_2O^-$ is a weaker nucleophile.]

(iii) Diethyl sulfide is a good nucleophile.

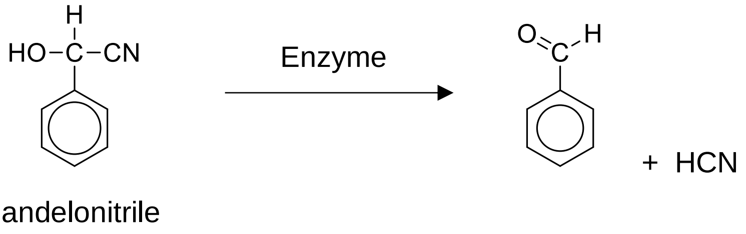
In Reaction 2, a side product, $C_6H_{15}SCl$, is formed when chloroethane is used in excess. $C_6H_{15}SCl$ gives a white precipitate with aqueous silver nitrate.

Suggest the structural formula of the side product $C_6H_{15}SCl$. [1]

Free Cl^- anion is present and the white ppt formed is AgCl

• $(CH_3CH_2)_3S^+ Cl^-$ (Similar to RX reaction with ammonia)

(e) The millipede *Apheeloria corrugate* protects itself by secreting the cyanohydrin mandelonitrile and an enzyme that decompose mandelonitrile into benzaldehyde and HCN.



(i) State the type of reaction for the formation of Mandelonitrile from benzaldehyde. [1]

• Nucleophilic addition

(ii) Suggest a chemical test that will give a positive test for Mandelonitrile but not for benzaldehyde. [2]

1. **Na(s),**

   Observation: H_2(g) evolved with Mandelonitrile but not benzaldehyde

2. **PCl_5(s)**

   Observation: White fumes of HCl(g) evolved with Mandelonitrile but not benzaldehyde

3. **NaOH(aq), heat**

   Observation: NH_3(g) evolved with Mandelonitrile but not benzaldehyde

(iii) A student made the following statement, “benzaldehyde can be directly synthesized from phenylmethanol, $C_6H_5CH_2OH$, but not from benzoic acid.”

Based on your knowledge of the reagents and conditions for each reaction, deduce if the statement is true. [2]

The statement made by the student is true.

• Benzaldehyde can be formed from phenylmethanol via oxidation using acidified $K_2Cr_2O_7$ warm with immediate distillation. Upon distillation, the aldehyde can be separated and not be further oxidized to propanoic acid.

• Benzoic acid can only be reduced by $LiAlH_4$ and it reduces directly back to phenylmethanol and benzaldehyde cannot be isolated.

[Total: 20]

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

1 Determination of the concentration of a solution of hydrogen peroxide

Hydrogen peroxide, H_2O_2, can be oxidised to give oxygen, O_2. This reaction happens rapidly in the presence of acidified potassium manganate(VII), $KMnO_4$.

$$2MnO_4^-(aq) + 5H_2O_2(aq) + 6H^+(aq) \longrightarrow 2Mn^{2+}(aq) + 5O_2(g) + 8H_2O(l)$$

To determine the concentration of a solution of hydrogen peroxide, you will first dilute the solution and then carry out a titration using acidified potassium manganate(VII), $KMnO_4$.

FA 1 is aqueous hydrogen peroxide.
FA 2 is 0.0200 mol dm^{-3} potassium manganate(VII), $KMnO_4$.
FA 3 is 1.0 mol dm^{-3} sulfuric acid, H_2SO_4.

Keep **FA 1** for use in **Question 3**

(a) Method

Dilution

- Pipette 25.0 cm^3 of **FA 1** into the 250 cm^3 volumetric flask.
- Add distilled water to make 250 cm^3 of solution and shake the flask thoroughly.
- Label this diluted solution of hydrogen peroxide as **FA 4**.

Titration

- Fill the burette with **FA 2**.
- Pipette 25.0 cm^3 of **FA 4** into a conical flask.
- Use the measuring cylinder to add 25 cm^3 of **FA 3** to the conical flask.
- Titrate **FA 4** against **FA 2** and record your readings in the space below.
- Carry out as many accurate titrations as you think necessary.

Results

[5]

(b) From your titrations, obtain a suitable volume of **FA 2** to be used in your calculations.

Show clearly how you obtained this volume.

25.0 cm^3 of **FA 4** required _____________ cm^3 of **FA 2** for titration [1]

(c) Calculations

Show your working and give appropriate significant figures in the final answer for **each** step of your calculations.

(i) Calculate the amount of potassium manganate(VII) present in the volume of **FA 2** calculated in **(b).**

amount of $KMnO_4$ = _________________ [1]

(ii) Calculate the amount of hydrogen peroxide present in 25.0 cm^3 of **FA 4**.

amount of H_2O_2 in 25.0 cm^3 of **FA4** = _________________ [1]

(iii) Calculate the concentration, in mol dm^{-3}, of H_2O_2 in **FA 4.**

concentration of H_2O_2 in **FA 4** = _________________ [1]

(iv) Calculate the concentration, in mol dm^{-3}, of H_2O_2 in **FA 1.**

concentration of H_2O_2 in **FA 1** = ________________ [1]

(d) Another experiment was conducted to determine the concentration of hydrogen peroxide. Different volumes of hydrogen peroxide were added to identical 25.0 cm^3 samples of 0.0400 mol dm^{-3} aqueous iron(II) solution. Iron(II) is oxidised by hydrogen peroxide as shown by the following equation.

$$2Fe^{2+} + H_2O_2 + 2H^+ \rightarrow 2Fe^{3+} + 2H_2O$$

The remaining iron(II) ions in each of the resulting mixtures were then titrated against potassium manganate(VII) and the results were shown in the table below:

Volume of H_2O_2 added / cm^3	**Volume of $KMnO_4$ / cm^3**
2.00	11.60
12.00	5.20
16.00	2.60
25.00	3.40
30.00	6.70
35.00	10.00

(i) Plot, on the grid on page 5, the values for the volume of potassium manganate(VII) (*y-axis*) against the volume of hydrogen peroxide added (*x-axis*).

Draw two straight lines of best fit, taking into account all of your plotted points.

Your graph should enable you to determine the values for **(d)(ii)**.

[3]

(ii) Hence obtain values for

- the volume of potassium manganate(VII) required, $V_{max}(KMnO_4)$, to react completely with 25.0 cm^3 of iron(II) solution if no hydrogen peroxide is added.
- the volume of hydrogen peroxide required, $V_{max}(H_2O_2)$, to react completely with 25.0 cm^3 of iron(II) solution if no potassium manganate(VII) is added.

$V_{max}(KMnO_4)$ = ____________________

$V_{max}(H_2O_2)$ = ____________________

[1]

[Turn over

(iii) Determine the concentration of hydrogen peroxide, in mol dm^{-3}, in this experiment.

Concentration of hydrogen peroxide = ________________

[4]

[Total: 18]

2 Determination of the enthalpy change of reaction, ΔH$_r$

You are to determine the enthalpy change of reaction, ΔH$_r$, for the following reactions:

$$Na_2CO_3(s) + 2HCl(aq) \rightarrow 2NaCl(aq) + CO_2(g) + H_2O(l) \qquad \Delta H_1$$

$$NaHCO_3(s) + HCl(aq) \rightarrow NaCl(aq) + CO_2(g) + H_2O(l) \qquad \Delta H_2$$

FA 5 is anhydrous sodium carbonate, Na_2CO_3

FA 6 is solid sodium hydrogen carbonate, $NaHCO_3$

You are also provided with 2.0 mol dm^{-3} HC*l*

(a) Reaction of FA 5, Na_2CO_3, with an excess of 2.0 mol dm^{-3} hydrochloric acid

Method

Read through the instructions carefully before starting any practical work.

1. Support the styrofoam cup in the 250 cm^3 beaker.
2. Use the measuring cylinder to transfer 50 cm^3 of 2.0 mol dm^{-3} hydrochloric acid into the styrofoam cup.
3. Place the thermometer in the styrofoam cup and record the temperature of the solution.
4. Weigh the weighing bottle containing **FA 5**, anhydrous sodium carbonate.
5. With the aid of a dry spatula, add the contents of the weighing bottle to the styrofoam cup in **three separate portions**, taking care that the mixture does not overflow.

[Safety precaution: DO NOT add FA 5 all at once. The reaction is very vigourous.]

6. Stir and record the highest temperature obtained.
7. Reweigh the weighing bottle containing residual **FA 5**.

Record in an appropriate form below, all of your weighings and temperature measurements together with the mass, **m$_1$**, of **FA 5** added and the maximum temperature rise, **ΔT$_1$**.

[Turn over]

Results

[2]

(b) **(i)** Calculate the temperature rise per gram of **FA 5**, Na_2CO_3, used in the experiment.

$\frac{\Delta T_1}{m_1}$ = ____________________

[2]

(ii) Calculate the enthalpy change, ΔH_1, for the reaction

$$Na_2CO_3(s) + 2HCl(aq) \rightarrow 2NaCl(aq) + CO_2(g) + H_2O(l)$$

$$\Delta H_1 = -\left(22.79 \times \frac{\Delta T_1}{m_1}\right) \text{ kJ mol}^{-1}$$

ΔH_1 = ____________________

[1]

[Turn over

(c) Reaction of FA 6, $NaHCO_3$, with an excess of 2.0 mol dm^{-3} hydrochloric acid

Method

Read through the instructions carefully before starting any practical work.

1. Support another styrofoam cup in the 250 cm^3 beaker provided.
2. Use the measuring cylinder to transfer 50 cm^3 of 2.0 mol dm^{-3} hydrochloric acid into the styrofoam cup.
3. Place the thermometer in the styrofoam cup and record the temperature of the solution.
4. Weigh the empty weighing bottle labelled **"FA 6"**.
5. Weigh approximately 7.0 – 8.0 g of **FA 6**, anhydrous sodium hydrogen carbonate into the empty weighing bottle labelled **"FA 6"**.
6. With the aid of a dry spatula, add the contents of the weighing bottle to the styrofoam cup in **three separate portions**, taking care that the mixture does not overflow.

[Safety precaution: DO NOT add FA6 all at once. The reaction is very vigourous.]

7. Stir and record the lowest temperature obtained.
8. Reweigh the weighing bottle containing residual **FA 6**.

Record in an appropriate form below, all of your weighings and temperature measurements together with the mass, **m_2**, of **FA 6** added and the maximum temperature fall, **ΔT_2**.

<u>Results</u>

[Turn over

(d) **(i)** Calculate the temperature fall per gram of **FA 6**, $NaHCO_3$, used in the experiment.

$\frac{\Delta T_2}{m_2}$ = ______________________ [2]

(ii) Calculate the enthalpy change, ΔH_2, for the reaction

$$NaHCO_3(s) + HCl(aq) \rightarrow NaCl(aq) + CO_2(g) + H_2O(l)$$

$$\Delta H_2 = +\left(18.06 \times \frac{\Delta T_2}{m_2}\right) \text{ kJ mol}^{-1}$$

ΔH_2 = ______________________ [1]

(e) **(i)** The smallest graduation in reading a –10 °C to +110 °C thermometer is 1.0 °C

Suggest the maximum error of a temperature change calculated with two temperature readings.

Maximum error = ______________________ [1]

(ii)

> The expected fall in temperature when 1.0 g of $NaHCO_3(s)$ is added to 50 cm^3 of 2.0 mol dm^{-3} hydrochloric acid is approximately 1.5°C

Determine the maximum percentage error in the calculated temperature change when 1.0 g of $NaHCO_3$ is added to 50 cm^3 of 2.0 mol dm^{-3} hydrochloric acid.

Maximum percentage error = ______________________ [1]

[Turn over

(f) It is not possible to measure experimentally the enthalpy change, ΔH$_3$, for the following reaction as it does not take place in the laboratory.

$$Na_2CO_3(s) + CO_2(g) + H_2O(l) \rightarrow 2NaHCO_3(s)$$

It is possible, however, to calculate a "theoretical" value of ΔH$_3$ for this reaction from the results of the experiments you have carried out.

Using an energy cycle and your results from **(b)(ii)** and **(d)(ii),** calculate a value for ΔH$_3$.

ΔH$_3$ = ____________________

[2]

[Total: 12]

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 reagents are selected for use in a test, the **name or correct formula** of the element or compound must be given.

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.

No additional tests for ions present should be attempted.

Rinse and reuse test-tubes where possible.

[Turn over

(a) **FA 7, FA 8** and **FA 9** are aqueous solutions that each have an ion containing one of the metals from those listed in the Qualitative Analysis Notes.

FA 1 from Question 1 is to be used in some of these tests.

Carry out the following tests and record your observations.

	Test	*Observation*
(i)	To a 1 cm depth of **FA 7** in a test-tube, add a 1 cm depth aqueous sodium hydroxide.	
	Then, add several drops of **FA 1**.	
(ii)	To a 1 cm depth of **FA 8** in a test-tube, add a few drops of aqueous sodium hydroxide.	
	Then, add excess aqueous sodium hydroxide.	
(iii)	To a 1 cm depth of **FA 8** in a test-tube, add several drops of **FA 1.**	
	Then, add aqueous sodium hydroxide until in excess.	
(iv)	To a 1 cm depth of **FA 8** in a test-tube, add a 1 cm depth of dilute sulfuric acid, and then a few drops of **FA 9**.	

[Turn over

(v)	To a 1 cm depth of aqueous potassium iodide in a test-tube, add a few drops of **FA 9**.	
	Then, add a few drops of starch solution	

[5]

(b) Identify the cation present in **FA 7** and **FA 8**.

The cation present in **FA 7** is ______________________

The cation present in **FA 8** is ______________________

[2]

(c) Explain the chemistry involved in the effervescence observed in both **(a)(i)** and **(a)(iii).**

[1]

(d) A student added 1 cm^3 of **FA 9** to a test-tube containing **FA 8**. A strip of magnesium ribbon was then added to the mixture. Effervescence was observed.

Deduce the identity of the gas evolved and explain the chemistry involved in this reaction.

[3]

(e) **Figure 1** below shows the thermal decomposition of **FA 10**, which is a solid sample of the compound present in the aqueous solution of **FA 9**.

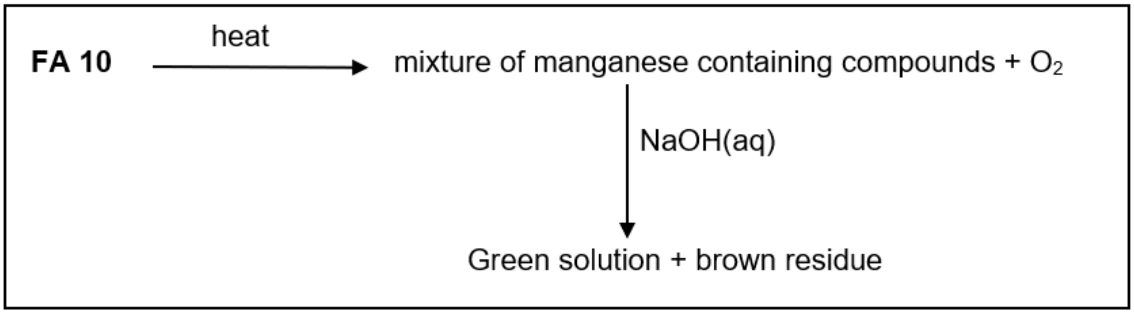


Figure 1

Consider the observations in **Figure 1**, suggest the identity of the manganese-containing species in the green solution and the residue.

[1]

(f) **FA 8** contains one of the anions Cl^-, Br^-, I^-, SO_4^{2-} or SO_3^{2-}.

Plan an experiment to determine the reagents you would use to identify which anion is present in **FA 8**.

Carry out your tests on **FA 8** to identify the anion present. Record your observations in the table below.

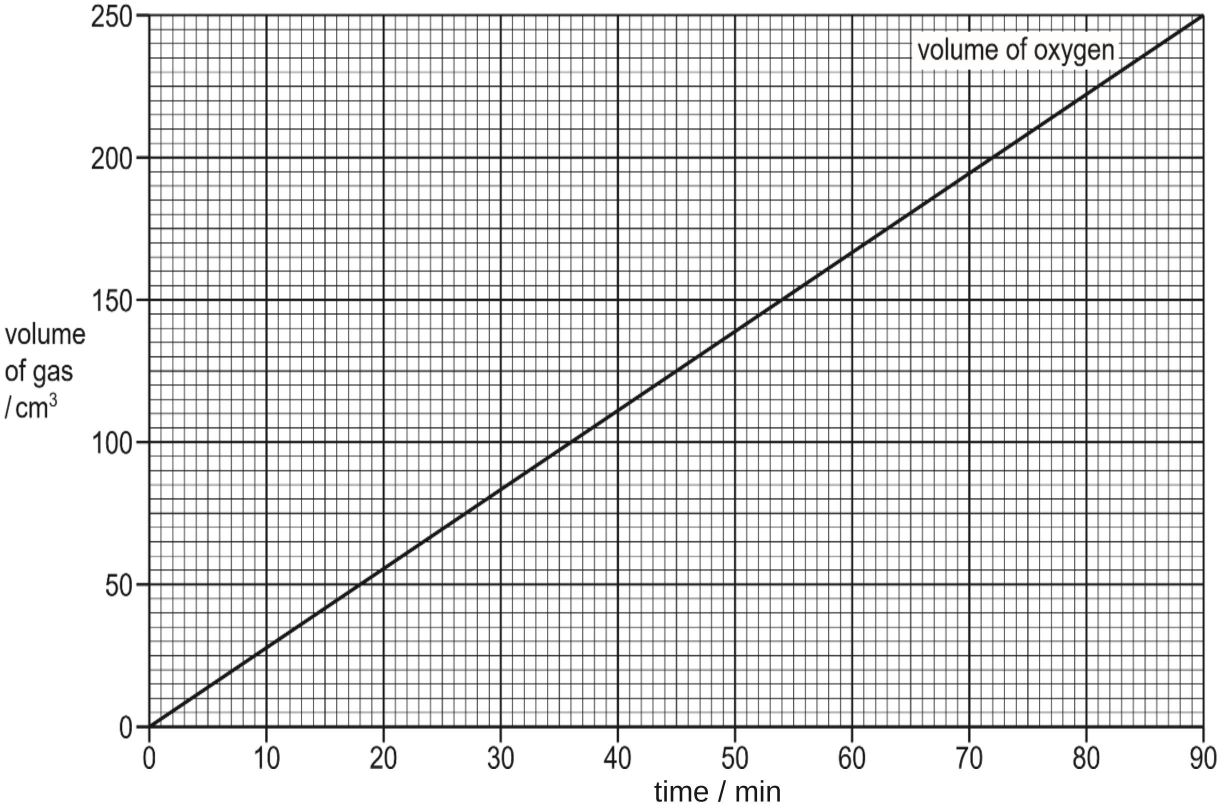
Test	**Observation**

Suggest the identity of the anion present in **FA 8**.

[3]
[Total:15]

4 **(a)** This question is about the electrolysis of different compounds.

During the electrolysis of dilute sulfuric acid using a current of 0.75 A for 90 minutes, the volume of oxygen gas collected was recorded and is shown in the graph below.



(i) **Table 1** below gives some standard electrode potential values

Electrode reaction	**E⊖ / V**
$2H^+ + 2e^- \rightleftharpoons H_2$	0.00
$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	+1.23
$O_2 + 2H_2O + 4e^- \rightleftharpoons 4OH^-$	+0.40
$2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-$	–0.83
$SO_4^{2-} + 4H^+ + 2e^- \rightleftharpoons SO_2 + 2H_2O$	+0.17
$S_2O_8^{2-} + 2e^- \rightleftharpoons 2SO_4^{2-}$	+2.01

Table 1

With reference to the values in the **Table 1**, write equations for the reactions that occur at each electrode in the electrolysis of sulfuric acid.

Cathode: ______________________________

Anode: ______________________________

[2]

[Turn over

On the graph on page 14,

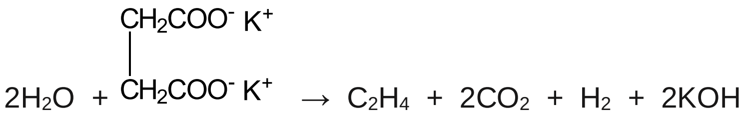
(ii) Draw a straight line to show the volume of hydrogen evolved in the same experiment. Label the line as “hydrogen”.

[1]

(iii) Draw a straight line to show the volume of oxygen evolved if a current of 0.45 A was used instead of the 0.75 A used in the original experiment. Label the line as “oxygen”.

[1]

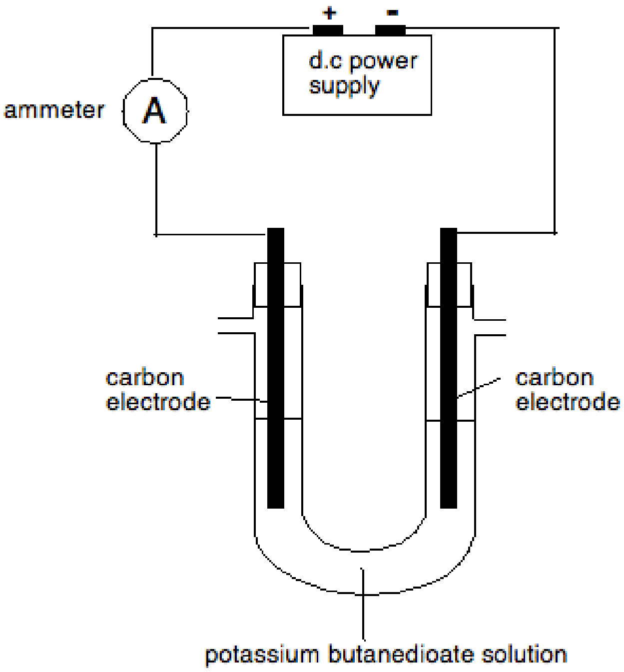
(b) During the electrolysis of potassium butanedioate, the following reaction occurs.



$$2H_2O + \begin{array}{l} CH_2COO^- K^+ \\ | \\ CH_2COO^- K^+ \end{array} \rightarrow C_2H_4 + 2CO_2 + H_2 + 2KOH$$

potassium
butanedioate

An experiment can be conducted to verify the stoichiometric ratio between hydrogen gas and ethene gas collected using the following set-up.



Hydrogen is produced at one electrode, ethene and carbon dioxide are produced at the other. The carbon dioxide can be separated from the ethene by absorbing it using a suitable reagent before the volume of ethene is measured.

[Turn over

(i) Complete the diagram on page 15 to show how:

- the hydrogen could be collected and its volume measured,
- the carbon dioxide could be removed,
- the volume of ethene could be measured.

Your diagram should include appropriate apparatus and the identity of the suitable reagent used to remove carbon dioxide.

[3]

(ii) Calculate the number of coulombs, **N**, that would be required to produce **V** cm^3 of hydrogen at room temperature and pressure.

[Faraday constant, $F = 9.65 \times 10^4$ C mol^{-1}] [1]

(iii) Write an equation for the reaction that takes place for the removal of carbon dioxide.

[1]

(iv) Predict the organic product that would be obtained at the electrode when a solution of potassium *hexanedioate* is electrolysed.

[1]
[Total: 10]

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

DO NOT WRITE IN THIS MARGIN

DO NOT WRITE IN THIS MARGIN

(b) Reactions of anions

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

DO NOT WRITE IN THIS MARGIN

(c) Test 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

DO NOT WRITE IN THIS MARGIN

(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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2019 JC2 PRELIMINARY EXAMINATIONS

HIGHER 2

CANDIDATE NAME	
CIVICS GROUP	☐ ☐ / ☐ ☐
CENTRE NO. / INDEX NO.	☐ ☐ ☐ ☐ / ☐ ☐ ☐ ☐

CHEMISTRY **9729/04**

Paper 4 Practical **2 September 2019**

2 hours 30 minutes

Candidates answer on the Question Paper.

READ THESE INSTRUCTIONS FIRST

Write your Civics Group and name on all the work you hand in.
Give details of the practical shift and laboratory where appropriate, in the boxes provided.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

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

The use of an approved scientific calculator is expected, where appropriate.
You may lose marks if you do not show your working or if you do not use appropriate units.
Qualitative Analysis Notes are printed on pages 17 and 18.
At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

Shift
Laboratory

For Examiner's Use	
1	/ 18
2	/12
3	/15
4	/ 10
Total	/ 55

This document consists of 18 printed pages and 2 blank pages.

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

1 **Determination of the concentration of a solution of hydrogen peroxide**

Hydrogen peroxide, H_2O_2, can be oxidised to give oxygen, O_2. This reaction happens rapidly in the presence of acidified potassium manganate(VII), $KMnO_4$.

$$2MnO_4^-(aq) + 5H_2O_2(aq) + 6H^+(aq) \longrightarrow 2Mn^{2+}(aq) + 5O_2(g) + 8H_2O(l)$$

To determine the concentration of a solution of hydrogen peroxide, you will first dilute the solution and then carry out a titration using acidified potassium manganate(VII), $KMnO_4$.

FA 1 is aqueous hydrogen peroxide.
FA 2 is 0.0200 mol dm^{-3} potassium manganate(VII), $KMnO_4$.
FA 3 is 1.0 mol dm^{-3} sulfuric acid, H_2SO_4.

Keep **FA 1** for use in **Question 4.**

(a) **Method**

Dilution

- Pipette 25.0 cm^3 of **FA 1** into the 250 cm^3 volumetric flask.
- Add distilled water to make 250 cm^3 of solution and shake the flask thoroughly.
- Label this diluted solution of hydrogen peroxide as **FA 4**.

Titration

- Fill the burette with **FA 2**.
- Pipette 25.0 cm^3 of **FA 4** into a conical flask.
- Use the measuring cylinder to add 25 cm^3 of **FA 3** to the conical flask.
- Titrate **FA 4** against **FA 2** and record your readings in the space below.
- Carry out as many accurate titrations as you think necessary.

Results

Final burette reading /cm^3	**20.70**	**20.80**
Initial burette reading /cm^3	**0.00**	**0.00**
Volume of FA 2 /cm^3	**20.70**	**20.80**
	√	√

- Appropriate headings and units.
- All accurate burette readings recorded to 0.05 cm^3.
- Has two uncorrected, accurate titres value within ±0.10 cm^3.

●● 2m – accuracy

[5]

(b) From your titrations, obtain a suitable volume of **FA 2** to be used in your calculations.

Show clearly how you obtained this volume.

- **Average titre =** $\frac{20.70+20.80}{2}$

= 20.75 cm^3

25.0 cm^3 of **FA 4** required **20.75** cm^3 of **FA 2** for titration

[1]

(c) **Calculations**

Show your working and give appropriate significant figures in the final answer for **each** step of your calculations.

(i) Calculate the amount of potassium manganate(VII) present in the volume of **FA 2** calculated in **(b).**

- **Amount of MnO_4^- present in 20.75 cm^3 of FA 2**

= $\frac{20.75}{1000} \times 0.0200$

= 4.15 x 10^{-4} mol

amount of $KMnO_4$ = **4.15 x 10^{-4} mol** [1]

(ii) Calculate the amount of hydrogen peroxide present in 25.0 cm^3 of **FA 4**.

$2MnO_4^-(aq) \equiv 5H_2O_2(aq)$

- **Amount of H_2O_2 in 25 cm^3 of FA 4**

= 4.15 x 10^{-4} x $\frac{5}{2}$

= 1.04 x 10^{-3} mol (3sf)

amount of H_2O_2 in 25.0 cm^3 of **FA4** = **1.04 x 10^{-3} mol** [1]

(iii) Calculate the concentration, in mol dm^{-3}, of H_2O_2 in **FA 4.**

- **Concentration of H_2O_2 in FA 4**

= 1.04 x 10^{-3} x $\frac{1000}{25}$

= 0.0415 mol dm^{-3} (3sf)

concentration of H_2O_2 in **FA 4** = **0.0415 mol dm^{-3}** [1]

(iv) Calculate the concentration, in mol dm^{-3}, of H_2O_2 in **FA 1.**

Amount of H_2O_2 in 250 cm^3 of FA 4 = Amount of H_2O_2 in 25 cm^3 of FA 1

= $1.04 \times 10^{-3} \times \frac{250}{25}$ mol

= 0.0104 mol

● Concentration of H_2O_2 in FA 1

= $0.0104 \times \frac{1000}{25}$

= 0.415 mol dm^{-3} (3sf)

OR

Dilution factor = 250 / 25 = 10

● Concentration of H_2O_2 in FA 1 = 0.0415 x 10 = 0.415 mol dm^{-3}

concentration of H_2O_2 in **FA 1** = **0.415 mol dm^{-3}** [1]

(d) Another experiment was conducted to determine the concentration of hydrogen peroxide. Different volumes of hydrogen peroxide were added to identical 25.0 cm^3 samples of 0.0400 mol dm^{-3} aqueous iron(II) solution. Iron (II) is oxidised by hydrogen peroxide as shown by the following equation.

$$2Fe^{2+} + H_2O_2 + 2H^+ \rightarrow 2Fe^{3+} + 2H_2O$$

The remaining iron(II) ions in each of the resulting mixtures were then titrated against potassium manganate(VII) and the results are shown in the table below:

Volume of H_2O_2 added / cm^3	**Volume of $KMnO_4$ / cm^3**
2.00	11.60
12.00	5.20
16.00	2.60
25.00	3.40
30.00	6.70
35.00	10.00

(i) Plot, on the grid on page 5, your values for the volume of potassium manganate(VII) (*y-axis*) against the volume of hydrogen peroxide added (*x-axis*).

Draw two straight lines of best fit, taking into account all of your plotted points.

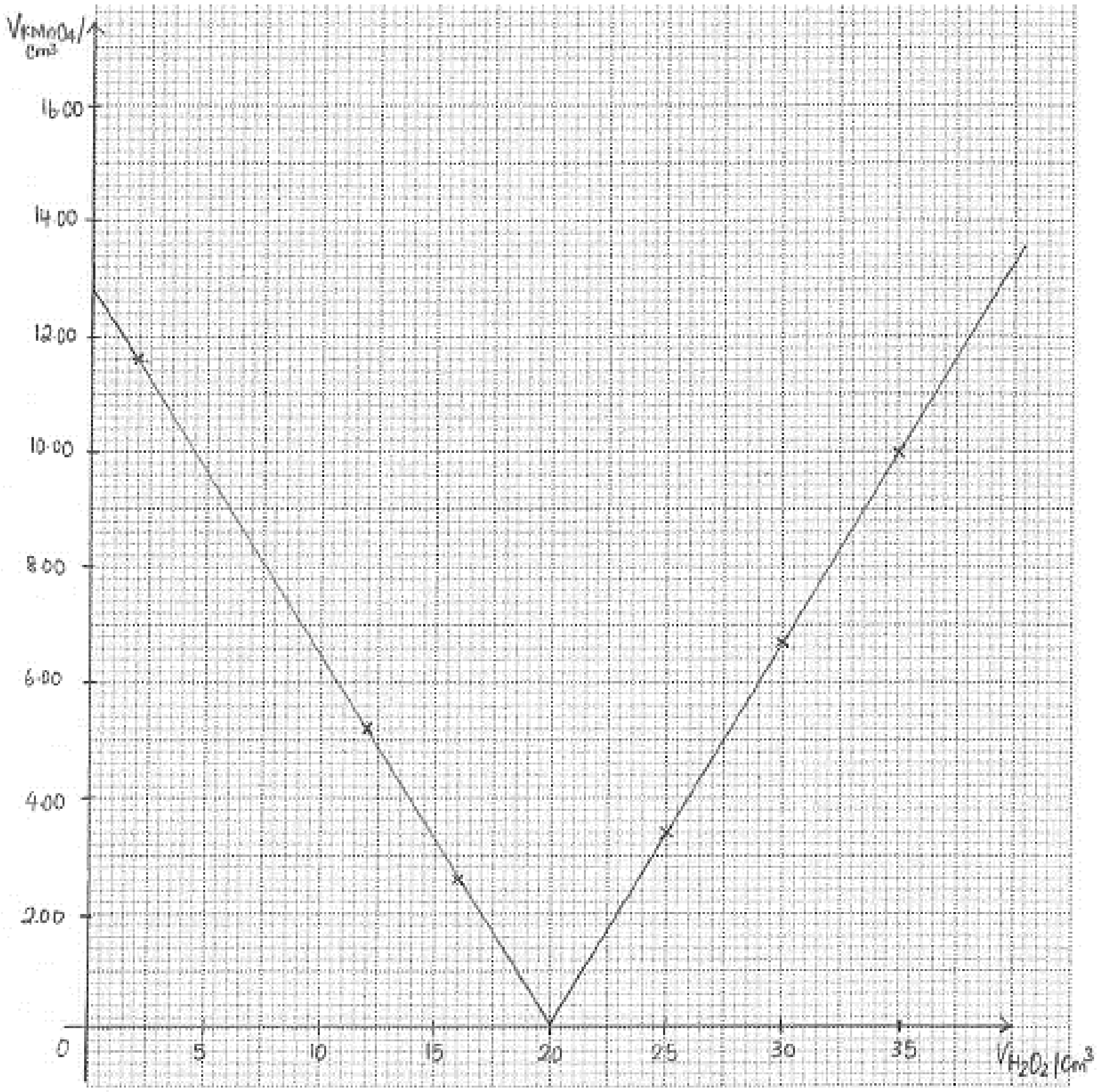
Your graph should enable you to determine the values for **(d)(ii)**.

[3]

(ii) Hence obtain values for

- the volume of potassium manganate(VII) required, $V_{max}(KMnO_4)$, to react completely with 25.0 cm^3 of iron(II) solution if no hydrogen peroxide is added.
- the volume of hydrogen peroxide required, $V_{max}(H_2O_2)$, to react completely with 25.0 cm^3 of iron(II) solution if no potassium manganate(VII) is added.

[1]



●Clearly labelled axes. Appropriate scale starting from origin and allowing the plotted points to be more than half given grid.

●correctly plotted points

●2 best-fit straight lines

$V_{max}(KMnO_4)$ = **12.8 cm^3**

$V_{max}(H_2O_2)$ = **20.0 cm^3**

● 1 mark for both values (only if the 2 lines intersect at x-axis)

(iii) Determine the concentration of hydrogen peroxide in mol dm^{-3} in this experiment.

$2Fe^{2+} \equiv H_2O_2$

Amount of Fe^{2+} in 25.0 cm^3 of solution = $\frac{25}{1000} \times 0.04$ = 1.00 x 10^{-3} mol

●Amount of H_2O_2 in 20 cm^3 of solution = 1.00 x 10^{-3} x ½ = 5.00 x 10^{-4} mol

(●using Vmax(H_2O_2)) Concentration of H_2O_2 solution = 5.00 x 10^{-4} x $\frac{1000}{20}$

= 0.0250 mol dm^{-3}

(allow ecf from (ii))

● All calculations to 3 significant figures

● correct units for all calculated values

Concentration of hydrogen peroxide = **0.0250 mol dm^{-3}**

[4]
[Total: 18]

2 Determination of the enthalpy change of reaction, ΔH$_r$

You are to determine the enthalpy change of reaction, ΔH$_r$, for the following reactions:

$$Na_2CO_3(s) + 2HCl(aq) \rightarrow 2NaCl(aq) + CO_2(g) + H_2O(l) \qquad \Delta H_1$$
$$NaHCO_3(s) + HCl(aq) \rightarrow NaCl(aq) + CO_2(g) + H_2O(l) \qquad \Delta H_2$$

FA 5 is anhydrous sodium carbonate, Na_2CO_3

FA 6 is solid sodium hydrogen carbonate, $NaHCO_3$

You are also provided with 2.0 mol dm^{-3} HC*l*

(a) Reaction of FA 5, Na_2CO_3, with an excess of 2.0 mol dm^{-3} hydrochloric acid

Method

Read through the instructions carefully before starting any practical work.

1. Support the styrofoam cup in the 250 cm^3 beaker.
2. Use the measuring cylinder to transfer 50 cm^3 of 2.0 mol dm^{-3} hydrochloric acid into the styrofoam cup.
3. Place the thermometer in the styrofoam cup and record the temperature of the solution.
4. Weigh the weighing bottle containing **FA 5**, anhydrous sodium carbonate.
5. With the aid of a dry spatula, add the contents of the weighing bottle to the styrofoam cup in **three separate portions**, taking care that the mixture does not overflow.

[Safety precaution: DO NOT add FA 5 all at once. The reaction is very vigourous.]

6. Stir and record the highest temperature obtained.
7. Reweigh the weighing bottle containing residual **FA 5**.

Record in an appropriate form below, all of your weighings and temperature measurements together with the mass, **m_1**, of **FA 5** added and the maximum temperature rise, **ΔT_1**.

Results

Mass of weighing bottle and FA 5	**/ g**	**51.64**
Mass of weighing bottle and residual FA 5	**/ g**	**45.60**
Mass of FA5 (Na_2CO_3) added to acid (m_1)	**/ g**	**6.04**

Initial temperature of HC*l*	**/ °C**	**29.5**
Maximum temperature	**/ °C**	**37.5**
Maximum temperature rise (ΔT_1)	**/ °C**	**8.0**

- **(for both (a) and (c)): mass table and table recording temperature changes with appropriate headers**
- **Record every mass reading to 2 dp and temperature recorded to 1dp**

[2]

(b) **(i)** Calculate the temperature rise per gram of **FA 5**, Na_2CO_3, used in the experiment.

- **$\frac{\Delta T_1}{m_1}$ = 8.0 / 6.04 = 1.32 °C g^{-1}**
- **Accuracy**

Calculate the difference between the Supervisor and candidate values of $\Delta T/m$. Give 1 mark for a difference up to ±0.2 °C g^{-1}.

$\frac{\Delta T_1}{m_1}$ = **1.32 °C g^{-1}**

[2]

(ii) Calculate the enthalpy change, ΔH_1, for the reaction

$$Na_2CO_3(s) + 2HCl(aq) \rightarrow 2NaCl\ (aq) + CO_2\ (g) + H_2O(l)$$

$$\Delta H_1 = -\left(22.79 \times \frac{\Delta T_1}{m_1}\right) \text{ kJ mol}^{-1}$$

$\Delta H_1 = -\left(22.79 \times \frac{\Delta T_1}{m_1}\right)$

- **$\Delta H_1 = -(22.79 \times 1.32) = \underline{-30.2 \text{ kJ mol}^{-1}}$**

ΔH_1 = **– 30.2 kJ mol^{-1}**

[1]

(c) Reaction of FA 6, $NaHCO_3$, with an excess of 2.0 mol dm^{-3} hydrochloric acid

Method

Read through the instructions carefully before starting any practical work.

1. Support another styrofoam cup in the 250 cm^3 beaker provided.
2. Use the measuring cylinder to transfer 50 cm^3 of 2.0 mol dm^{-3} hydrochloric acid into the styrofoam cup.
3. Place the thermometer in the styrofoam cup and record the temperature of the solution.
4. Weigh the empty weighing bottle labelled **"FA 6"**.
5. Weigh approximately 7.0 – 8.0 g of **FA 6**, anhydrous sodium hydrogen carbonate into the empty weighing bottle labelled **"FA 6"**.
6. With the aid of a dry spatula, add the contents of the weighing bottle to the styrofoam cup in **three separate portions**, taking care that the mixture does not overflow.

[Safety precaution: DO NOT add FA6 all at once. The reaction is very vigourous.]

7. Stir and record the lowest temperature obtained.
8. Reweigh the weighing bottle containing residual **FA 6**.

Record in an appropriate form below, all of your weighings and temperature measurements together with the mass, **m_2**, of **FA 6** added and the maximum temperature fall, **ΔT_2**.

Results

Mass of empty weighing bottle	**/ g**	**44.89**
Mass of weighing bottle and FA 6	**/ g**	**52.49**
Mass of weighing bottle and residual FA 6	**/ g**	**44.90**
Mass of FA 6 ($NaHCO_3$) added to acid (m_2)	**/ g**	**7.59**

Initial temperature of HC*l*	**/ °C**	**29.5**
Minimum temperature	**/ °C**	**18.0**
Fall in temperature (ΔT_2)	**/ °C**	**11.5**

[Marks awarded together with (a)]:

mass table and table recording temperature changes with appropriate headers
Record every mass reading to 2 dp and temperature recorded to 1dp

(d) (i) Calculate the temperature fall per gram of **FA 6**, $NaHCO_3$, used in the experiment.

●$\frac{\Delta T_2}{m_2}$ **= (11.5/ 7.59) = 1.52 °C g^{-1}.**

●**Accuracy**

Calculate the difference between supervisors' value and the candidate's value of ΔT/m.

Give 1 mark for a difference up to ±0.2 °C g^{-1}

$\frac{\Delta T_2}{m_2}$ = **1.52 °C g^{-1}**

[2]

(ii) Calculate the enthalpy change, ΔH_2, for the reaction

$$NaHCO_3(s) + HCl(aq) \rightarrow NaCl(aq) + CO_2(g) + H_2O(l)$$

$$\Delta H_2 = +\left(18.06 \times \frac{\Delta T_2}{m_2}\right) \text{ kJ mol}^{-1}$$

$\Delta H_2 = +\left(18.06 \times \frac{\Delta T_2}{m_2}\right)$

- **$\Delta H_2 = +(18.06 \times 1.52)$ = $\underline{+ 27.5 \text{ kJ mol}^{-1}}$**

ΔH_2 = **$\underline{+ 27.5 \text{ kJ mol}^{-1}}$**

[1]

(e) **(i)** The smallest graduation in reading a –10 °C to +110 °C thermometer is 1.0 °C

Suggest the maximum error of the temperature change calculated with two temperature readings.

Error = ½ of smallest graduation = ±0.5 °C

- **Maximum error = 2 x 0.5 = ±1.0°C**

Maximum error = **±1.0°C**

[1]

(ii)

The expected fall in temperature when 1.0 g of $NaHCO_3(s)$ is added to 50 cm^3 of 2.0 mol dm^{-3} hydrochloric acid is approximately 1.5°C

Determine the maximum percentage error in the calculated temperature change when 1.0 g of $NaHCO_3$ is added to 50 cm^3 of 2.0 mol dm^{-3} hydrochloric acid.

- **% error = $\frac{1.0}{1.5}$ x 100% = 66.7%**

Maximum percentage error = **66.7%**

[1]

(f) It is not possible to measure experimentally the enthalpy change, ΔH_3, for the following reaction as it does not take place in the laboratory.

$$Na_2CO_3(s) + CO_2(g) + H_2O(l) \rightarrow 2NaHCO_3(s)$$

It is possible, however, to calculate a "theoretical" value of ΔH_3 for this reaction from the results of the experiments you have carried out.

Using an energy cycle and your results from **(b)(ii)** and **(d)(ii),** calculate a value for ΔH_3.

●Energy cycle with state symbols

$$\begin{tikzcd}
2HCl(aq) + Na_2CO_3(s) + H_2O(l) + CO_2(g) \arrow[rr, "\Delta H_3"] \arrow[dr, "\Delta H_1"'] & & 2NaHCO_3(s) + 2HCl(aq) \arrow[dl, "2\Delta H_2"] \\
& 2NaCl(aq) + 2CO_2(g) + 2H_2O(l) &
\end{tikzcd}$$

● By Hess' Law,

$\Delta H_3 = \Delta H_1 - (2 \times \Delta H_2)$

$\Delta H_3 = (-30.2) - 2(+27.5) = -85.2\ \text{kJ mol}^{-1}$

ΔH_3 = $-85.2\ \text{kJ mol}^{-1}$

[2]

[Total: 12]

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 reagents are selected for use in a test, the **name or correct formula** of the element or compound must be given.

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.

No additional tests for ions present should be attempted.

Rinse and reuse test-tubes and boiling tubes where possible.

(a) **FA 7, FA 8** and **FA 9** are aqueous solutions that each have an ion containing one of the metals from those listed in the Qualitative Analysis Notes.

FA 1 from Question 1 are to be used in some of these tests.

Carry out the following tests and record your observations.

	Test	*Observation*
(i)	To a 1 cm depth of **FA 7** in a test-tube, add a 1 cm depth aqueous sodium hydroxide. Then, add several drops of **FA 1**.	√ **Off-white ppt formed turns brown on contact with air, insoluble in excess NaOH** √ **Black or brown solid (ppt) formed** **Effervescence seen.** √(Colourless, odourless) **gas evolved relights a glowing splint**
(ii)	To a 1 cm depth of **FA 8** in a test-tube, add a few drops of aqueous sodium hydroxide. Then, add excess aqueous sodium hydroxide.	√ **Green ppt formed, turns brown on standing, insoluble in excess NaOH**
(iii)	To a 1 cm depth of **FA 8** in a test-tube, add several drops of **FA 1,** and then add aqueous sodium hydroxide.	√ **Solution turned darker yellow.** √ **Red-brown ppt formed insoluble in excess NaOH** **Effervescence seen.** √ **(colourless, odourless) gas evolved relights a glowing splint**
(iv)	To a 1 cm depth of **FA 8** in a test-tube, add a 1 cm depth of dilute sulfuric acid, and then a few drops of **FA 9**.	√ **Purple FA 9 decolourises to form a colourless/ (pale-yellow/ pale-orange) solution.**
(v)	To a 1 cm depth of aqueous potassium iodide in a test-tube, add a few drops of **FA 9**. Then, add a few drops of starch solution	√ **Brown solution formed / black ppt formed.** √**Solution turned blue-black** **Every 2 √ = 1m**

[5]

(b) Identify the cation present in **FA 7** and **FA 8**.

The cation present in **FA 7** is **●Mn^{2+}**

The cation present in **FA 8** is **●Fe^{2+}**

[2]

(c) Explain the chemistry involved in the effervescence observed in both **(a)(i)** and **(a)(iii).**

[1]

●Gas evolved is O_2. Mn^{2+} and Fe^{3+} present in the solution acts as a catalyst for the decomposition of H_2O_2. Hence, O_2 is produced.

(d) A student added 1 cm^3 of **FA 9** to a test-tube containing **FA 8**. A strip of magnesium ribbon was then added to the mixture. Effervescence was observed.

Deduce the identity of the gas evolved and explain the chemistry involved in this reaction.

[3]

●Gas evolved is H_2.

●Fe^{2+} in FA 8 was oxidized to Fe^{3+} by FA 9 (oxidizing agent)

●Fe^{3+} has a high polarizing power (high charge density), thus polarize the electron cloud of water, weaken the O-H bond, releasing H^+ into the solution, thus FA8 is acidic. Reactive metal Mg reacts with an acidic solution to release H_2 (g).

(e) **Figure 1** below shows the process of thermal decomposition of **FA 10**, which is a solid sample of the compound present in the aqueous solution of **FA 9**.

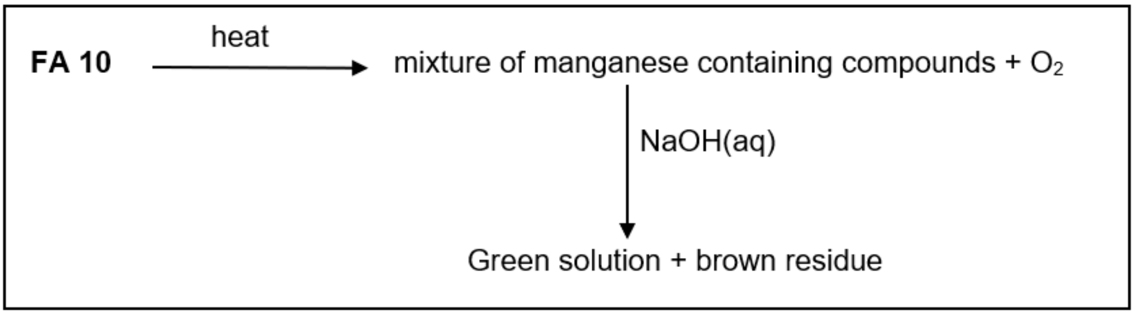


Figure 1

Consider the observations in **Figure 1**, suggest the identity of the manganese-containing species in the green solution and the residue.

● MnO_4^{2-}(solution) and MnO_2(residue)

[1]

(f) **FA 8** contains one of the anions Cl^-, Br^-, I^-, SO_4^{2-} or SO_3^{2-}.

Plan an experiment to determine the reagents you would use to identify which anion is present in **FA 8**.

Carry out your tests on **FA 8** to identify the anion present. Record your observations in the table below.

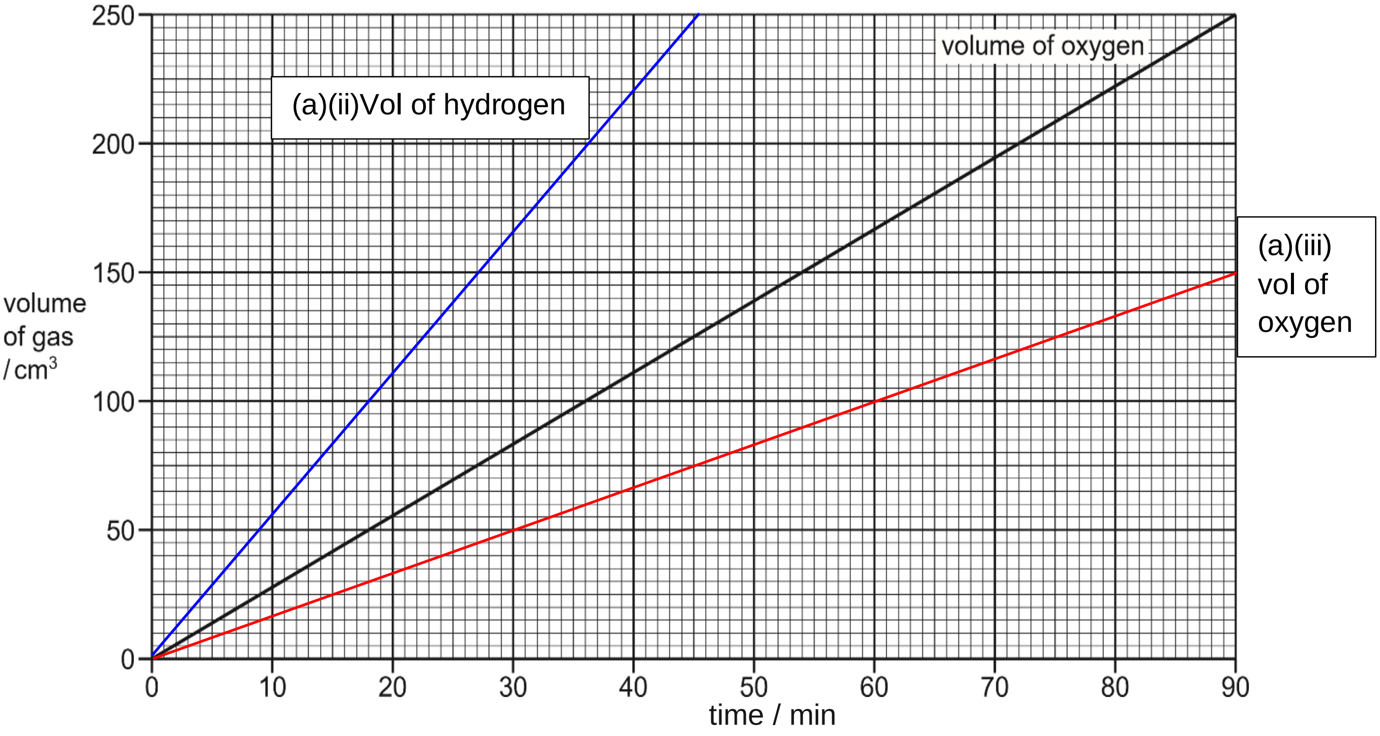
	Test	*Observations*
(i)	**To a 1 cm depth of FA 8, add 1 cm^3 of aqueous silver nitrate.**	**No ppt formed**
(ii)	**To a 1 cm depth of FA 8, add 1 cm^3 of √ aqueous barium nitrate, √ followed by nitric acid.** *[Note: cannot use sulfuric acid. Hydrochloric acid is acceptable]*	**√ White ppt formed,** **√ insoluble in HNO_3.**

Suggest the identity of the anion present in **FA 8**.

●sulfate / SO_4^{2-}

[3]
[Total:15]

4 **(a)** This question is about the electrolysis of different compounds.
During the electrolysis of dilute sulfuric acid using a current of 0.75 A for 90 minutes, the volume of oxygen gas collected was recorded and is shown in the graph below.



(i) Table 1 below gives some standard electrode potential values

Electrode reaction	**$E^{\ominus}$ / V**
$2H^+ + 2e^- \rightleftharpoons H_2$	0.00
$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	+1.23
$O_2 + 2H_2O + 4e^- \rightleftharpoons 4OH^-$	+0.40
$2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-$	–0.83
$SO_4^{2-} + 4H^+ + 2e^- \rightleftharpoons SO_2 + 2H_2O$	+0.17
$S_2O_8^{2-} + 2e^- \rightleftharpoons 2SO_4^{2-}$	+2.01

Table 1

With reference to the values in the Table 1, write equations for the reactions that occur at each electrode in the electrolysis of sulfuric acid.

[2]

- **Cathode :** $2H^+(aq) + 2e \longrightarrow H_2(g)$
- **Anode :** $2H_2O(l) \longrightarrow O_2(g) + 4H^+(aq) + 4e$

On the graph on page 14,

(ii) Draw a straight line to show the volume of hydrogen evolved in the same experiment. Label the line as “hydrogen”.

[1]

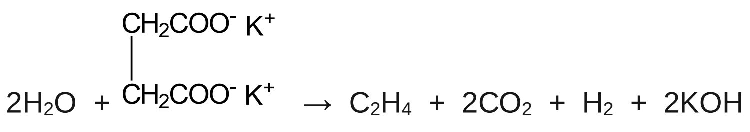
- **Straight line drawn from origin that has double the volume of oxygen at a given time.**

(iii) Draw a straight line to show the volume of oxygen evolved if a current of 0.45 A was used instead of the 0.75 A used in the original experiment. Label the line as “oxygen”.

[1]

- **Straight line drawn from origin which has 0.45/0.75 x volume of oxygen at a given time.**

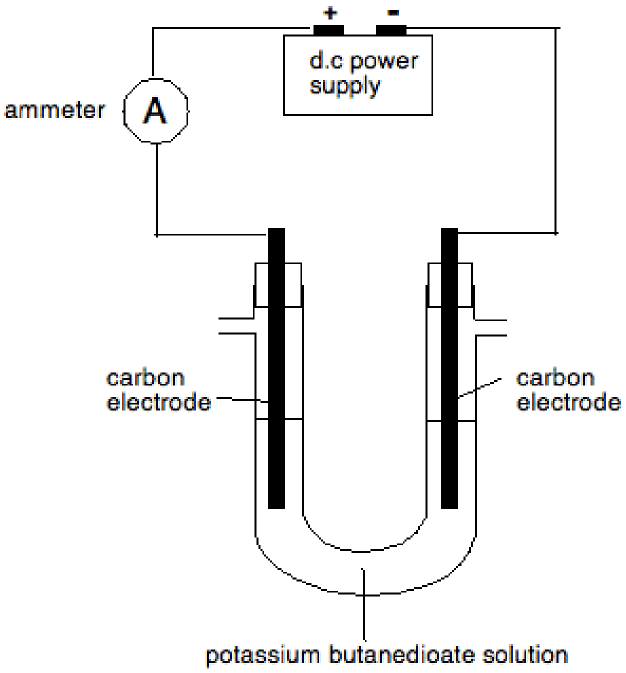
(b) During the electrolysis of potassium butanedioate, the following reaction occurs.



$$2H_2O + \begin{array}{l} CH_2COO^- K^+ \\ | \\ CH_2COO^- K^+ \end{array} \rightarrow C_2H_4 + 2CO_2 + H_2 + 2KOH$$

potassium
butanedioate

An experiment can be conducted to verify the stoichiometric ratio between hydrogen gas and ethene gas collected using the following set-up.



Hydrogen is produced at one electrode, ethene and carbon dioxide are produced at the other. The carbon dioxide can be separated from the ethene by absorbing it using a suitable reagent before the volume of ethene is measured.

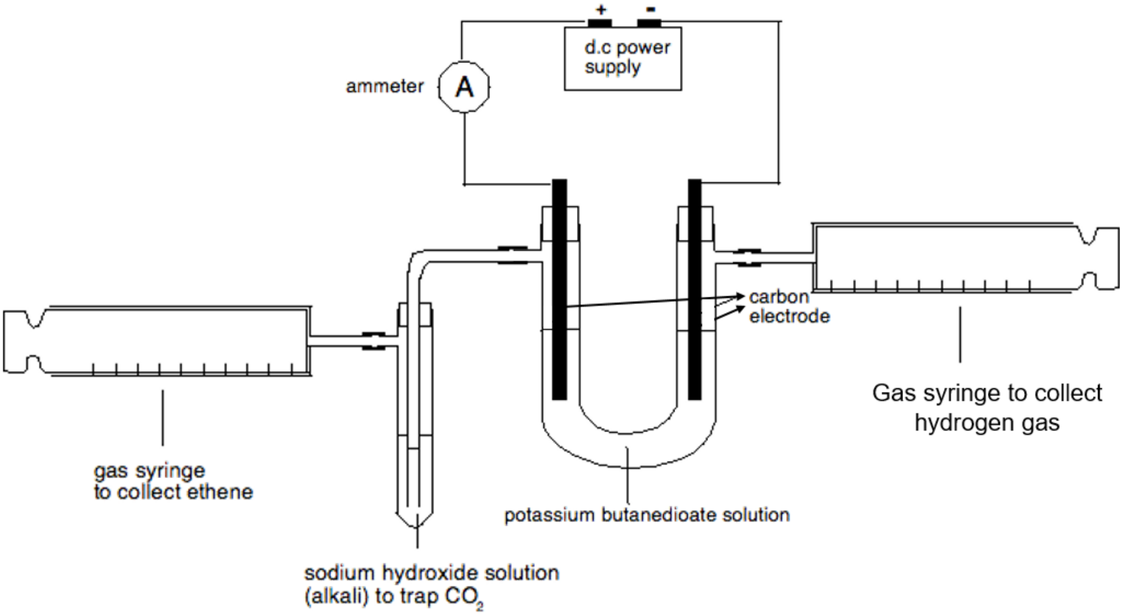
(i) Complete the diagram on page 15 to show how:

- the hydrogen could be collected and its volume measured,
- the carbon dioxide could be removed,
- the volume of ethene could be measured.

Your diagram should include appropriate apparatus and the identity of the suitable reagent used to remove carbon dioxide.

[3]

Answers:



√ Gases are released at the correct electrode (polarity)
√ Diagram shows collection of hydrogen using a means of measuring the volume of the gas
√ Diagram shows carbon dioxide from the anode being absorbed using an alkaline solution
√ Diagram shows ethene being collected using a means of measuring the volume of the gas

4√ : 3 m
2-3√ : 2m
1√ : 1 m
If use limewater not penalised here.

(ii) Calculate the number of coulombs, **N**, that would be required to produce **V** cm^3 of hydrogen at room temperature and pressure.

[1]

Amount of hydrogen = V/24000 mol

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

Amount of electrons required = 2 x V/24000

• N = 2 x V/24000 x 96500 C

= 8.04V C

(iv) Write the equation for the reaction that takes place for the removal of carbon dioxide.

[1]

- **$2NaOH + CO_2 \longrightarrow Na_2CO_3 + H_2O$**

(vi) Predict the organic product that would be obtained at the electrode when a solution of potassium *hexanedioate* is electrolysed.

[1]

- **But-2-ene**

[Total: 10]

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

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

Apparatus List

1. In addition to the fittings ordinarily contained in a chemical laboratory, the apparatus, and materials specified below will be necessary.

2. Pipette fillers (or equivalent safety devices), safety goggles and disposable plastic gloves should be used where necessary.

3. *For each candidate*

For each candidate

1 x burettes (50 cm^3);
1 x pipette (25.0 cm^3);
1 x pipette filler;
1 x retort stands and burette clamps;
1 x 50 cm^3 measuring cylinder;
1 x funnels (for filling burette);
1 x 250cm^3 volumetric (graduated) flask
2 x 250 cm^3 conical flasks;
1 x 250cm^3 beaker
1 x white tile;
1 x thermometer with range -10 °C to +110 °C, graduated to 1 °C;
2 x styrofoam cup
4 plastic dropping pipettes;
5 test-tubes;
1 x test-tube rack;
1 x test-tube holder;
1 x delivery-tube (small one – for test-tube)
1 x small spatula
1 x wash bottle containing deionised water;
1 x Bunsen burner;
1 x lighter (per bench)
Water-soluble marker
wooden splinters
red and blue litmus paper
paper towels

Additional pipette filler, test-tubes and dropping pipettes should be available.

Chemicals Required

Question 1-3:

Label	Per candidate	Identity	Notes (preparation)
FA 1	70 cm^3	5 'vol' hydrogen peroxide	Dilute 50cm^3 of 100 'vol' hydrogen peroxide to 1 dm^3
FA 2	150 cm^3	0.02 mol dm^{-3} potassium managanate (VII)	
FA 3	200 cm^3	1.0 mol dm^{-3} sulfuric acid	
FA 5	6.0 g – 7.0 g	Anhydrous sodium carbonate	Between 6.0 - 7.0 g of powdered Na_2CO_3 in a stoppered weighing bottle, labelled **FA 5.**
FA 6	6.0 g – 7.0 g	Sodium hydrogen carbonate	Place powdered $NaHCO_3$ beside weighing balance in lab (4 weighing balance in each lab). Each student would have 1 empty stoppered weighing bottle, labelled **FA6**.
2.0 mol dm^{-3} HCl	150 cm^3	2.0 mol dm^{-3} HC*l*	Bottled and labelled separately from QA reagents Labelled as '2.0 mol dm^{-3} HC*l*'.
FA 7	10 cm^3	0.2 mol dm^{-3} manganese (II) chloride	Dissolve 25.2 g of $MnCl_2$ (or 39.6g of $MnCl_2$•$4H_2O$) in each dm^3 of solution
FA 8	20 cm^3	0.1 mol dm^{-3} iron (II) ammonium sulfate	Dissolve 39.2 g of $Fe(NH_4)_2(SO_4)_2$•$6H_2O$ in acid Note: Cannot not prepare in acid as the solution gets oxidized quickly. If dissolve in acid, the solution is colourless.
FA 9	10 cm^3	0.02 mol dm^{-3} potassium managanate (VII)	Labelled separately as '**FA 9'**. Different from **FA 2** labels.
Aqueous Starch	5 cm^3	Starch solution	
Potassium iodide	5 cm^3	0.1 mol dm^{-3} potassium iodide	

QA reagents required:

1. Dilute HC*l*
2. Dilute HNO_3
3. Dilute H_2SO_4
4. Aqueous NH_3
5. Aqueous NaOH
6. 0.1 mol dm^{-3} of Aqueous $Ba(NO_3)_2$
7. 0.05 mol dm^{-3} of aqueous silver nitrate ($AgNO_3$)
8. Limewater