EUNOIA JUNIOR COLLEGE
JC2 Preliminary Examination 2018
General Certificate of Education Advanced Level
Higher 2

CHEMISTRY

9729/01

Paper 1 Multiple Choice

24 September 2018

1 hour

Additional Materials: Multiple Choice Answer Sheet
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write in soft pencil.
Do not use staples, paper clips, glue or correction fluid.
Write your name, civics group and registration number on the Answer Sheet in the spaces provided unless this has been done for you.

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.

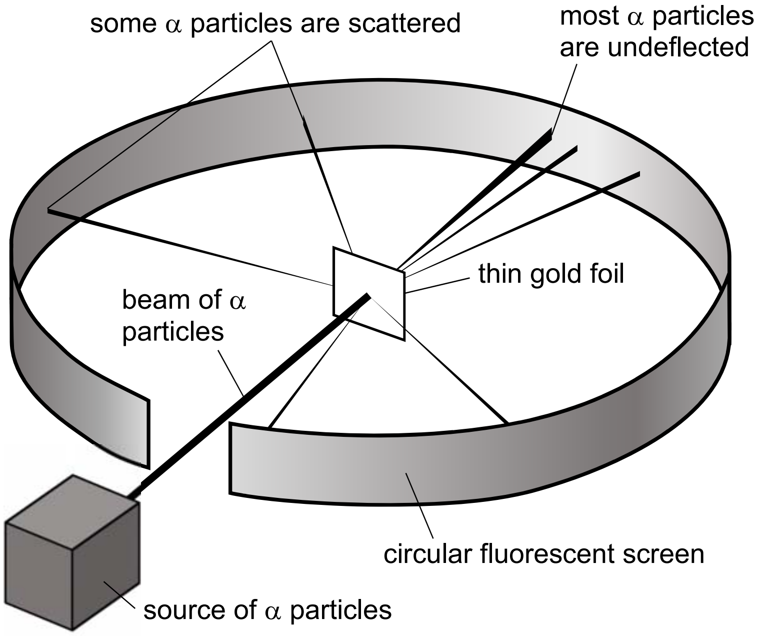
Read the instructions on the Answer Sheet very carefully.

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

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

1 Following J. J. Thomson's discovery of the electron in 1897, Ernest Rutherford devised the celebrated gold foil experiment, which led to a better understanding of the structure of the atom. In the experiment, a beam of heavy α particles, ${}^{4}_{2}He^{2+}$, was fired at a piece of thin gold foil as target.

As expected, most of the α particles passed straight through the gold foil undeflected. However, some α particles are scattered, and a small number in fact deflected right back to the source.



Which of the following conclusions **cannot** be drawn from the gold foil experiment?

A Atom is mostly empty space.

B Atom possesses a region of positive charge.

C Electrons in atom orbit around a dense positively charged region.

D The positive charge in an atom is concentrated within a very small volume.

2 The most common oxidation state of americium, Am, in aqueous solution is +*n*.

Recently, Cu^{3+} has been shown to quantitatively oxidise Am^{n+}(aq) in dilute HNO_3 to the +2*n* oxidation state, while itself is reduced to Cu^{2+}.

In an experiment, 25.0 cm^3 of 0.0100 mol dm^{-3} Am^{n+}(aq) was found to require 15.0 cm^3 of 0.0500 mol dm^{-3} Cu^{3+} for complete oxidation.

What is the formula of the americium containing species formed?

A Am^{2+} **B** AmO_2 **C** AmO_2^{+} **D** AmO_2^{2+}

3 In which sequences are the molecules quoted in order of increasing bond angle around the central atom within the molecule?

A	OF_2	CH_4	SF_6
B	H_2O	O_3	N_2O
C	PF_3	BF_3	IF_3
D	NO_2	SO_2	CO_2

4 Unlike the reaction of ammonia with hydrogen chloride to give ammonium chloride, the reaction of ammonia with hydrogen fluoride produces colourless crystals of ammonium bifluoride, NH_4HF_2, which contains the bifluoride ion, HF_2^-:

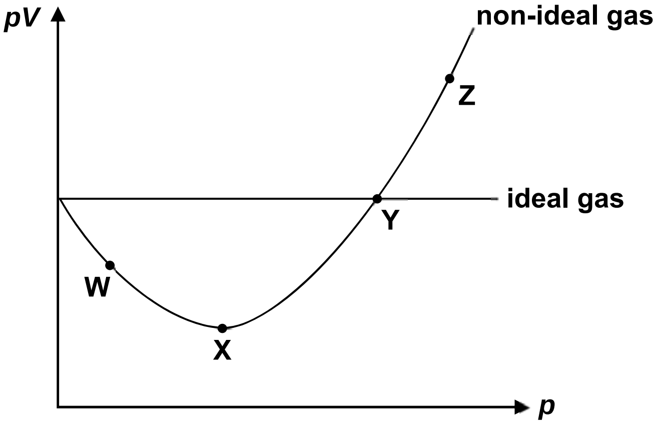
$$NH_3(g) + 2HF(g) \rightarrow NH_4HF_2(s)$$

Which of the following chemical bonds are present in the ammonium bifluoride crystals?

1 ionic bond
2 dative bond
3 hydrogen bond

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

5 The value of pV is plotted against p for two gases, an ideal gas and a non-ideal gas, where p is the pressure and V is the volume of the gas.



At which points on the graph, is the intermolecular forces of attraction within the non-ideal gas, the dominant factor accounting for deviation from ideal gas behavior?

A **W** only
B **W** and **X** only
C **W**, **X** and **Y** only
D **W**, **X** and **Z** only

6 There are conflicting interpretations for the origin of the acidity of aqueous boric acid, $B(OH)_3$. Some believe that the acidity is exclusively from the following equilibria:

$$B(OH)_3(aq) + H_2O(l) \rightleftharpoons B(OH)_4^-(aq) + H^+(aq)$$

Which of the following statements pertaining to this interpretation of the acidity of boric acid is **incorrect**?

A Boric acid is an Arrhenius acid.

B Boric acid is a Brønsted-Lowry acid.

C Boric acid is a Lewis acid.

D Boric acid is a weak monobasic acid.

7 Chlorides of Period 3 elements dissolve in water to form aqueous solutions.

Which of the following sequence shows the order of increasing pH of the resultant solutions formed when these compounds are dissolved in water?

A $Al_2Cl_6 < MgCl_2 < NaCl$

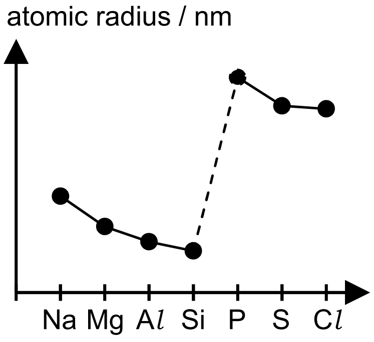
B $MgCl_2 < Al_2Cl_6 < SiCl_4$

C $PCl_5 < MgCl_2 < Al_2Cl_6$

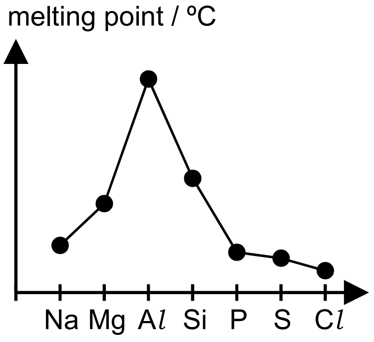
D $SiCl_4 < Al_2Cl_6 < PCl_5$

8 For the elements in Period 3 of the Periodic Table, which of the following sketches shows the correct trend in the stated property?

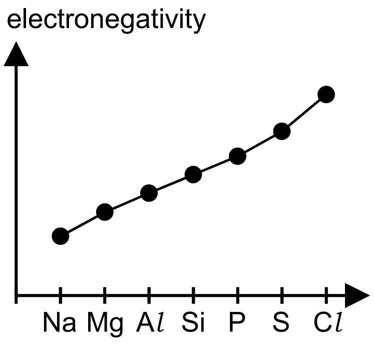
A



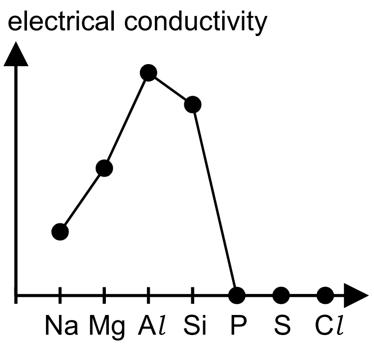
B



C



D



9 Sodium reacts with water to form sodium hydroxide and hydrogen.

$$2Na(s) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2(g) \qquad \Delta H_1^\ominus$$

What information is needed in order to calculate the standard enthalpy change of reaction, $\Delta H_1^\ominus$?

1 $\Delta H_c^\ominus$ for $H_2(g)$

2 $\Delta H_c^\ominus$ for $H_2O(l)$

3 $\Delta H_f^\ominus$ for $NaOH(aq)$

4 $\Delta H_c^\ominus$ for $Na(s)$

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

10 Which reaction represents a standard enthalpy change at 298 K?

A $\frac{1}{2}O_2(g) \rightarrow O(g)$

B $C(g) + O_2(g) \rightarrow CO_2(g)$

C $2C(s) + 6H(g) \rightarrow C_2H_6(g)$

D $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$

11 The reaction between $A(aq)$ and $B(aq)$ has a rate constant of 9×10^{-3} $mol^{-2}\,dm^6\,s^{-1}$.

Which one of the following is a possible rate equation for this reaction?

A $rate = k[B(aq)]$

B $rate = k[A(aq)]^2$

C $rate = k[A(aq)][B(aq)]^2$

D $rate = k[A(aq)]^2[B(aq)]^2$

12 The half-life of the first order gaseous reaction in which X_2 molecules become converted into X atoms is 20 minutes.

1 mol of X_2 is put into a sealed vessel at pressure *p*.

Which of the following will be correct when 87.5% of X_2 has been converted into X atoms?

1 60 minutes have elapsed.

2 1.75 mol of X atoms have been formed.

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

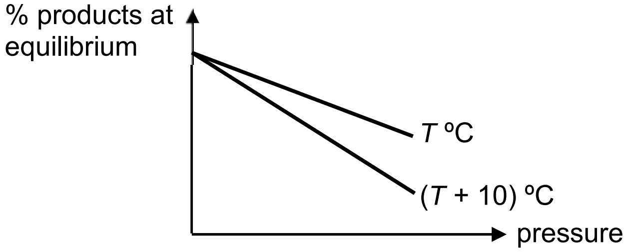
A **1** only is correct

B **1** and **2** only are correct

C **2** and **3** only are correct

D **1**, **2** and **3** are correct

13 The graphs below show how the percentage of gaseous products present at equilibrium vary with temperature and pressure.



Which one of the following reactions could the graph represent?

A $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ $\Delta H = +57\ \text{kJ mol}^{-1}$

B $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ $\Delta H = +53\ \text{kJ mol}^{-1}$

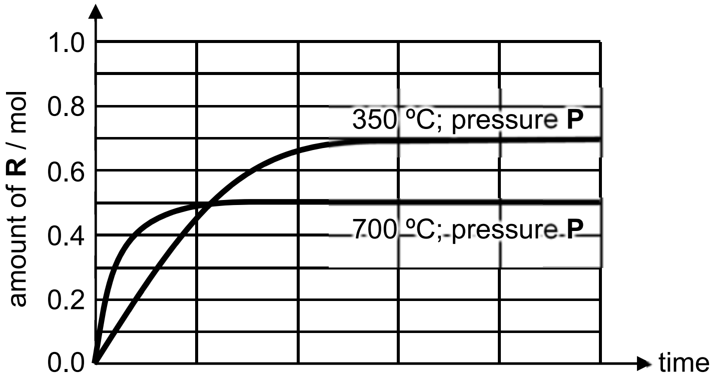
C $2C(s) + O_2(g) \rightleftharpoons 2CO(g)$ $\Delta H = -221\ \text{kJ mol}^{-1}$

D $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ $\Delta H = -92\ \text{kJ mol}^{-1}$

14 **L** and **M** can react together to reach equilibrium in the reaction below.

$$\mathbf{L}(g) + \mathbf{M}(g) \rightleftharpoons \mathbf{Q}(g) + \mathbf{R}(g)$$

In an experiment, 1.0 mole each of **L** and **M** were reacted at constant pressure **P** and temperature 350 ºC. The amount of **R** present in the mixture at intervals of time was recorded. The experiment was repeated at the same pressure **P**, but at a temperature of 700 ºC. The results for both experiments are shown below.



Which one of the following information **cannot** be deduced from the graph?

A The value of K_p at 350 ºC.

B The forward reaction is exothermic.

C The activation energy of the forward reaction is high.

D The equilibrium is achieved at a faster rate at higher temperatures.

15 The table gives the concentrations and pH values of the aqueous solutions of three compounds, **X**, **Y** and **Z** at 25 ºC. Each compound could be an acid or a base.

	X	**Y**	**Z**
concentration	1.00×10^{-4} mol dm^{-3}	1.00 mol dm^{-3}	1.00 mol dm^{-3}
pH	4	3	14

A final year student made the following conclusions:

1 **X** is a strong acid and **Z** is a strong base.
2 The extent of dissociation of **X**(aq) is higher than in **Y**(aq).
3 Mixture of equal volume of **Y** and **Z** will give a resulting solution of pH > 7.

Which of the above conclusions are **correct**?

A Conclusion **1** only

B Conclusion **2** only

C Conclusions **2** and **3** only

D All three conclusions are correct

16 In which of the following solution will solid silver phosphate, Ag_3PO_4, be the least soluble at 25 ºC?

Given that the numerical value of $K_{sp}(Ag_3PO_4) = 8.89 \times 10^{-17}$.

A pure water

B 0.10 mol dm^{-3} $AgNO_3(aq)$

C 0.10 mol dm^{-3} $NH_3(aq)$

D 0.10 mol dm^{-3} $Na_3PO_4(aq)$

17 Which compound exhibits both *cis-trans* and enantiomerism?

A $CH_3CH_2CHBrCH{=}CHBr$

B $CH_3CH{=}CHCH_2CH_3$

C $CH_3CHBrCH{=}CH_2$

D $CH_3CBr{=}CBrCH_3$

18 Which structural formula represents 2,2-dimethylpentane?

A $(CH_3)_3CCH(CH_3)_2$

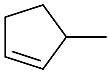
B $(CH_3)_3CCH_2C(CH_3)_3$

C $CH_3CH_2CH_2C(CH_3)_3$

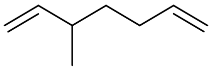
D $(CH_3)_2CHCH_2CH(CH_3)_2$

19 Which of the following hydrocarbons would give the same organic product upon oxidation with hot acidified $KMnO_4$?

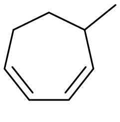
1



2



3



A **1**, **2** and **3** are correct

B **1** and **2** only are correct

C **2** and **3** only are correct

D **1** and **3** only are correct

20 Which of the following compounds reacts with benzene under suitable conditions to form $C_6H_5COC_6H_5$?

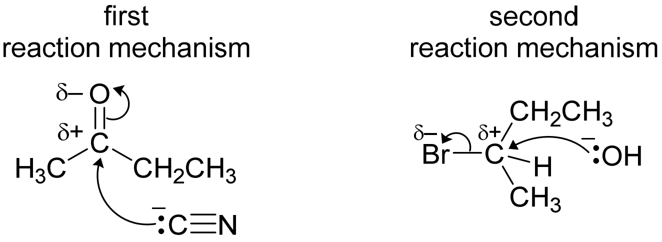
A C_6H_5CHO

B C_6H_5COOH

C $C_6H_5CH_2OH$

D C_6H_5COCl

21 The **rate-determining step** of two different reaction mechanisms are shown below:



What do both reaction mechanism steps have in common?

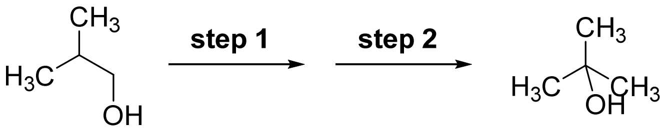
A Intermediates are formed.

B They involve addition of nucleophile.

C The overall rate of reaction is second order.

D The products formed can rotate plane polarised light.

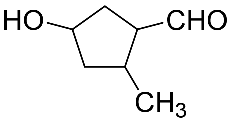
22 2-methylpropan-1-ol can be converted into 2-methylpropan-2-ol in two steps.



Which one of the following sequences may be used for the conversion?

	step 1	step 2
A	PCl_5 at r.t.p.	NaOH(aq), heat
B	conc. H_2SO_4, heat	alkaline $KMnO_4$, cold
C	Al_2O_3 with heating	H_2O with H_3PO_4 at high temperature and pressure
D	alcoholic NaOH	dilute H_2SO_4

23 Tollens' reagent is added to the following organic compound and warmed. What are the products formed as a result?



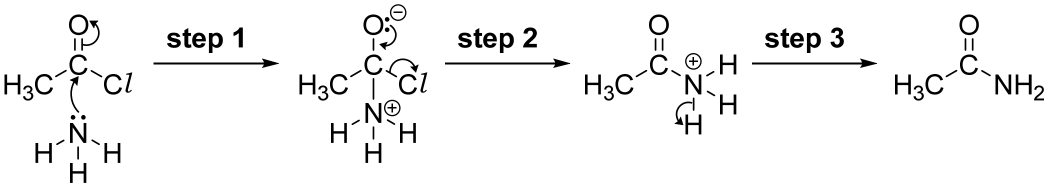
A Silver mirror and an organic compound containing a carboxylic acid

B Silver mirror and an organic compound containing a carboxylate salt

C Silver mirror and an organic compound containing a ketone and a carboxylic acid

D Silver mirror and an organic compound containing a ketone and a carboxylic salt

24 The reaction between ammonia and ethanoyl chloride proceeds *via* the nucleophilic acyl substitution mechanism shown below.



Which of the statements is **incorrect** about the above mechanism?

A Ammonia behaves as a nucleophile.

B Arrow pushing in **step 2** has been shown correctly.

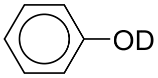
C Ethanoyl chloride behaves as an electrophile.

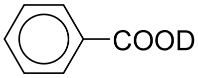
D Proton loss in **step 3** has been shown correctly.

25 Phenyl propanoate undergoes acid hydrolysis in the presence of water labelled with the deuterium ^2D isotope.

Which of the following products are formed?

1 CH_3CH_2COOD

2 

3 

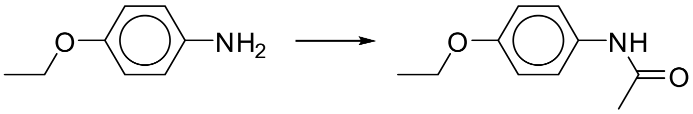
A Only **1**

B **1** and **2** only

C **1** and **3** only

D **1**, **2** and **3**

26 The synthesis of an aromatic amide from compound **X** is shown below.



What is the most suitable reagent to use in this synthesis?

A CH_3COCl

B CH_3COCH_3

C CH_3CONH_2

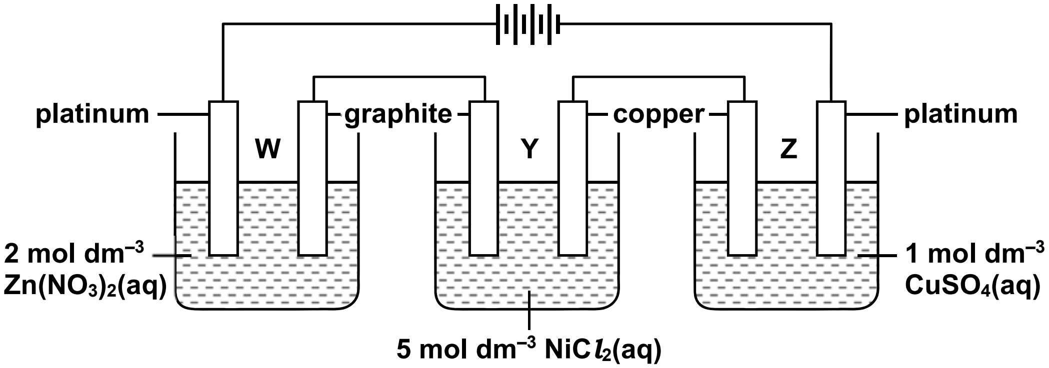
D CH_3COOH

27 Which of the following shows the nitrogen compounds arranged in order of increasing pK_b values?

A	NH_3	<	CH_3NH_2	<	$(CH_3)_2NH$
B	$CH_3CH_2NH_2$	<	NH_3	<	$C_6H_5NH_2$
C	$CH_3CH_2NH_2$	<	$(C_2H_5)_2NH$	<	$C_6H_5NH_2$
D	$C_6H_5NH_2$	<	NH_3	<	$CH_3CH_2NH_2$

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

The following electrolytic cell is set up.

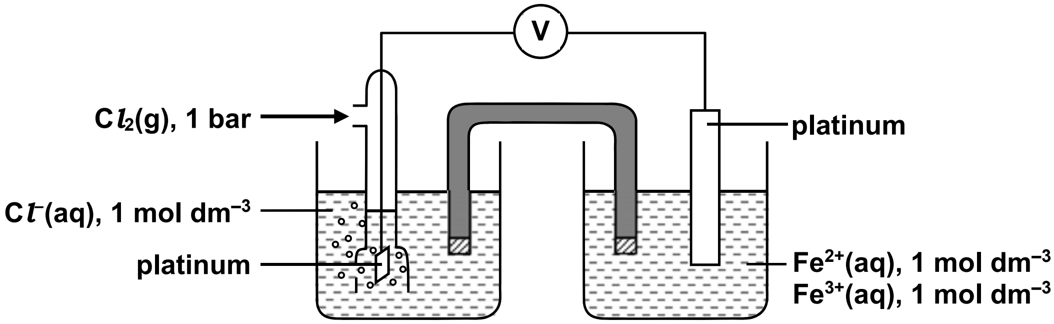


What is the ratio of the volume of gas formed at the anode in cell **W** : cell **Y** : cell **Z**?

A 1 : 1 : 1 **B** 1 : 2 : 1 **C** 1 : 1 : 0 **D** 1 : 2 : 0

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

The cell shown below is set up.



Which statements are correct?

1 The voltmeter will register an initial reading of 0.59 V, which decreases gradually with time.

2 Addition of a few crystals of silver(I) nitrate to the left-hand-side half-cell will cause the voltmeter reading to increase.

3 Addition of excess solid sodium cyanide to the right-hand-side half-cell will cause the voltmeter reading to increase.

A **1** only is correct

B **1** and **2** only are correct

C **2** and **3** only are correct

D **1**, **2** and **3** are correct

30 Which of the following processes is **not** involved in the following reaction between the two transition metal complexes in acidic medium?

$$[CoCl(NH_3)_5]^{2+} + [Cr(OH_2)_6]^{2+} + 5H_3O^+ \rightarrow [CrCl(OH_2)_5]^{2+} + [Co(OH_2)_6]^{2+} + 5NH_4^+$$

A electron transfer

B hydration

C ligand exchange

D neutralisation

Answer :

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

2018 JC2 Preliminary Examination
H2 Chemistry 9729
Paper 1 Worked Solution

1 The positive α particles either passes straight through the empty space or are occasionally repelled by the dense positive nucleus. They are not affected by the much smaller electrons and hence does not provide any information about the electrons.

$\Rightarrow$ **C**

2 [O] : $Am^{n+} \rightarrow Am^{2n+} + ne^-$

[R] : $nCu^{3+} + ne^- \rightarrow nCu^{2+}$

So, $Am^{n+} + nCu^{3+} \rightarrow Am^{2n+} + nCu^{2+}$

$$n_{Am^{n+}} = \frac{25.0}{1000} \times 0.0100 = 2.5 \times 10^{-4} \text{ mol}$$

$$n_{Cu^{3+}} = \frac{15.0}{1000} \times 0.0500 = 7.5 \times 10^{-4} \text{ mol}$$

$$n_{Am^{n+}} : n_{Cu} = 1 : n = 1 : 3 \Rightarrow n = 3$$

Am species formed has O.S. of +6 $\left(AmO_2^{2+}\right)$

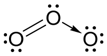
$\Rightarrow$ **D**

3 OF_2 : 2 b.p. + 2 l.p. $\Rightarrow$ bent $\Rightarrow$ 105º

CH_4 : 4 b.p. + 0 l.p. $\Rightarrow$ tetrahedral $\Rightarrow$ 109.5º

SF_6 : 6 b.p. + 0 l.p. $\Rightarrow$ octahedral $\Rightarrow$ 90º

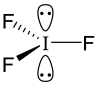
H_2O : 2 b.p. + 2 l.p. $\Rightarrow$ bent $\Rightarrow$ 105º

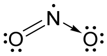
O_3 :  $\Rightarrow$ bent $\Rightarrow$ <120º

N_2O :  $\Rightarrow$ linear $\Rightarrow$ 180º

PF_3 : 3 b.p. + 1 l.p. $\Rightarrow$ trig. pyr. $\Rightarrow$ 107º

BF_3 : 3 b.p. + 0 l.p. $\Rightarrow$ trig. planar $\Rightarrow$ 120º

IF_3 :  $\Rightarrow$ trig. planar $\Rightarrow$ 120º

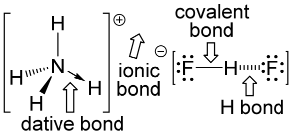
NO_2 :  $\Rightarrow$ bent $\Rightarrow$ >120º

SO_2 : 2 b.p. + 1 l.p. $\Rightarrow$ bent $\Rightarrow$ <120º

CO_2 : 2 b.p. + 0 1.p. $\Rightarrow$ linear $\Rightarrow$ 180º

$\Rightarrow$ **B**

4 Bonding in solid NH_4HF_2:



$\Rightarrow$ **A**

5 At low pressure, gas particles are far apart. IMF between particles causes force they impinge on wall to be smaller and thus pressure is lower than ideal gas $\Rightarrow$ $pV_{real} < pV_{ideal}$

At higher pressure, gas particles are close together and the volume occupied by particles is significant compared to volume of container. Hence the gas occupies a larger volume than ideal gas $\Rightarrow$ $pV_{real} > pV_{ideal}$

$\Rightarrow$ **B**

6
- ✓Arrhenius acid: Produces $H^+(aq)$ in water
- ✗ Brønsted-Lowry acid: H^+ donor; $B(OH)_3$ accepts a OH^- and does not donate H^+
- ✓Lewis acid: Lone pair acceptor; accepts a lone pair fron OH^-
- ✓Monobasic acid: each mole of $B(OH)_3$ reacts with one mole of OH^-

$\Rightarrow$ **B**

7 $NaCl$: no hydrolysis $\Rightarrow$ pH = 7

$MgCl_2$: slight hydrolysis $\Rightarrow$ pH $\approx$ 6.5

$$MgCl_2 + H_2O \rightleftharpoons Mg(OH)Cl + HCl$$

$AlCl_3$: extensive hydrolysis $\Rightarrow$ pH $\approx$ 3

$$AlCl_3 + 3H_2O \rightarrow Al(OH)_3 + 3HCl$$

$SiCl_4$: complete hydrolysis $\Rightarrow$ pH $\approx$ 1

$$SiCl_4 + 2H_2O \rightarrow SiO_2 + 4HCl$$

PCl_5 : complete hydrolysis $\Rightarrow$ pH $\approx$ 1

$$PCl_5 + 4H_2O \rightarrow H_3PO_4 + 5HCl$$

$\Rightarrow$ **A**

8 **A** ✗: Graph is for ionic radii

B ✗: Melting point of Si should be highest due to extensive strong Si–Si covalent bonds within giant molecular structure

C ✓: Nuclear charge increases across period while shielding effect is the same, hence ENC increases across the period resulting in increase in electronegativity

D ✗: Silicon being a metalloid should only have conductivity below that of the metals (Na, Mg, Al)

$\Rightarrow$ **C**

9
$$\begin{aligned}\Delta H_1^\ominus &= \sum \Delta H_f^\ominus(\text{products}) - \sum \Delta H_f^\ominus(\text{reactants}) \\ &= 2\Delta H_f^\ominus(NaOH(aq)) + \Delta H_f^\ominus(H_2(g)) - \\ &\quad 2\Delta H_f^\ominus(Na(s)) - 2\Delta H_f^\ominus(H_2O(l)) \\ &= 2\Delta H_f^\ominus(NaOH(aq)) + 0 - \\ &\quad 0 - 2\Delta H_f^\ominus(H_2O(l)) \\ &= 2\Delta H_f^\ominus(NaOH(aq)) - 2\Delta H_f^\ominus(H_2O(l))\end{aligned}$$

$\Delta H_f^\ominus(H_2O(l)) = \Delta H_c^\ominus(H_2(g))$ as both corresponds to the same reaction:

$$H_2(g) + ½O_2(g) \rightarrow H_2O(l)$$

$\Rightarrow$ **B**

10 **B** ✗: At 298 K, C is a solid

C ✗: Hydrogen exists as H_2 under std state

D ✗: At 298 K, H_2O is a liquid

$\Rightarrow$ **A**

11 Units for rate is concentration per unit time, in this case, mol dm^{-3} s^{-1}

If k has units of mol^{-2} dm^6 s^{-1}, the reaction must be overall third order:

$$\text{mol dm}^{-3}\text{ s}^{-1} = \left(\text{mol}^{-2}\text{ dm}^3\text{ s}^{-1}\right)\left(\text{mol dm}^{-3}\right)^3$$

$\Rightarrow$ **C**

12 Given $X_2(g) \rightarrow 2X(g)$,

$\text{rate} = k[X_2]$, $t_{\frac{1}{2}} = 20$ min

1 ✓: 12.5% X_2 is left after 3 $t_{\frac{1}{2}}$ (60 min).

i.e. 87.5% of X_2 had reacted

$$X_2 \xrightarrow{t_{\frac{1}{2}}} \underset{50\%\ X_2}{\frac{1}{2}X_2} \xrightarrow{t_{\frac{1}{2}}} \underset{25\%\ X_2}{\frac{1}{4}X_2} \xrightarrow{t_{\frac{1}{2}}} \underset{12.5\%\ X_2}{\frac{1}{8}X_2}$$

2 ✓: $n_X = 2n_{X_2 \text{ reacted}} = 2 \times \frac{87.5}{100} \times 1 = 1.75$ mol

3 ✓: $n_{gas} = n_{X_2} + n_X = \frac{12.5}{100} \times 1 + 1.75 = \frac{15}{8}$ mol

At constant temperature and volume,

$$\frac{p_1}{n_1} = \frac{p_2}{n_2} \Rightarrow p_2 = \frac{p_1}{n_1} \times n_2 = \frac{p}{1} \times \frac{15}{8} = \frac{15}{8}p$$

$\Rightarrow$ **D**

13 From the graph,

As pressure increases, % products decreases. Hence, there must be more gaseous particles on the product side, since backward reaction is favoured to decreases the pressure

As temperature increases, % products decreases. Hence the forward reaction must be exothermic, since backward reaction is favoured to absorb heat

$\Rightarrow$ **C**

14 **A** ✗: $n_\mathbf{Q} = n_\mathbf{R}$; $n_\mathbf{L} = n_\mathbf{M} = 1.0 - n_\mathbf{R}$

Since $n_\mathbf{R}$ at eqm can be read from the graph, the partial pressures of **L**, **M**, **Q** and **R** can be obtained. Hence K_p can be obtained.

B ✗: Since the amount of product **R** decreases when temperature is increased, the forward reaction must be exothermic since the backward reaction is favoured to absorb heat.

C ✓: The position of eqm does not provide information about the kinetics of the reaction

D ✗: From the graph, it can seen that it takes a shorter time to plateau at higher temperature, hence eqm is achieved at a faster rate

$\Rightarrow$ **C**

15 pH = 4 $\Rightarrow$ $\left[H^+\right] = 10^{-pH} = 10^{-4}$ mol dm^{-3}

$\Rightarrow$ **X** is fully dissociated, *i.e.* strong acid

pH = 3 $\Rightarrow$ $\left[H^+\right] = 10^{-pH} = 10^{-3}$ mol dm^{-3}

$\Rightarrow$ **Y** is not fully dissociated, *i.e.* weak acid

pH = 14 $\Rightarrow$ $\left[OH^-\right] = 10^{-pOH} = 10^{-(14-pH)} = 10^0$

$= 1$ mol dm^{-3}

$\Rightarrow$ **Z** is a fully ionised, *i.e.* strong base

$\Rightarrow$ **D**

16 Let the solubility of Ag_3PO_4 be s mol dm^{-3}

$$K_{sp} = \left[Ag^+\right]^3\left[PO_4^{3-}\right]$$

A : $K_{sp} = (3s)^3(s) \Rightarrow 27s^4 = K_{sp}$

$$s = \sqrt[4]{\frac{K_{sp}}{27}} = 4.26 \times 10^{-5}$$

B : $K_{sp} = (3s + 0.10)^3(s) \approx 0.10^3 s$

$$s = \frac{K_{sp}}{0.10^3} = 8.89 \times 10^{-14}$$

C : $Ag^+ + 2NH_3 \rightarrow \left[Ag(NH_3)_2\right]^+$

Formation of complex increases solubility of Ag_3PO_4

D : $K_{sp} = (3s)^3(s + 0.10) \approx (3s)^3\, 0.10$

$$s = \sqrt[3]{\frac{K_{sp}}{27 \times 0.10}} = 3.21 \times 10^{-6}$$

$\Rightarrow$ **B**

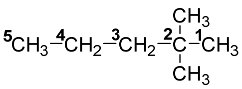
17 **B** ✗: No chiral centre

C ✗: $=CH_2$ $\Rightarrow$ no *cis-trans* isomerism

D ✗: No chiral centre

$\Rightarrow$ **A**

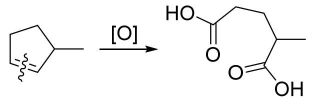
18 Structure of 2,2-dimethylpentane:



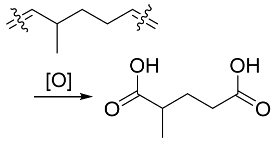
$$\overset{5}{C}H_3-\overset{4}{C}H_2-\overset{3}{C}H_2-\overset{2}{C}(CH_3)_2-\overset{1}{C}H_3$$

$\Rightarrow$ **C**

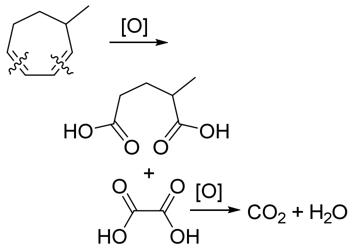
19 **1** ✓:



2 ✓:

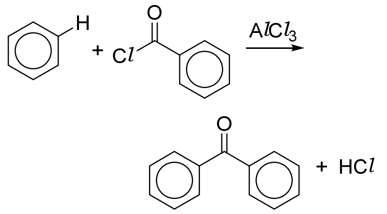


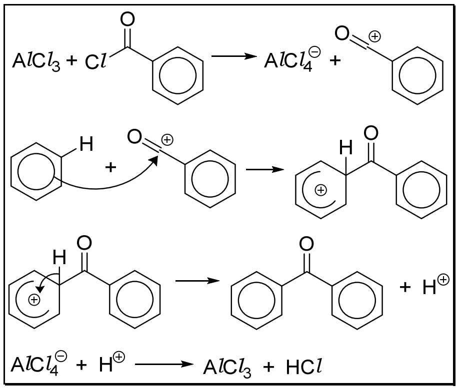
3 ✓:



$\Rightarrow$ **C**

20 Friedel-Crafts acylation, similar to Friedel-Crafts alkyation, using acyl chloride instead of alkyl chloride:





$\Rightarrow$ **D**

21 **A** ✗: Second mechanism is **single-step** S_N2 involving only a **transition state**

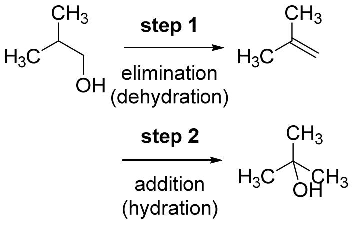
B ✗: Second mechanism is a nucleophilic **substitution** reaction

C ✓: Since both mechanisms involves two reacting species in the rate determining step, both reactions are second order

D ✗: The first mechanism involves addition of the CN^- to a trigonal planar C=O which can take place on both faces with equal chance, hence a racemic product will be obtained

$\Rightarrow$ **C**

22 The reaction involves



$\Rightarrow$ **C**

23 Tollens' reagent, $\left[Ag(NH_3)_2\right]^+ OH^-$, only oxidises the –CHO into –COO⁻ (the salt is obtained and not $–CO_2H$ since Tollens' reagent is alkaline), while itself is reduced to silver metal. Alcohols are **not** oxidised.

$\Rightarrow$ **B**

24 **A** ✗: NH_3 donates a pair of electrons to the electron-deficient acyl carbon, hence a nucleophile

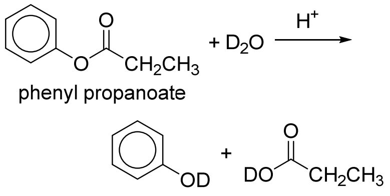
B ✗: The arrow pushing is correct, leading to the regeneration of C=O and expulsion of the Cl^- leaving group

C ✗: The acyl carbon is electron-deficient as it is bonded to two electronegative atoms, O and Cl, hence attracting the NH_3 nucleophile

D ✓: The arrow pushing is wrong as the pair of N–H electrons end up on the H, which will lead to formation of H^- and a doubly positive N instead

$\Rightarrow$ **D**

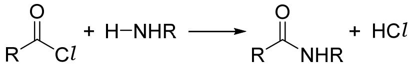
25



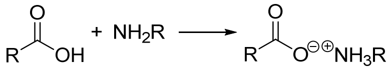
2 1

$\Rightarrow$ **B**

26 Amides are made from the reaction between an amine and an acyl chloride:



Amine and carboxylic acid gives an ammonium salt:



$\Rightarrow$ **A**

27 Basicity (availability of lone pair of electrons on N for donation to H^+) :

Generally $R_2NH > RNH_2 > NH_3 > ArNH_2$ as R groups exert electron-donating effect, rendering the lone pair more available for donation, while the lone pair is delocalised into the benzene ring of $ArNH_2$ rendering the lone pair less available for donation.

↓ing basicity $\Rightarrow$ ↑ing pK_b

So pK_b : $R_2NH < RNH_2 < NH_3 < ArNH_2$

$\Rightarrow$ **B**

28 **W** : Nitrogen in NO_3^- is already in the maximum oxidation of +5 and cannot be further oxidised. Oxidation of H_2O

$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$

Y : Due to the high concentration of chloride, oxidation of Cl^- occurs instead of H_2O

$2Cl^- \rightarrow Cl_2 + 2e^- \left(4Cl^- \rightarrow 2Cl_2 + 4e^-\right)$

Z : Oxidation of Cu instead of H_2O due to the less positive $E^\ominus$. **No gas** evolved

$Cu \rightarrow Cu^{2+} + 2e^- \qquad E^\ominus = +0.34$ V

$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \qquad E^\ominus = +1.23$ V

Since the same amount of charge passes through all three cells, $V_{O_2} : V_{Cl_2} = 1 : 2$

$\Rightarrow$ **D**

29 **1** ✓: [R]: $Cl_2 + 2e^- \rightleftharpoons 2Cl^- \quad E^\ominus = +1.36$ V

[O]: $Fe^{3+} + e^- \rightleftharpoons Fe^{2+} \quad E^\ominus = +0.77$ V

$$E^\ominus_{cell} = E^\ominus_{reduction} - E^\ominus_{oxidation}$$
$$= E^\ominus\left(Cl_2|Cl^-\right) - E^\ominus\left(Fe^{3+}|Fe^{2+}\right)$$
$$= +1.36 - (+0.77) = +0.59 \text{ V}$$

As reaction progresses, [Cl_2] ↓es and [Fe^{2+}] ↓es. So $E\left(Cl_2|Cl^-\right)$ ↓es, while $E\left(Fe^{3+}|Fe^{2+}\right)$ ↑es. Hence E_{cell} ↓es.

2 ✓: Addition of $AgNO_3$ causes AgCl to precipitate, hence [Cl^-] ↓es. Thus $E\left(Cl_2|Cl^-\right)$ ↑es, causing E_{cell} to ↑.

3 ✓: Fe^{2+} and Fe^{3+} forms the respective hexacyano complex with CN^-:

$$\left[Fe(CN)_6\right]^{3-} + e^- \rightleftharpoons \left[Fe(CN)_6\right]^{4-} \qquad E^\ominus = +0.36 \text{ V}$$

Since $E^\ominus_{oxidation}$ ↓es , hence $E^\ominus_{cell}$ ↑es

$\Rightarrow$ **D**

30 **A** ✗: Oxidations state of Co decreases from +3 in $\left[CoCl(NH_3)_5\right]^{2+}$ to +2 in $\left[Co(OH_2)_6\right]^{2+}$, while that of Cr increases from +2 in $\left[Cr(OH_2)_6\right]^{2+}$ to +3 in $\left[CrCl(OH_2)_5\right]^{2+}$. Hence electron is transferred from Cr to Co

B ✓: Hydration refers to the formation of the aqueous species from the gaseous species, which is not observed in the reaction

C ✗: The Cl^- and NH_3 ligands around the Co ion is replaced by H_2O, while one of the H_2O ligand around the Cr ion is replaced by Cl^-. Hence ligand exchange has taken place

D ✗: The ammonia ligands around Co^{3+} upon replacement by H_2O, reacted with H_3O^+ to give NH_4^+. Hence acid-base neutralisation had taken place

$\Rightarrow$ **B**

Answer Key

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

EUNOIA JUNIOR COLLEGE
JC2 Preliminary Examination 2018
General Certificate of Education Advanced Level
Higher 2

CANDIDATE NAME						
CIVICS GROUP	1	7	–			
INDEX NUMBER						

CHEMISTRY

9729/02

Paper 2 Structured Questions

13 September 2018

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, civics group and registration number on 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 paper clips, highlighters, 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	
2	
3	
4	
5	
6	
Total	

This document consists of **21** printed pages and **1** blank page.

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

1 The table below shows the melting points of some oxides of Period 3 elements.

compound	**chemical formula**	**melting point / ºC**
sodium oxide	Na_2O	1132
aluminium oxide	Al_2O_3	2980
sulfur trioxide	SO_3	16

(a) **(i)** Briefly relate the melting points of these oxides to their structure and bonding.

....

....

....

....

....

....

....

....

....

.... [2]

(ii) Describe the reactions, if any, of these oxides with water, stating the approximate pH of any solution formed.
Write equations for all the reactions that take place.

....

....

....

....

....

....

....

.... [4]

(b) Suggest a reason for each of the following observations:

(i) Effervescence is observed when aqueous sodium carbonate is added to an aqueous solution of aluminium chloride. Write equations for the reactions involved.

....

....

....

....

....

....

.... [2]

(ii) Silicon tetrachloride, $SiCl_4$, hydrolyses in water while carbon tetrachloride, CCl_4, remains insoluble in water.

....

....

....

....

....

.... [1]

(c) Gaseous N_2O_5 dissociates to form NO_2 and O_2 as shown in the following reaction equilibrium:

$$2N_2O_5(g) \rightleftharpoons 4NO_2(g) + O_2(g)$$

The value of the equilibrium constant, K_p, is 1.80×10^4 atm^3 at 750 K and 3.23×10^3 atm^3 at 700 K.

(i) Write an expression for K_p for the above dissociation.

[1]

(ii) Calculate the equilibrium constant in terms of pressure at 700 K for the reaction represented below:

$$\frac{1}{2}O_2(g) + 2NO_2(g) \rightleftharpoons N_2O_5(g)$$

[1]

(iii) Will the enthalpy change for the dissociation be a positive or negative value? Justify your answer briefly.

....

....

....

....

....

....

.... [2]

(iv) State and justify the effect on the position of equilibrium if the total volume of the system at equilibrium is increased at constant temperature.

....

....

....

....

....

.... [2]

[Total: 15]

2 Halogens have a wide range of uses, such as in water purification and as antiseptics. Halogens form compounds, such as halides and oxoanions which are used in photography and as oxidising agents respectively.

(a) State and explain the variation of the first ionisation energy of the halogens from chlorine to iodine.

....

....

....

....

.... [2]

(b) Halogens react with hydrogen gas to form hydrogen halides.
State and explain the trend in the thermal stability of hydrogen halides from HC*l* to HI.

....

....

....

....

.... [2]

(c) Halogens react with the thiosulfate ion, $S_2O_3^{2-}$. In acidic medium, bromine reacts with $S_2O_3^{2-}$ to form SO_4^{2-} and bromide ions, while iodine reacts with $S_2O_3^{2-}$ to form $S_4O_6^{2-}$ and iodide ions.

(i) Write an ionic equation for the reaction between iodine with the thiosulfate ion.

.... [1]

(ii) By quoting suitable values from the *Data Booklet*, explain the difference in the products formed.

....

....

....

....

....

.... [2]

(d) 5.0×10^{-4} mol of a bromate salt containing the BrO_4^{n-} anion was added to 25.0 cm^3 of acidified KI present in excess to yield iodine and bromide ions.

The resultant solution required 40.0 cm^3 of 0.10 mol dm^{-3} sodium thiosulfate, $Na_2S_2O_3$, for complete reaction.

Determine the value of ***n***.

[2]

(e) When chlorine reacts with magnesium, magnesium chloride, $MgCl_2$ is formed in preference of magnesium(I) chloride, $MgCl$. Attempts to isolate $MgCl$ have not been successful. It is proposed that the $MgCl$ formed undergoes disproportionation to form $MgCl_2$ and Mg.

$$2MgCl\,(s) \rightarrow MgCl_2\,(s) + Mg\,(s)$$

(i) Define the standard enthalpy change of formation of $MgCl$.

....

.... [1]

(ii) Using appropriate data from the *Data Booklet* and the information given below, construct a Born-Haber cycle to predict the lattice energy of magnesium(I) chloride, $MgCl$.

Enthalpy change of atomisation of magnesium = +148 kJ mol^{-1}
First electron affinity of chlorine = –349 kJ mol^{-1}
Standard enthalpy change of formation of magnesium(I) chloride = –130 kJ mol^{-1}

[4]

(iii) The preferential formation of $MgCl_2$ can also be explained through the use of lattice energy of both $MgCl_2$ and $MgCl$ and the relevant ionisation energies of magnesium.

Given that the experimental lattice energy of $MgCl_2$ is –2526 kJ mol^{-1}, explain why $MgCl_2$ is formed preferentially and $MgCl$ is not.

....

....

....

....

.... [1]

[Total: 15]

For Examiner's Use

3 The Haber Process is one of the landmark discoveries that converts nitrogen from the atmosphere to ammonia via a reversible reaction with hydrogen gas. This allows the agricultural industry to flourish due the increased accessibility of ammonia to synthesise nitrogen-containing fertilisers.

(a) (i) Write an equation, including state symbols, for the Haber Process.

.... [1]

(ii) Using the information in **(a)(i)**, predict and explain the sign of the entropy change for the conversion of nitrogen to ammonia.

....

....

....

....

....

.... [2]

(b) Often the behaviour of gases can be estimated using the ideal gas equation, which is based on the laws of Boyle, Charles and Avogadro. However, this is assuming that all gases behave ideally. These assumptions are based on the kinetic theory of gases.

(i) State **two** assumptions of the kinetic theory of gases.

....

....

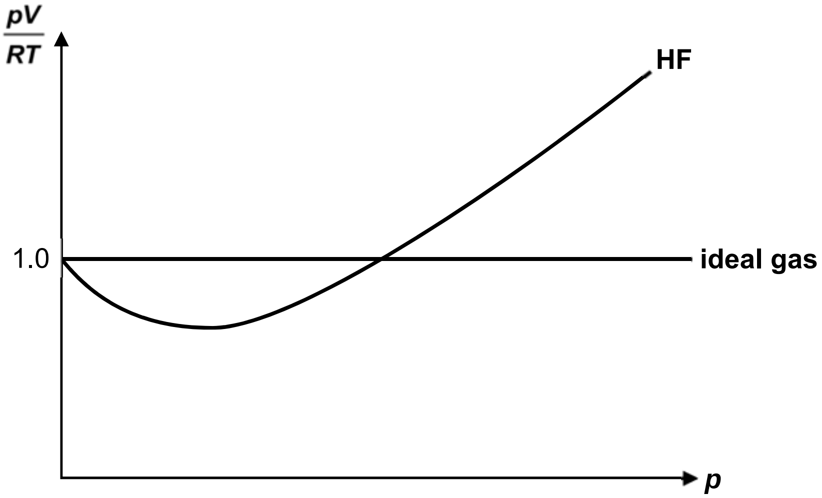
....

....

....

.... [2]

(ii) The plot of $\frac{pV}{RT}$ against p for one mole of an ideal gas and one mole of hydrogen fluoride gas at 300 K is given below.



Sketch on the graph above to show how one mole of ammonia gas (NH_3) will behave at 300 K. Explain your answer.

....

....

....

....

.... [2]

(iii) Under what conditions of temperature and pressure would ammonia behave like an ideal gas? Explain your answer.

....

....

....

....

....

....

....

.... [3]

[Total: 10]

4 Trimethylamine, $(CH_3)_3N$, is a base which is used as a starting material for the preparation of insecticides and pharmaceuticals.

(a) A 10.0 cm^3 of an aqueous solution of trimethylamine was placed in a conical flask. The pH of the solution was found to be 11.85. When a titration was performed, 16.00 cm^3 of 0.250 mol dm^{-3} dilute sulfuric acid was required to neutralise this base.

(i) Calculate the concentration of trimethylamine in the conical flask.

[1]

(ii) Use your answer in **(a)(i)** and the above data to show that trimethylamine is a weak base. Explain your answer.

....

....

....

....

.... [2]

(iii) Write an expression for the base dissociation constant, K_b, for trimethylamine. Hence determine its pK_b value.

[2]

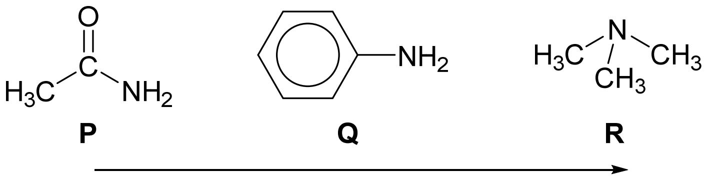
For Examiner's Use

(b) Sketch the pH curve that would be obtained for the titration reaction mentioned in **(a)**. Label clearly **any significant co-ordinates** on your sketch.

[2]

(c) The basicity of trimethylamine is different in comparison with other nitrogen organic compounds.

Account for the trend in basicity as shown below.



....

....

....

....

....

....

....

....

.... [3]

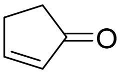
[Total: 10]

5 **(a)** This question is about Grignard reagents, compounds that are of great use in organic synthesis for forming carbon–carbon bonds.

Grignard reagents are compounds of general formula RMgX where X = Br or I. They are very reactive, giving rise to the highly nucleophilic ion R^-. When a solution of a Grignard reagent in dry ether is added to a carbonyl compound, the R^- attacks the carbonyl group.

The mechanism of this reaction involves **two steps**:

- The first step is the rate determining step which involves a nucleophilic attack of nucleophilic ion **R**$^-$ on the carbonyl carbon to form a tetrahedral intermediate.
- The second step involves an acid-base reaction with water.

(i) 2-cyclopentenone, , is treated with the Grignard reagent ethyl magnesium bromide, CH_3CH_2MgBr, followed by water. An organic compound **W**, $C_7H_{12}O$, is formed.

Name and draw the mechanism of the above reaction.

[3]

(ii) Does 2-cyclopentenone exhibit *cis-trans* isomerism? Explain your answer.

....

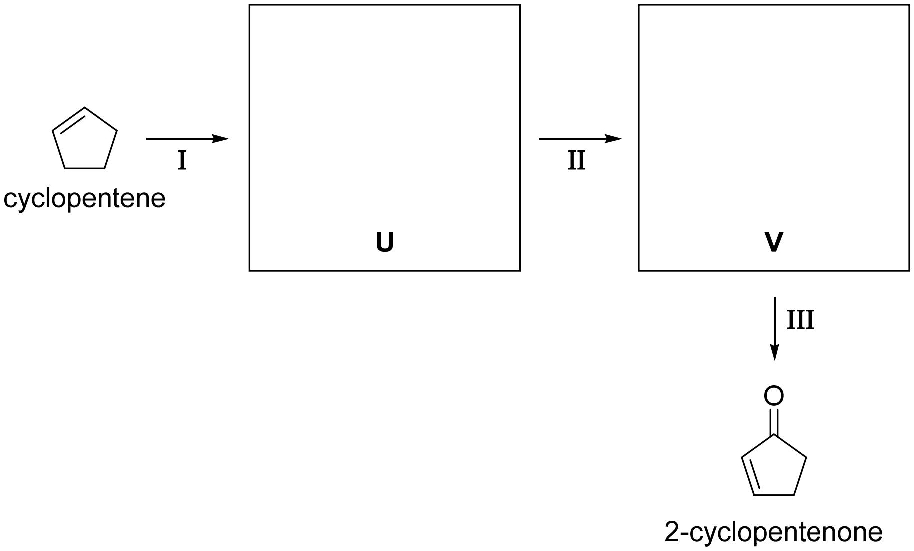
....

....

....

.... [1]

(iii) 2-cyclopentenone can be formed from cyclopentene. Propose a three-step synthetic route to obtain 2-cyclopentenone from cyclopentene. State the reagents and conditions required, and draw the structures of the intermediates **U** and **V** obtained in the boxes below.



Step I: ....

Step II: ....

Step III: .... [3]

(b) A six-membered cyclic compound **X**, an isomer of **W**, $C_7H_{12}O$, reacts with gaseous HBr at room temperature to form chiral compounds with molecular formula $C_7H_{13}OBr$. Compound **X** is readily oxidised by hot acidified potassium manganate(VII) to form an acidic compound **Y**, $C_7H_{12}O_5$. 1 mole of **Y** is exactly neutralised by 2 moles of sodium hydroxide. When **Y** is warmed with concentrated sulfuric acid, a sweet-smelling compound **Z**, $C_7H_{10}O_4$ is isolated.

Suggest the structures for compound **X**, **Y** and **Z**.

X	
Y	
Z	

[3]

[Total: 10]

6 Halogenoalkanes are compounds in which one or more hydrogen atoms in an alkane have been replaced by halogen atoms (fluorine, chlorine, bromine and iodine). They serves as important intermediates in organic synthesis due to the ease of cleavage of the polar C–X bond (X = C*l*, Br or I), leading to substitution of the halogen atom by a wide variety of nucleophiles.

(a) The reaction between the primary halogenoalkane, benzyl chloride, $C_6H_5CH_2Cl$, and sodium hydroxide is known follow the rate equation:

$$\text{rate} = k\,[\text{benzyl chloride}]$$

(i) Draw the mechanism of the reaction which is consistent with the rate equation.

[2]

(ii) Suggest a possible reason why despite being a primary halogenoalkane, benzyl chloride adopts the mechanism you have drawn in **(a)(i)**.

....

....

....

....

.... [1]

(b) Unlike halogenoalkanes, halogenoalkenes such as vinyl bromide, $CH_2{=}CHBr$, are inert towards nucleophilic substitution. Suggest a possible explanation for this inertness.

....

....

....

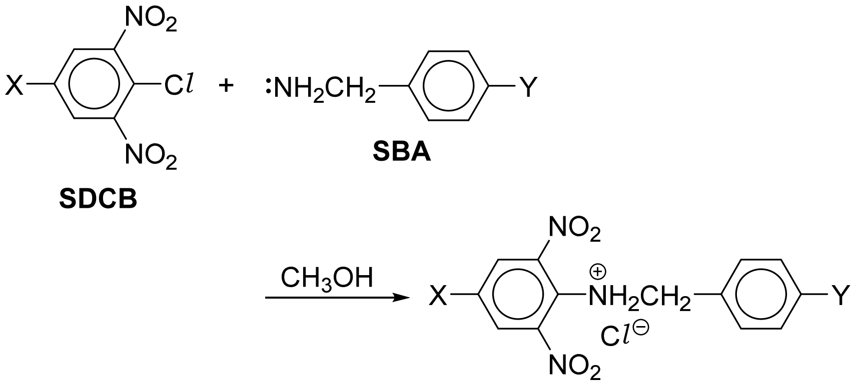
....

.... [1]

Like halogenoalkenes, halogenoarenes are also usually inert towards nucleophilic substitution reaction.

Nonetheless, when suitably tuned, halogenoarenes can be made to undergo nucleophilic substitution too, although the mechanism is different from the S_N1 and S_N2 mechanisms of aliphatic halogenoalkanes.

(c) 4-X-Substituted-2,6-dinitrochlorobenzenes (SDCB) react with 4-Y-substituted-benzylamines (SBA) in methanol to give benzylammonium chloride salt:



benzylammonium chloride

In the reaction, SDCB is regarded as the substrate, while SBA is the nucleophile.

(i) Suggest how it can be shown *chemically* that substitution reaction had indeed taken place with SDCB?

....

....

....

.... [1]

(ii) Suggest, with reason, one physical property which may be used to follow the progress of the reaction.

....

....

....

....

.... [1]

The reaction was found to follow overall second-order kinetics, with rate equation:

$$\text{rate} = k\left[\text{SDCB}\right]\left[\text{SBA}\right]$$

The rate constant, *k* ($\text{mol}^{-1}\ \text{dm}^{3}\ \text{s}^{-1}$), for the reaction of three 4-X-substituted-2,6-dinitrochlorobenzenes with four 4-Y-substituted-benzylamines in pure methanol at 25 ºC is given in Table 6.1 below.

Table 6.1

X (SDCB substrate)	**4-Y-benzylamine (SBA nucleophile)**			
	4-OCH_3	**4-CH_3**	**H**	**4-C*l***
NO_2	3.12	2.47	2.34	1.66
CN	0.748	0.563	0.498	
CF_3	0.100	0.0902	0.0744	0.0479

The values of the rate constant, *k*, can be obtained from suitable concentration–time plots such as those shown in Figure 6.1 on the next page.

Figure 6.1 is obtained by monitoring changes in the concentration of the nucleophile, 4-chlorobenzylamine, with time, using an **excess** of the three substrates separately. The initial concentrations of the three substrates are indicated on Figure 6.1.

(iii) With the aid of Figure 6.1, determine the rate constant, *k*, when X = CN, using 4-chlorobenzylamine as nucleophile, and fill in the blank in Table 6.1.

[2]

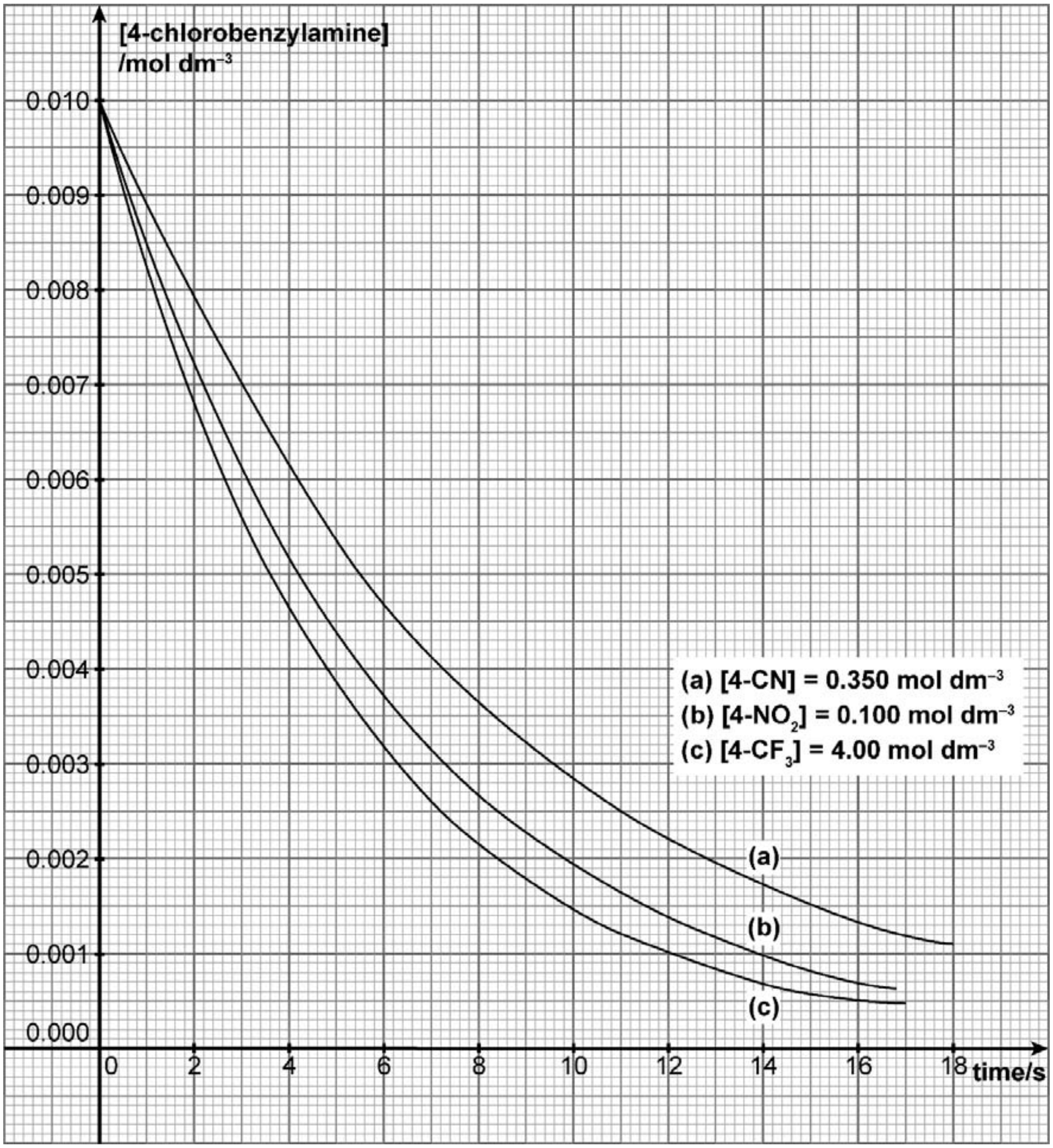
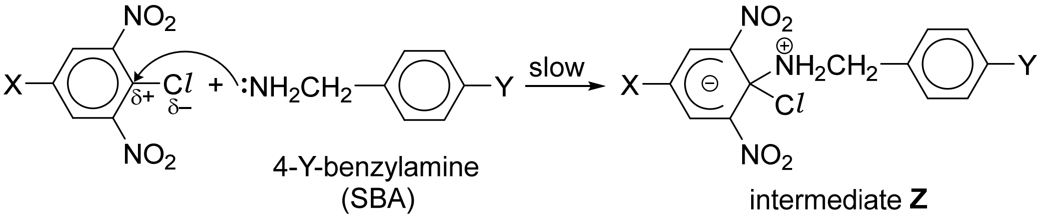
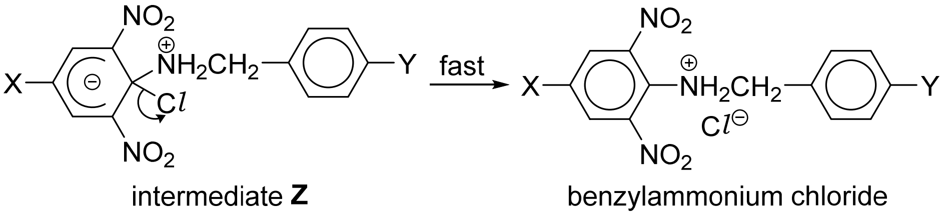

[4-chlorobenzylamine] /mol dm^{-3}
0.010
0.009
0.008
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0.000
0
2
4
6
8
10
12
14
16
18
time/s
(a) [4-CN] = 0.350 mol dm^{-3}
(b) [4-NO$_2$] = 0.100 mol dm^{-3}
(c) [4-CF$_3$] = 4.00 mol dm^{-3}
(a)
(b)
(c)

Figure 6.1

(d) Although the reaction is second-order, however, it is **not** a single-step reaction. Instead, SBA performs a rate-determining nucleophilic attack at the electrophilic C–C*l* carbon of SDCB, leading to the formation of resonance-stabilised intermediate **Z**:



Subsequently, intermediate **Z** rapidly expels a chloride ion to give the desired benzylammonium chloride:



This two-step mechanism is known as the S_NAr mechanism.

Using the mechanism given above and the data in Table 6.1, explain which of the three substituents X = NO_2, CN or CF_3, is the strongest electron-withdrawing group.

....

....

....

....

.... [1]

(e) The magnitude of the rate constant *k* can be used as a direct measure of the nucleophilicity of the 4-Y-benzylamine (SBA) nucleophile, that is, the larger the rate constant *k*, the more nucleophilic is the 4-Y-benzylamine.

Using the mechanism of the S_NAr mechanism described, explain why there is a positive correlation between the magnitude of the rate constant *k* and the nucleophilicity of the 4-Y-benzylamine.

....

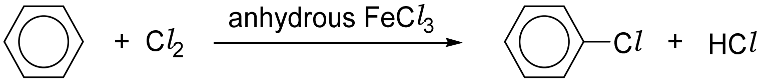
....

....

....

.... [1]

Chloroarenes can be prepared by the reaction of benzene and chlorine in the presence of anhydrous $FeCl_3$ as a Lewis acid catalyst:



(f) Describe the role of anhydrous $FeCl_3$ in the reaction, illustrating with an equation.

....

....

....

.... [1]

Anhydrous iron(III) chloride, $FeCl_3$, is an almost black crystalline solid and is very hygroscopic; it forms a series of hydrates when exposed to moist air. The common hydrate is yellow $FeCl_3 \cdot 6H_2O$, which contains $[FeCl_2(H_2O)_4]^+$. This is very soluble in water, and gives a strongly acidic solution.

The $[Fe(H_2O)_6]^{3+}$ ion exist only in strongly acidic solution in the absence of coordinating anion. The ion is violet in solution, although some hydrolysis may colour the solution yellow-brown.

(g) **(i)** Explain why $[FeCl_2(H_2O)_4]^+$ and $[Fe(H_2O)_6]^{3+}$ have different colours despite both containing iron(III).

....

....

....

....

....

.... [1]

(ii) Explain why the violet $[Fe(H_2O)_6]^{3+}$ ion is stable only in highly acidic solution.

....

....

....

....

.... [1]

(h) On the other hand, anhydrous iron(III) iodide, FeI_3, had only been prepared recently in non-aqueous medium via the reaction of 6-coordinated $Fe(CO)_4I_2$ in hexane:

$$Fe(CO)_4I_2 + \tfrac{1}{2}I_2 \xrightarrow[\text{hexane}]{\text{uv light}} FeI_3 + 4CO$$

(i) State and explain the type of reaction involved in the synthesis of iron(III) iodide.

....

....

....

.... [1]

A non-aqueous medium is required for the above synthesis as iron(III) iodide is completely decomposed in aqueous solution.

(ii) Using the *Data Booklet*, suggest possible products from the decomposition of iron(III) iodide in water.

....

....

....

.... [1]

[Total: 15]

BLANK PAGE

EUNOIA JUNIOR COLLEGE
JC2 Preliminary Examination 2018
General Certificate of Education Advanced Level
Higher 2

CANDIDATE NAME	

CIVICS GROUP	1	7	–			INDEX NUMBER		

CHEMISTRY

9729/02

Paper 2 Structured Questions

13 September 2018

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, civics group and registration number on 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 paper clips, highlighters, 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	
2	
3	
4	
5	
6	
Total	

This document consists of **21** printed pages and **1** blank page.

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

For Examiner's Use

1 The table below shows the melting points of some oxides of Period 3 elements.

compound	chemical formula	melting point / °C
sodium oxide	Na_2O	1132
aluminium oxide	Al_2O_3	2980
sulfur trioxide	SO_3	16

(a) **(i)** Briefly relate the melting points of these oxides to their structure and bonding.

Both Al_2O_3 and Na_2O **are of giant ionic lattice structure**. During melting, a lot of energy is required to break **strong electrostatic forces of attraction between oppositely charged ions** **[both, 1m]** in these two compounds, resulting in their high melting points. Al_2O_3 has higher melting point than Na_2O as Al_2O_3 has a larger magnitude of lattice energy (since Al^{3+} ion has higher charge and is smaller in size compared to Na^+ ion).

SO_3 has **covalent simple molecular structure** that has **weak intermolecular instantaneous dipole-induced dipole (id-id) interactions** **[both, 1m]** between SO_3 molecules, **requiring little amount of energy to overcome** during melting. Thus, SO_3 has the lowest melting point. [2]

(ii) Describe the reactions, if any, of these oxides with water, stating the approximate pH of any solution formed.
Write equations for all the reactions that take place.

Na_2O is an ionic oxide that reacts with water to form strongly alkaline solutions.

$Na_2O(s) + H_2O(l) \rightarrow 2NaOH(aq)$ **[1m]** (**pH ≈ 13–14**).

Al_2O_3 **does not dissolve in water** because its lattice energy is highly exothermic **[1m]**. (**pH = 7**)

SO_3 is an acidic oxide that react readily with water to form strongly acidic solutions.

$SO_3(l) + H_2O(l) \rightarrow H_2SO_4(aq)$ **[1m]** (**pH ≈ 1–2**)

[all three pH's correct – 1m] [4]

(b) Suggest a reason for each of the following observations:

(i) Effervescence is observed when aqueous sodium carbonate is added to an aqueous solution of aluminium chloride. Write equations for the reactions involved.

$A\ell^{3+}$ has a **high charge density** and **further polarises** and **weakens the O–H bonds** of the water ligands **[1m]**. Hence $[A\ell(H_2O)_6]^{3+}$ undergoes **appreciable hydrolysis**, giving an acidic solution that reacts with sodium carbonate to give carbon dioxide.

$[A\ell(H_2O)_6]^{3+}(aq) \rightleftharpoons [A\ell(H_2O)_5(OH)]^{2+}(aq) + H^+(aq)$

$CO_3^{2-}(aq) + 2H^+(aq) \rightarrow CO_2(g) + H_2O(\ell)$ **[both eqns – 1m]**

[2]

(ii) Silicon tetrachloride, $SiC\ell_4$, hydrolyses in water while carbon tetrachloride, $CC\ell_4$, remains insoluble in water.

Carbon in $CC\ell_4$, unlike silicon in $SiC\ell_4$, **does not have low-lying vacant orbitals** to accommodate the lone pair from water during hydrolysis.

In addition, **steric hindrance** from the 4 bulky chlorine atoms prevents approach/attack of water nucleophiles at the carbon atom in $CC\ell_4$.

[both, 1m]

[1]

(c) Gaseous N_2O_5 dissociates to form NO_2 and O_2 as shown in the following reaction equilibrium:

$$2N_2O_5(g) \rightleftharpoons 4NO_2(g) + O_2(g)$$

The value of the equilibrium constant, K_p, is 1.80×10^4 atm^3 at 750 K and 3.23×10^3 atm^3 at 700 K.

(i) Write an expression for K_p for the above dissociation.

$$K_p = \frac{p_{O_2} \times \left(p_{NO_2}\right)^4}{\left(p_{N_2O_5}\right)^2} \quad \textbf{[1m]}$$

[1]

(ii) Calculate the equilibrium constant in terms of pressure at 700 K for the reaction represented below:

$$\frac{1}{2}O_2(g) + 2NO_2(g) \rightleftharpoons N_2O_5(g)$$

$$K_p = \frac{p_{N_2O_5}}{(p_{O_2})^{\frac{1}{2}} \times (p_{NO_2})^2} = \left(\frac{1}{\frac{p_{O_2} \times (p_{NO_2})^4}{(p_{N_2O_5})^2}}\right)^{\frac{1}{2}}$$

$$= \left(\frac{1}{3.23 \times 10^3}\right)^{\frac{1}{2}} = \underline{\mathbf{1.76 \times 10^{-2}\ atm^{-\frac{3}{2}}}}\ \text{[1m]}$$

[1]

(iii) Will the enthalpy change for the dissociation be a positive or negative value? Justify your answer briefly.

The enthalpy change will have a **positive value** [1m].

The value of K_p for the dissociation **increases** with **increasing** temperature.

Therefore **the amounts of products (O_2 and NO_2) will increase while the amount of reactant (N_2O_5) will decrease** [1m] when temperature increases.

According to Le Chatelier's Principle, the forward reaction must be endothermic as it is favoured when temperature increases.

[2]

(iv) State and justify the effect on the position of equilibrium if the total volume of the system at equilibrium is increased at constant temperature.

Increasing the volume decreases the total pressure of the system.

This shifts the position of equilibrium to the **right** [1m] to **form more gaseous particles** to **increase pressure** as there are **more gaseous particles on the right** [1m].

[2]

[Total: 15]

2 Halogens have a wide range of uses, such as in water purification and as antiseptics. Halogens form compounds, such as halides and oxoanions which are used in photography and as oxidising agents respectively.

(a) State and explain the variation of the first ionisation energy of the halogens from chlorine to iodine.

From chlorine to iodine,

- Valence electrons are **further away** from the nucleus.
- **Weaker electrostatic attraction** between nucleus and the valence electrons.
- **Less** energy is required to remove the valence electron. **[1m] for explanation**

Hence, first ionisation energy generally **decreases** down the group. **[1m]** [2]

(b) Halogens react with hydrogen gas to form hydrogen halides.
State and explain the trend in the thermal stability of hydrogen halides from HC*l* to HI.

From HC*l* to HI,

- Covalent **bond length of H—X increases**
- Covalent **bond strength decreases** *or* **bond (dissociation) energy decreases**

[1m] for both

- **Thermal stability decreases** **[1m]** [2]

(c) Halogens react with the thiosulfate ion, $S_2O_3^{2-}$. In acidic medium, bromine reacts with $S_2O_3^{2-}$ to form SO_4^{2-} and bromide ions, while iodine reacts with $S_2O_3^{2-}$ to form $S_4O_6^{2-}$ and iodide ions.

(i) Write an ionic equation for the reaction between iodine with the thiosulfate ion.

$I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$ **[1m] ss optional** [1]

(ii) By quoting suitable values from the *Data Booklet*, explain the difference in the products formed.

$I_2 + 2e^- \rightleftharpoons 2I^-$ $E^\ominus = +0.54$ V

$Br_2 + 2e^- \rightleftharpoons 2Br^-$ $E^\ominus = +1.07$ V

As $E^\ominus(Br_2|Br^-)$ is **more positive** than $E^\ominus(I_2|I^-)$, **I_2 is the weaker oxidising agent** **[1m, with correct $E^\ominus$ values]** and oxidation number of S **increases** from **+2** in $S_2O_3^{2-}$ to **+2.5** in $S_4O_6^{2-}$. Bromine is the stronger oxidising agent and oxidation number of S **increases** from **+2** in $S_2O_3^{2-}$ to **+6** in SO_4^{2-}. **[1m]** [2]

(d) 5.0×10^{-4} mol of a bromate salt containing the BrO_4^{n-} anion was added to 25.0 cm^3 of acidified KI present in excess to yield iodine and bromide ions.

The resultant solution required 40.0 cm^3 of 0.10 mol dm^{-3} sodium thiosulfate, $Na_2S_2O_3$, for complete reaction.

Determine the value of ***n***.

Iodometric equation: $2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$

$$n_{I_2}\text{ formed} = n_{I_2}\text{ reacted with }S_2O_3^{2-}$$

$$= \frac{1}{2}\times(0.0400\times0.10)$$

$$= \underline{\mathbf{2.00\times10^{-3}\ mol}}\ \textbf{[1m] ecf from eqn in (c)(i)}$$

$$\frac{n_{I_2}}{n_{BrO_4^{n-}}} = \frac{2.00\times10^{-3}}{5.0\times10^{-4}} = 4$$

Oxidation: $2I^- \rightarrow I_2 + 2e^-$

Mole ratio: $\mathbf{BrO_4^{n-} \equiv 4I_2 \equiv 8e^-}$

1 mole of BrO_4^{n-} gains 8 moles of electrons.

Oxidation number of Br in BrO_4^{n-} decreases by 8 to –1 in Br^-

Oxidation number of Br in BrO_4^{n-} = +7

$+7 + 4(-2) = n(-1)$

n **=** **<u>1</u>** **[1m] with logical working to deduce this**

[2]

(e) When chlorine reacts with magnesium, magnesium chloride, $MgCl_2$ is formed in preference of magnesium(I) chloride, $MgCl$. Attempts to isolate $MgCl$ have not been successful. It is proposed that the $MgCl$ formed undergoes disproportionation to form $MgCl_2$ and Mg.

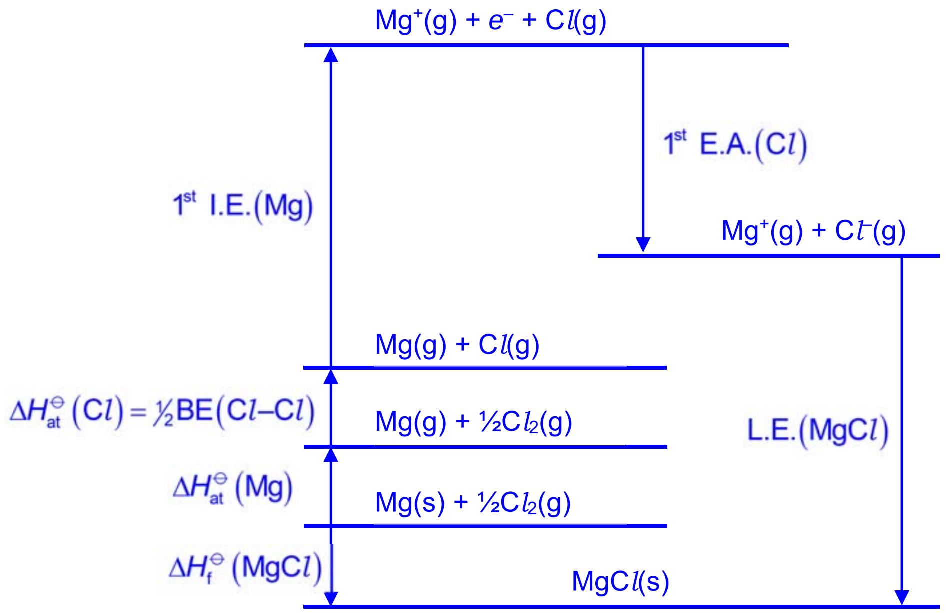
$$2MgCl\,(s) \rightarrow MgCl_2\,(s) + Mg\,(s)$$

(i) Define the standard enthalpy change of formation of $MgCl$.

The enthalpy change when **<u>1 mole of MgC*l*</u>** is formed from its **<u>constituent elements in their standard states</u>** at 298 K and 1 bar **[1m]** [1]

(ii) Using appropriate data from the *Data Booklet* and the information given below, construct a Born-Haber cycle to predict the lattice energy of magnesium(I) chloride, $MgCl$.

Enthalpy change of atomisation of magnesium = +148 kJ mol^{-1}
First electron affinity of chlorine = –349 kJ mol^{-1}
Standard enthalpy change of formation of magnesium(I) chloride = –130 kJ mol^{-1}



[2m]

By Hess' Law,

$$\Delta H^{\ominus}_{at}(Mg) + \frac{1}{2}BE(Cl–Cl) + 1^{st}\ I.E.(Mg) + 1^{st}\ E.A.(Cl) + L.E.(MgCl) = \Delta H^{\ominus}_f(MgCl)$$

$$L.E.(MgCl) = -130 - (+148) - \frac{1}{2}(+244) - (+736) - (-349)$$ **[1m]**

$$= \underline{\mathbf{-787\ kJ\ mol^{-1}}}$$ **[1m]**

[4]

(iii) The preferential formation of $MgCl_2$ can also be explained through the use of lattice energy of both $MgCl_2$ and $MgCl$ and the relevant ionisation energies of magnesium.

Given that the experimental lattice energy of $MgCl_2$ is –2526 kJ mol^{-1}, explain why $MgCl_2$ is formed preferentially and $MgCl$ is not.

- The ionisation energy required to produce Mg^{2+} (1^{st} IE(Mg) = +736 kJ mol^{-1} and 2^{nd} IE(Mg) = +1450 kJ mol^{-1}) can be compensated reasonably well by the higher magnitude of lattice energy (higher amount of energy (–2526 kJ mol^{-1}) is released during the formation of $MgCl_2$). **[1m]**
  or
- Whereas the ionisation energy required to produce Mg^+ is only merely compensated by the formation of $MgCl$ due to its lower lattice energy (–787 kJ mol^{-1}). **[1m]**
  Therefore $MgCl_2$ is formed preferentially. [1]

[Total: 15]

For Examiner's Use

3 The Haber Process is one of the landmark discoveries that converts nitrogen from the atmosphere to ammonia via a reversible reaction with hydrogen gas. This allows the agricultural industry to flourish due the increased accessibility of ammonia to synthesise nitrogen-containing fertilisers.

(a) **(i)** Write an equation, including state symbols, for the Haber Process.

N_2 (g) + $3H_2$ (g) $\rightleftharpoons$ $2NH_3$ (g) **[1m]** [1]

(ii) Using the information in **(a)(i)**, predict and explain the sign of the entropy change for the conversion of nitrogen to ammonia.

In the reaction in **(a)(i)**, there is a **decrease in the number of gas molecules**, **reducing** the number of ways that the **particles and energy can be distributed**. **[1m] for gas molecules and particles/energy distributed**

Hence, there is a **decrease in entropy**. The sign of the entropy change should **be negative**. **[1m] for entropy and sign of entropy change**

[2]

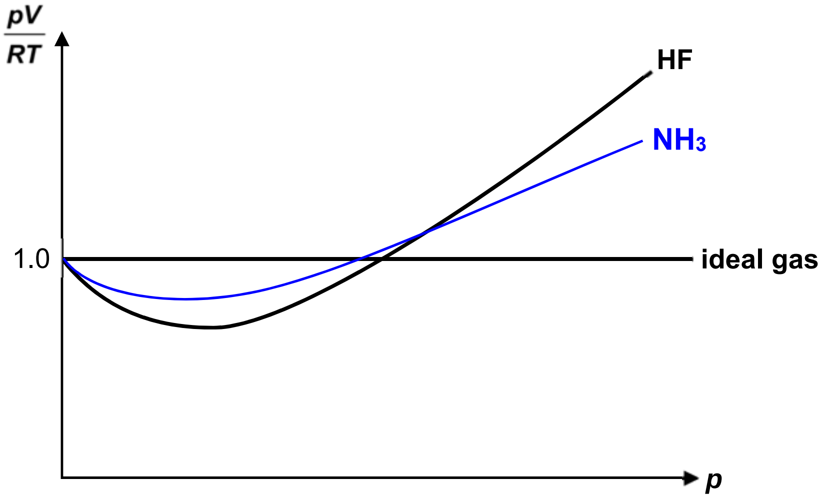
(b) Often the behaviour of gases can be estimated using the ideal gas equation, which is based on the laws of Boyle, Charles and Avogadro. However, this is assuming that all gases behave ideally. These assumptions are based on the kinetic theory of gases.

(i) State **two** assumptions of the kinetic theory of gases.

- There are **no/negligible intermolecular forces of attraction** between the gas molecules.
- Gas molecules **does not occupy any volume**. (volume is negligible compared to the volume of container)
- Collisions between gas molecules are **"perfectly elastic"**.

[2m] any 2 [2]

(ii) The plot of $\frac{pV}{RT}$ against p for one mole of an ideal gas and one mole of hydrogen fluoride gas at 300 K is given below.



Sketch on the graph above to show how one mole of ammonia gas (NH_3) will behave at 300 K. Explain your answer.

The **hydrogen bonds** between NH_3 are **weaker** than that between HF molecules since **N–H bond is less polar than H–F bond**. **[1m] for concept of weaker hydrogen bonding between molecules**

Hence, NH_3 **deviates less** from ideal gas behaviour. **[1m] for correct sketching of line** [2]

(iii) Under what conditions of temperature and pressure would ammonia behave like an ideal gas? Explain your answer.

Under **low pressure and high temperature**. **[1m] for stating both conditions**

At lower pressure, NH_3 molecules are **far apart**, such that **volume of gas molecules becomes insignificant compared to the volume of the container** **[1m]** in which the gas is held.

At high temperature, NH_3 molecules **moves faster** (or have higher average kinetic energy). As such, **the intermolecular forces of attraction between the molecules become negligible** **[1m]**.

[3]

[Total: 10]

4 Trimethylamine, $(CH_3)_3N$, is a base which is used as a starting material for the preparation of insecticides and pharmaceuticals.

(a) A 10.0 cm^3 of an aqueous solution of trimethylamine was placed in a conical flask. The pH of the solution was found to be 11.85. When a titration was performed, 16.00 cm^3 of 0.250 mol dm^{-3} dilute sulfuric acid was required to neutralise this base.

(i) Calculate the concentration of trimethylamine in the conical flask.

$$\text{Concentration of triethylamine} = \frac{2\times\left(\frac{16.00}{1000}\times 0.250\right)}{\frac{10.0}{1000}} = \underline{\mathbf{0.800\ mol\ dm^{-3}}}\ \mathbf{[1m]}$$

[1]

(ii) Use your answer in **(a)(i)** and the above data to show that trimethylamine is a weak base. Explain your answer.

pOH = 14 – 11.85 = 2.15

$[OH^-(aq)] = 10^{-pOH} = 7.079\times10^{-3}$ mol dm^{-3} ≈ $\underline{\mathbf{7.08\times10^{-3}\ mol\ dm^{-3}}}$ **[1m]**

Since $[OH^-(aq)]$ is **less than** [trimethylamine (aq)], trimethylamine is **not fully ionised** in solution **[1m]** and hence is a weak base.

[2]

(iii) Write an expression for the base dissociation constant, K_b, for trimethylamine. Hence determine its pK_b value.

$$K_b = \frac{[(CH_3)_3NH^+(aq)][OH^-(aq)]}{[(CH_3)_3N\ (aq)]}\ \mathbf{[1m]}$$

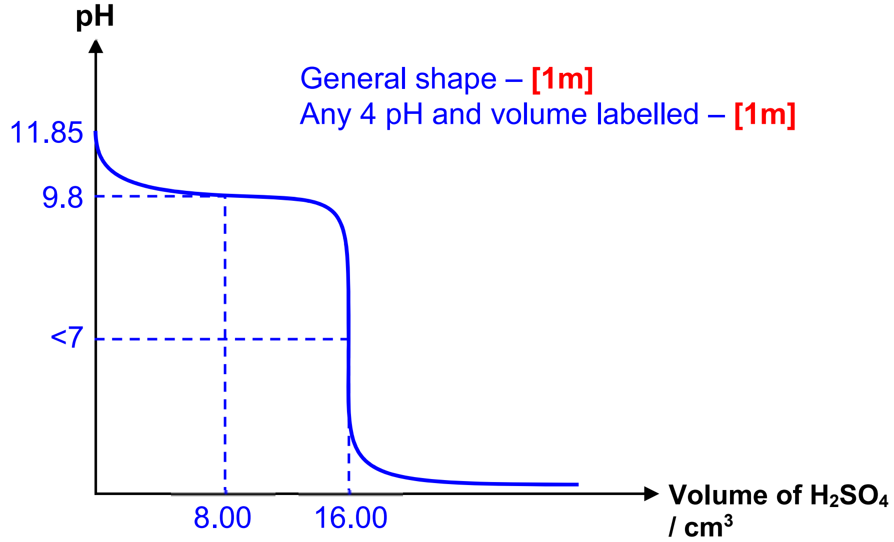
$$= \frac{(7.079\times10^{-3})(7.079\times10^{-3})}{(0.800 - 7.079\times10^{-3})} = 6.321\times10^{-5}\ \text{mol}$$

$pK_b = -\log(6.321\times10^{-5}) = 4.199 = \underline{\mathbf{4.20}}$ (3 sf) **[1m]**

[If assuming the dissociation to be very small, and approximating $0.800 - 7.079\times10^{-3} \approx 0.800$, then pK_b = **4.203** or **4.20** (3sf)]

[2]

(b) Sketch the pH curve that would be obtained for the titration reaction mentioned in **(a)**. Label clearly **any significant co-ordinates** on your sketch.

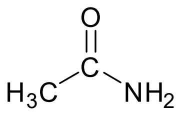


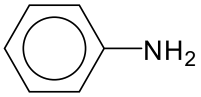
General shape – [1m]
Any 4 pH and volume labelled – [1m]

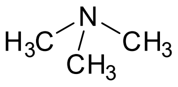
[2]

(c) The basicity of trimethylamine is different in comparison with other nitrogen organic compounds.

Account for the trend in basicity as shown below.


P


Q


R

increasing basicity →

amide P: lone pair of electrons on N is delocalised into the neighbouring carbonyl group with δ+ C and highly electronegative O due to overlap of p orbital of N with the π electron cloud of C=O

⇒ not readily available for donation [1m]

aryl amine Q: lone pair of electron delocalised into the benzene ring

⇒ less readily available for donation [1m]

tertiary amine R: alkyl groups are electron donating, increases the electron density around N

⇒ lone pair of electrons more easily donated, increased basic strength [1m]

[3]

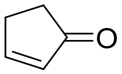
[Total: 10]

5 (a) This question is about Grignard reagents, compounds that are of great use in organic synthesis for forming carbon–carbon bonds.

Grignard reagents are compounds of general formula RMgX where X = Br or I. They are very reactive, giving rise to the highly nucleophilic ion R^-. When a solution of a Grignard reagent in dry ether is added to a carbonyl compound, the R^- attacks the carbonyl group.

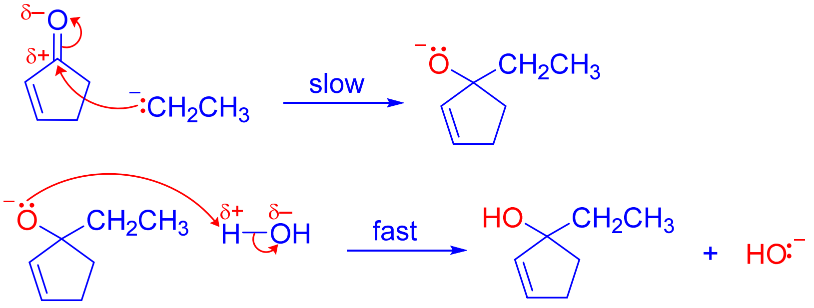
The mechanism of this reaction involves **two steps**:

- The first step is the rate determining step which involves a nucleophilic attack of nucleophilic ion **R**$^-$ on the carbonyl carbon to form a tetrahedral intermediate.
- The second step involves an acid-base reaction with water.

(i) 2-cyclopentenone,  , is treated with the Grignard reagent ethyl magnesium bromide, CH_3CH_2MgBr, followed by water. An organic compound **W**, $C_7H_{12}O$, is formed.

Name and draw the mechanism of the above reaction.

Nucleophilic addition **[1m]**



W

[1m] curly arrows, partial charges, lone pair
[1m] intermediate and slow step products

[3]

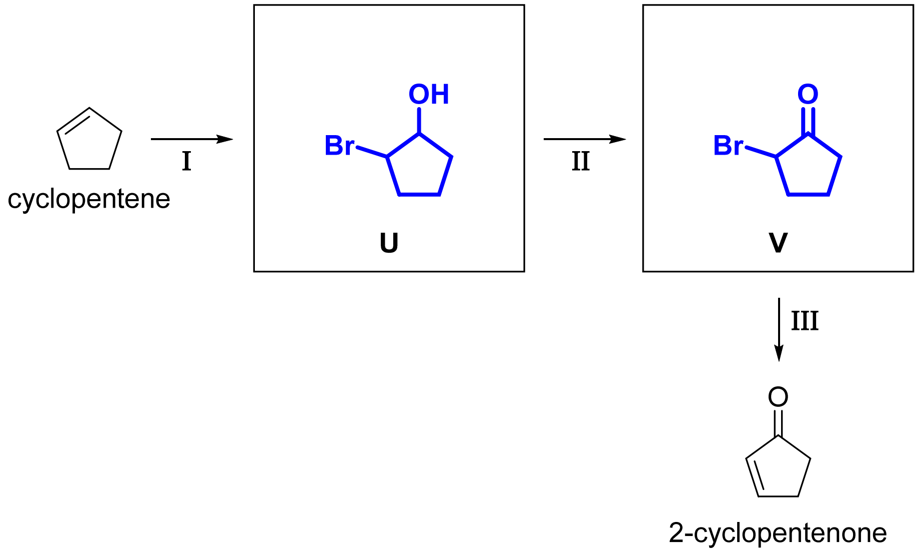
(ii) Does 2-cyclopentenone exhibit *cis-trans* isomerism? Explain your answer.

No. There is no *cis-trans* isomerism as the C=C is in a small cyclic ring, so only the *cis* isomer is present due to **ring strain**. **[1m]**

[1]

For Examiner's Use

(iii) 2-cyclopentenone can be formed from cyclopentene. Propose a three-step synthetic route to obtain 2-cyclopentenone from cyclopentene. State the reagents and conditions required, and draw the structures of the intermediates **U** and **V** obtained in the boxes below.



Step I: **Br_2 (aq), room temperature**

Step II: **$KMnO_4$(aq) or $K_2Cr_2O_7$(aq), H_2SO_4(aq), heat**

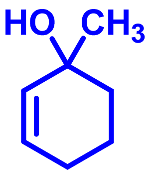
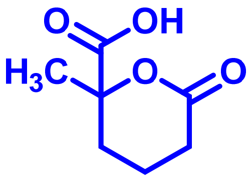
Step III: **ethanolic KOH, heat** [3]

[1m] for each step and intermediate

For Examiner's Use

(b) A six-membered cyclic compound **X**, an isomer of **W**, $C_7H_{12}O$, reacts with gaseous HBr at room temperature to form chiral compounds with molecular formula $C_7H_{13}OBr$. Compound **X** is readily oxidised by hot acidified potassium manganate(VII) to form an acidic compound **Y**, $C_7H_{12}O_5$. 1 mole of **Y** is exactly neutralised by 2 moles of sodium hydroxide. When **Y** is warmed with concentrated sulfuric acid, a sweet-smelling compound **Z**, $C_7H_{10}O_4$ is isolated.

Suggest the structures for compound **X**, **Y** and **Z**.

X	
Y	
Z	

[1m] for each compound

[3]

[Total: 10]

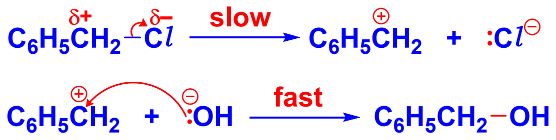
6 Halogenoalkanes are compounds in which one or more hydrogen atoms in an alkane have been replaced by halogen atoms (fluorine, chlorine, bromine and iodine). They serves as important intermediates in organic synthesis due to the ease of cleavage of the polar C–X bond (X = C*l*, Br or I), leading to substitution of the halogen atom by a wide variety of nucleophiles.

(a) The reaction between the primary halogenoalkane, benzyl chloride, $C_6H_5CH_2Cl$, and sodium hydroxide is known follow the rate equation:

$$\text{rate} = k\,[\text{benzyl chloride}]$$

(i) Draw the mechanism of the reaction which is consistent with the rate equation.

S_N1 Nucleophilic substitution



$$C_6H_5\overset{\delta+}{C}H_2-\overset{\delta-}{Cl} \xrightarrow{\text{slow}} C_6H_5\overset{\oplus}{C}H_2 + :Cl^{\ominus}$$

$$C_6H_5\overset{\oplus}{C}H_2 + \overset{\ominus}{:}OH \xrightarrow{\text{fast}} C_6H_5CH_2-OH$$

[1m] curly arrows, partial charges, lone pair
[1m] benzyl cation intermediate and slow step products

[2]

(ii) Suggest a possible reason why despite being a primary halogenoalkane, benzyl chloride adopts the mechanism you have drawn in **(a)(i)**.

The benzyl cation, **$C_6H_5CH_2^+$, intermediate** formed although is a primary cation, is **stabilised by delocalisation of the electrons from the benzene ring** **[1m]** onto the carbocationic carbon, hence favouring the S_N1 mechanism instead of S_N2 mechanism.

[1]

(b) Unlike halogenoalkanes, halogenoalkenes such as vinyl bromide, $CH_2{=}CHBr$, are inert towards nucleophilic substitution. Suggest a possible explanation for this inertness.

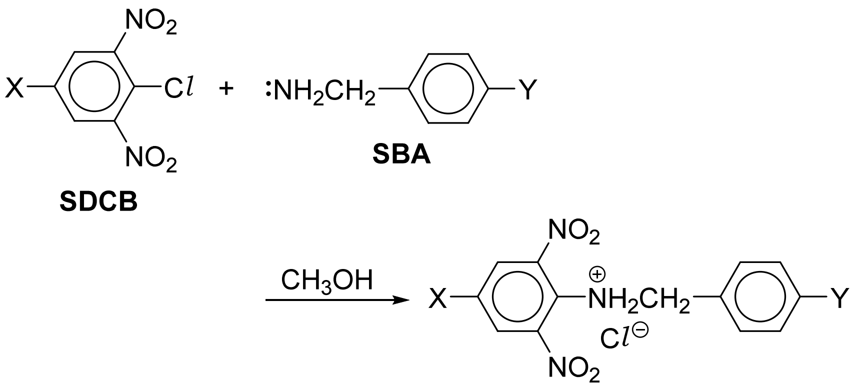
The **lone pair of electrons on Br is delocalised into the C=C**, imparting **partial double bond character** to the C–Br, and **strengthening the C–Br bond**, hence rendering cleavage of the C–Br bond difficult. **[1m]** In addition, this lowers the electron-deficiency of the α-carbon, making vinyl bromide less susceptible to nucleophilic attack.

[1]

Like halogenoalkenes, halogenoarenes are also usually inert towards nucleophilic substitution reaction.

Nonetheless, when suitably tuned, halogenoarenes can be made to undergo nucleophilic substitution too, although the mechanism is different from the S_N1 and S_N2 mechanisms of aliphatic halogenoalkanes.

(c) 4-X-Substituted-2,6-dinitrochlorobenzenes (SDCB) react with 4-Y-substituted-benzylamines (SBA) in methanol to give benzylammonium chloride salt:



benzylammonium chloride

In the reaction, SDCB is regarded as the substrate, while SBA is the nucleophile.

(i) Suggest how it can be shown *chemically* that substitution reaction had indeed taken place with SDCB?

Addition of **aqueous silver nitrate** to the reaction mixture will produce an **immediate white precipitate of AgC*l*** if the substitution reaction had taken place. Otherwise, no precipitate will be observed. **[1m] for both reagent and immediate ppt** [1]

(ii) Suggest, with reason, one physical property which may be used to follow the progress of the reaction.

Since the reaction **produces an ionic product** from electrically neutral reactants, the **electrical conductivity** **[1m]** of the mixture will increase with the amount of the product formed, allowing the progress of the reaction to be followed.

[1]

The reaction was found to follow overall second-order kinetics, with rate equation:

$$\text{rate} = k[\text{SDCB}][\text{SBA}]$$

The rate constant, k ($\text{mol}^{-1}\ \text{dm}^3\ \text{s}^{-1}$), for the reaction of three 4-X-substituted-2,6-dinitrochlorobenzenes with four 4-Y-substituted-benzylamines in pure methanol at 25 °C is given in Table 6.1 below.

Table 6.1

X (SDCB substrate)	**4-Y-benzylamine (SBA nucleophile)**			
	4-OCH_3	**4-CH_3**	**H**	**4-Cl**
NO_2	3.12	2.47	2.34	1.66
CN	0.748	0.563	0.498	**0.357**
CF_3	0.100	0.0902	0.0744	0.0479

The values of the rate constant, k, can be obtained from suitable concentration–time plots such as those shown in Figure 6.1 on the next page.

Figure 6.1 is obtained by monitoring changes in the concentration of the nucleophile, 4-chlorobenzylamine, with time, using an **excess** of the three substrates separately. The initial concentrations of the three substrates are indicated on Figure 6.1.

(iii) With the aid of Figure 6.1, determine the rate constant, k, when X = CN, using 4-chlorobenzylamine as nucleophile, and fill in the blank in Table 6.1.

From the graph,

$$\text{initial rate} = \left|\frac{0.010 - 0}{0 - 8}\right| = 1.25 \times 10^{-3}\ \text{mol dm}^{-3}\ \text{s}^{-1}$$ **[1m]**

$$\text{Hence, } k = \frac{\text{rate}}{[\text{SDCB}][\text{SBA}]} = \frac{1.25 \times 10^{-3}}{0.350 \times 0.010} = 0.3571 \approx \underline{\mathbf{0.357}}\ \text{mol}^{-1}\ \text{dm}^{3}\ \text{s}^{-1}$$ **[1m]**

[2]

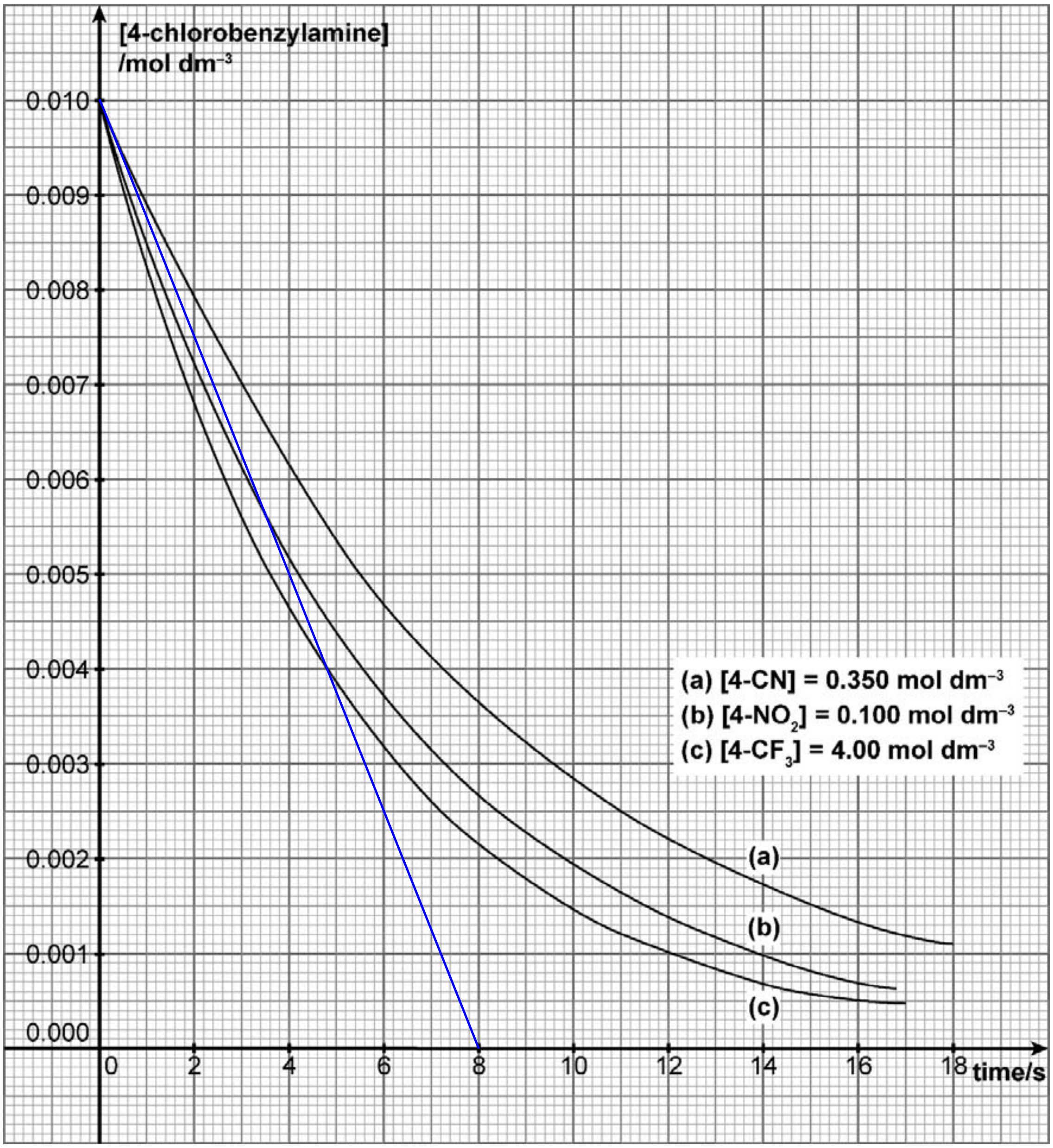
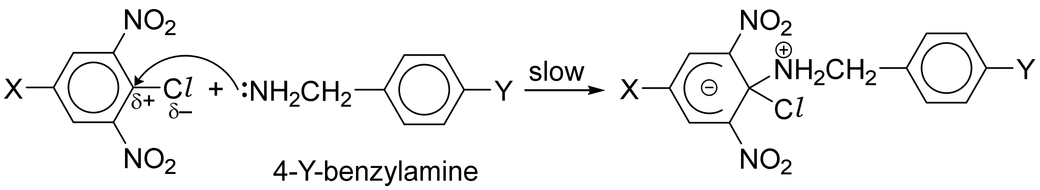

[4-chlorobenzylamine] /mol dm^{-3}
0.010
0.009
0.008
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0.000
0
2
4
6
8
10
12
14
16
18
time/s
(a) [4-CN] = 0.350 mol dm^{-3}
(b) [4-NO$_2$] = 0.100 mol dm^{-3}
(c) [4-CF$_3$] = 4.00 mol dm^{-3}
(a)
(b)
(c)

Figure 6.1

For Examiner's Use

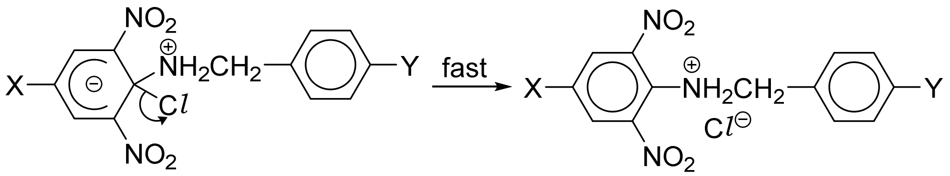
(d) Although the reaction is second-order, however, it is **not** a single-step reaction. Instead, SBA performs a rate-determining nucleophilic attack at the electrophilic C–Cl carbon of SDCB, leading to the formation of resonance-stabilised intermediate **Z**:



4-Y-benzylamine (SBA)

intermediate **Z**

Subsequently, intermediate **Z** rapidly expels a chloride ion to give the desired benzylammonium chloride:



intermediate **Z**

benzylammonium chloride

This two-step mechanism is known as the S_NAr mechanism.

Using the mechanism given above and the data in Table 6.1, explain which of the three substituents X = NO_2, CN or CF_3, is the strongest electron-withdrawing group.

From the mechanism, since the slow step involves the formation of intermediate **Z**, the **more stable Z** is, the **faster** the reaction will be.

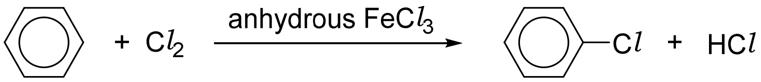
The **negative charge** of intermediate **Z** will be **stabilised** by the presence of **electron-withdrawing substituents**. Since the reaction is fastest (largest *k*) with X = NO_2, **NO_2** must be the strongest electron-withdrawing group. **[1m]** [1]

(e) The magnitude of the rate constant *k* can be used as a direct measure of the nucleophilicity of the 4-Y-benzylamine (SBA) nucleophile, that is, the larger the rate constant *k*, the more nucleophilic is the 4-Y-benzylamine.

Using the mechanism of the S_NAr mechanism described, explain why there is a positive correlation between the magnitude of the rate constant *k* and the nucleophilicity of the 4-Y-benzylamine.

From the mechanism, since the **slow step** involves the **nucleophilic attack** of the 4-Y-benzylamine at the electrophilic carbon of the benzene ring, the **more nucleophilic** the 4-Y-benzylamine, the **lower** will be the **activation energy**, and hence **larger** the **rate constant** *k*. **[1m] for nucleophilic attack being slow step and lower activation energy** [1]

Chloroarenes can be prepared by the reaction of benzene and chlorine in the presence of anhydrous $FeCl_3$ as a Lewis acid catalyst:



(f) Describe the role of anhydrous $FeCl_3$ in the reaction, illustrating with an equation.

The role of anhydrous $FeCl_3$ is to serve as a halogen carrier to **generate the strong electrophile**, the chlorine cation, from chlorine:

$$Cl_2 + FeCl_3 \rightarrow Cl^+ + FeCl_4^-$$

[1m] for strong electrophile and equation [1]

Anhydrous iron(III) chloride, $FeCl_3$, is an almost black crystalline solid and is very hygroscopic; it forms a series of hydrates when exposed to moist air. The common hydrate is yellow $FeCl_3 \cdot 6H_2O$, which contains $[FeCl_2(H_2O)_4]^+$. This is very soluble in water, and gives a strongly acidic solution.

The $[Fe(H_2O)_6]^{3+}$ ion exist only in strongly acidic solution in the absence of coordinating anion. The ion is violet in solution, although some hydrolysis may colour the solution yellow-brown.

(g) **(i)** Explain why $[FeCl_2(H_2O)_4]^+$ and $[Fe(H_2O)_6]^{3+}$ have different colours despite both containing iron(III).

Despite containing iron(III), the two complexes possesses **different ligands** and hence, the 3d orbitals of iron(III) is **split** into two different energy levels by **different extent**, resulting in **different energy gaps** between the two levels. **[1m]**

[1]

(ii) Explain why the violet $[Fe(H_2O)_6]^{3+}$ ion is stable only in highly acidic solution.

Due to the high charge density of the Fe^{3+} ion, $[Fe(H_2O)_6]^{3+}$ undergoes **hydrolysis** readily: $[Fe(H_2O)_6]^{3+}(aq) \rightleftharpoons [Fe(H_2O)_5(OH)]^{2+}(aq) + H^+(aq)$

Hence, a **high concentration of $H^+(aq)$** is needed to **suppress the hydrolysis**, to stabilise the $[Fe(H_2O)_6]^{3+}$ ion. **[1m]**

[1]

(h) On the other hand, anhydrous iron(III) iodide, FeI_3, had only been prepared recently in non-aqueous medium via the reaction of 6-coordinated $Fe(CO)_4I_2$ in hexane:

$$Fe(CO)_4I_2 + \tfrac{1}{2}I_2 \xrightarrow[\text{hexane}]{\text{uv light}} FeI_3 + 4CO$$

(i) State and explain the type of reaction involved in the synthesis of iron(III) iodide.

Redox reaction. The oxidation state of iron in $Fe(CO)_4I_2$ is +2, which is increased to +3 in FeI_3, while the oxidation state of iodine in I_2 is 0 which is decreased to –1 in FeI_3 **[1m] with correct explanation**

[1]

A non-aqueous medium is required for the above synthesis as iron(III) iodide is completely decomposed in aqueous solution.

(ii) Using the *Data Booklet*, suggest possible products from the decomposition of iron(III) iodide in water.

Since $E^{\ominus}(Fe^{3+}|Fe^{2+}) = +0.77\text{ V} > E^{\ominus}(I_2|I^-) = +0.54\text{ V}$, Fe^{3+} is capable of oxidising I^- to I_2, while itself reduced to Fe^{2+}:

$$FeI_3 \rightarrow FeI_2 + \tfrac{1}{2}I_2$$

The possible products are **FeI_2** and **I_2**. **[1m] for both products** [1]

[Total: 15]

BLANK PAGE

EUNOIA JUNIOR COLLEGE
JC2 Preliminary Examination 2018
General Certificate of Education Advanced Level
Higher 2

CHEMISTRY

9729/03

Paper 3 Free Response

19 September 2018

2 hours

Candidates answer on separate paper.

Additional Materials:	Answer Paper Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, civics group and registration number on 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 paper clips, highlighters, glue or correction fluid.

Section A
Answer **all** questions.

Section B
Answer **one** question.

Begin **each question** on a **fresh** piece of answer paper.

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 **13** printed pages and **1** blank page.

Section A

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

1 This question concerns acid-base properties of organic compounds and compounds of some elements in the Periodic Table.

(a) The behaviour of a molecular specie as an acid or base is dependent of the surrounding medium and its interaction with another reacting specie.

Using the symbol **HZ** to represent a Brønsted-Lowry acid and the symbol **B⁻** to represent a Brønsted-Lowry base, write equations to show the following:

(i) CH_3OH acting as a Brønsted-Lowry base. [1]

(ii) NH_3 acting as a Brønsted-Lowry acid. [1]

(b) In an acid-base reaction, conjugate acid-base pairs can be determined. Copy the table below onto your writing paper and complete it by writing the formula of the conjugate acid-base pairs of the species listed, assuming the acids/bases are monobasic/monoacidic in nature respectively.

	acid	**base**
I		H_2O
II	H_2	

[1]

(c) A particular weak monobasic acid HA has a dissociation constant, K_a, of 1.0×10^{-5} mol dm^{-3}. The un-ionised acid molecules are blue and the anions are yellow.

(i) Calculate the pH at which a solution containing HA molecules and A^- ions is green, *i.e.* midway between blue and yellow. [1]

(ii) Describe qualitatively how the answer in **(c)(i)** would be affected by the addition of solid sodium salt of the acid, NaA. [2]

A solution mixture is prepared by adding 50 cm^3 of 0.10 mol dm^{-3} of the acid HA to 50 cm^3 of 0.10 mol dm^{-3} of the sodium salt NaA.

(iii) Calculate the final pH of the above solution mixture if 0.04 g of NaOH(s) was added. [3]

(d) Elements and their compounds of the Periodic Table display varied chemical and physical properties.

(i) The peroxide ion has the formula O_2^{2-}. Group 2 peroxides, on heating, decompose to the oxides and oxygen as exemplified by barium peroxide below:

$$BaO_2(s) \longrightarrow BaO(s) + \tfrac{1}{2}O_2(g)$$

Predict how the temperature of decomposition of calcium peroxide would differ from that of barium peroxide. Support your prediction with a brief explanation. [2]

(ii) Explain why the melting point of Al_2O_3, is higher than that of P_4O_{10}, but lower than that of SiO_2. [3]

(e) Bromine occurs as bromide ion in low concentration in sea-water. It is extracted commercially by the following series of steps.

I Chlorine is passed into acidified sea-water and bromine is then removed in a stream of air. The concentration of bromine in the gas phase is too low at this stage for it to be condensed efficiently.

II Therefore it is converted to hydrogen bromide by reaction with added sulfur dioxide and a small excess of water vapour:

$$Br_2(g) + SO_2(g) + 2H_2O(g) \rightarrow 2HBr(g) + H_2SO_4(g)$$

A moderately concentrated, aqueous mixture of hydrobromic and sulfuric acids is obtained when the vapour is cooled and condensed.

III The concentrated mixture of acids is treated with chlorine and steam, producing a bromine vapour from which liquid bromine is obtained through condensation on cooling. The sulfuric acid remains in the solution.

IV The crude bromine is purified by fractional distillation.

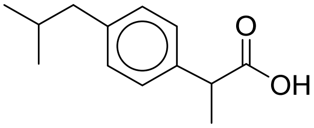
(i) Explain in terms of the relevant standard electrode potentials the feasibility of the reactions taking place in Steps **I** and **II**. [3]

(ii) Discuss the difference between the polarity of SO_2 and Br_2. [2]

(iii) Explain in terms of bonding, why, in Step **III**, the sulfuric acid remains in the solution. [1]

[Total: 20]

2 (a) Ibuprofen is a nonsteroidal anti-inflammatory drug (NSAID) that is commonly used as a painkiller and for fever reduction. The structure of ibuprofen is as shown below.



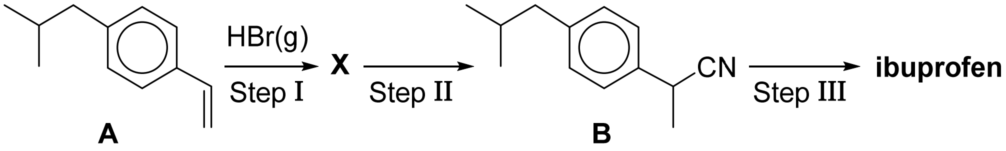
(i) Describe what is a chiral carbon. [1]

(ii) Draw the pair of enantiomers of ibuprofen. You may represent the aryl substituent using **Ar**. [2]

In the laboratory, the enantiomers of ibuprofen have been separated into their enantiomerically pure forms. However, the bottles containing these pure enantiomers were not labelled.

(iii) State a suitable physical property that you could use to identify the two different enantiomers. Explain your answer. [2]

There are a few routes that can be used to synthesis ibuprofen. Below is a reaction scheme proposed by a student to synthesise ibuprofen from the hydrocarbon **A**, *via* two intermediates **X** and **B**.



(iv) Suggest the identity of intermediate **X**. [1]

(v) Name and outline the mechanism for Step **I**, including curly arrows, showing the movement of electrons, and all charges. [3]

(vi) State the reagents and conditions for Step **II** and Step **III**. [2]

(b) Methylbenzene, an important starting material in synthetic chemistry, can be manufactured from heptane *via* catalytic reforming:

$$C_7H_{16}(l) \rightarrow C_7H_8(l) + 4H_2(g)$$

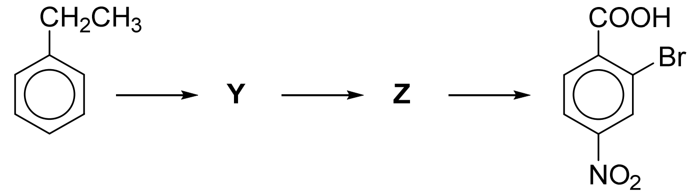
At T = 27 °C, the enthalpy of reaction, $\Delta H^{\ominus}$, is +211 kJ mol^{-1}, and the change in Gibbs free energy of reaction, $\Delta G^{\ominus}$, is +110 kJ mol^{-1}.

(i) Using the information above, calculate for $\Delta S^{\ominus}$ in J mol^{-1} K^{-1}. [2]

(ii) Calculate for $\Delta G^{\ominus}$ at T = 627 °C, in kJ mol^{-1}. [1]

(iii) Hence, comment on the effect of temperature on the spontaneity of the reaction. State any assumption that must be made for your comment to be valid. [2]

(c) The position of an incoming electrophile in electrophilic substitution is dependent upon nature and position of the substituent(s) already bonded to the benzene ring. Ethylbenzene undergoes a three-step reaction as shown below.



(i) Suggest the structures of intermediate **Y** and **Z**. [2]

(ii) With reference to the substituents on the benzene ring, explain the rationale behind the order of substitution in determining the identity of **Y** and **Z**. [2]

[Total: 20]

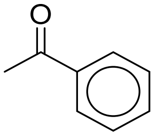
3 Ethanal used to be manufactured from ethyne, HC≡CH. This process is now being replaced by a method based on ethene. Widely known as the Wacker Oxidation, the overall process amounts to oxidation. Ethene and oxygen are bubbled together through an aqueous solution containing $CuCl_2$ and $PdCl_2$ catalysts:

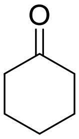
$$CH_2{=}CH_2 + \tfrac{1}{2}O_2 \xrightarrow[CuCl_2]{PdCl_2} CH_3CHO$$

The laboratory scale modification – the Wacker-Tsuji Oxidation – is useful for the synthesis of various ketone:

$$RCH{=}CH_2 + \tfrac{1}{2}O_2 \xrightarrow[CuCl_2]{PdCl_2} RCOCH_3$$

(a) **(i)** Draw the structure of the starting material to manufacture the following ketones using the Wacker-Tsuji Oxidation:

(**I**) acetophenone, 

(**II**) cyclohexanone,  [2]

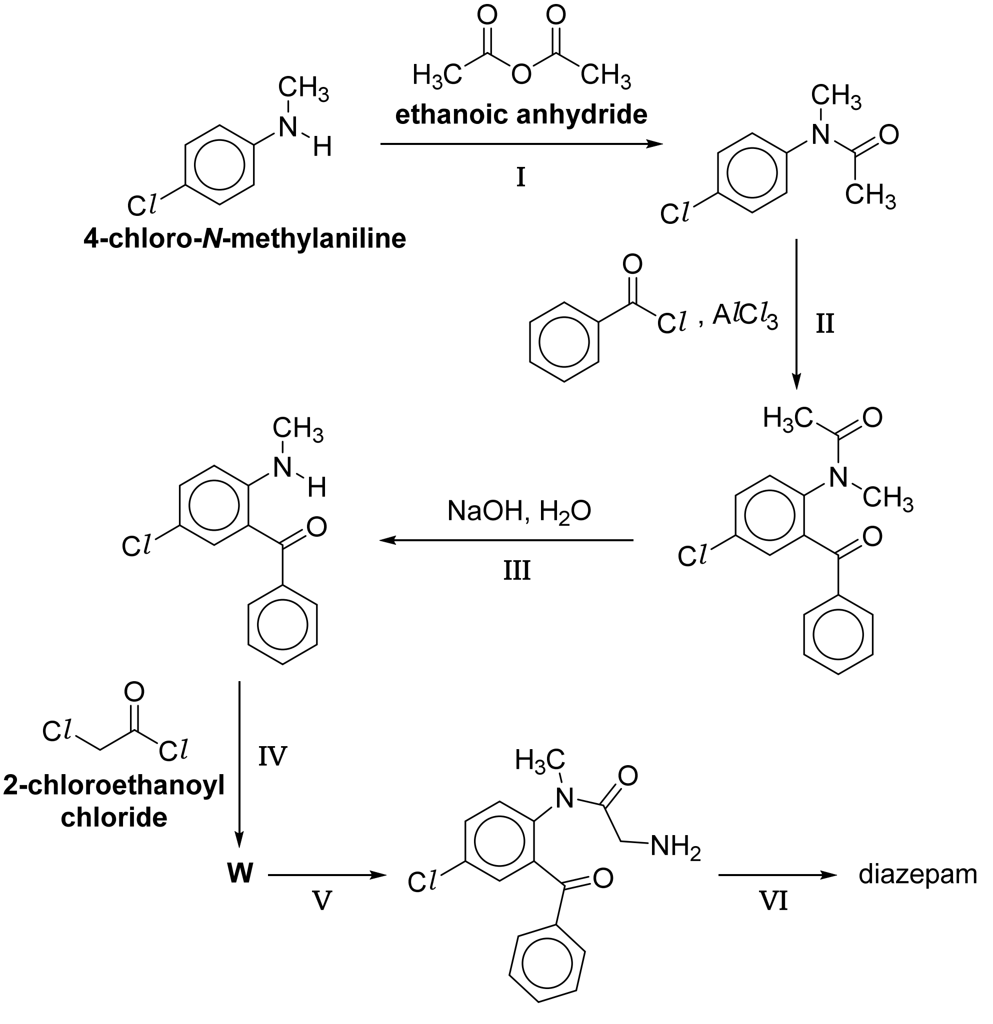
(ii) Describe one simple chemical test to distinguish between the above two ketones. You should state the reagents, conditions and the expected observations with each compound. [2]

(b) Ethanal is often used in the manufacture of 2-chloroethanoyl chloride, $ClCH_2COCl$.

(i) Propose a 3-step synthetic route for the formation of 2-chloroethanoyl chloride from ethanal, stating clearly the reagents and conditions for each step. [3]

2-chloroethanoyl chloride is an important reagent in the manufacture of diazepam, a drug that is commonly used to treat a range of conditions including anxiety and alcohol withdrawal syndrome.

The following reaction scheme shows the synthesis of diazepam from 4-chloro-*N*-methylaniline.

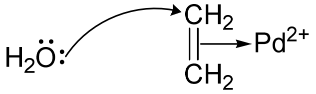


(ii) The mechanism for Step **II** is similar to that of Friedel-Crafts alkylation. Suggest the mechanism for this step, including curly arrows, showing the movement of electrons, and all charges. [2]

(iii) Draw the structure of compound **W** and state the reagent for Step **V**. [2]

(iv) Step **VI** occurs spontaneously at room temperature, without the need of any reagents. This reaction is similar to the reaction of carbonyl compounds with 2,4-dinitrophenylhydrazine. Draw the structure of diazepam. [1]

(c) The suggested mechanism of the Wacker Oxidation involves the formation of a complex between ethene and Pd^{2+}, whereby ethene acts as a *ligand*. This is then followed by nucleophilic attack of water at the complexed ethene molecule:



The resulting complex breaks down by a number of stages to form ethanal and palladium metal. The palladium metal is oxidised back to Pd^{2+} by oxygen. The $CuCl_2$ is a catalyst for this oxidation.

(i) What is meant by the term *ligand* in the context of transition element chemistry? [1]

(ii) Suggest a reason why the formation of this complex renders ethene attractive to nucleophiles rather than the usual electrophiles. [1]

(iii) Aqueous $CuCl_2$ is commonly observed as a blue solution. Explain this phenomenon. [3]

(d) A mixture containing 0.200 mol dm^{-3} Cu^{2+} and 0.200 mol dm^{-3} Pd^{2+} is treated with solid potassium hydroxide in attempt to separate the two cations, by precipitating out $Pd(OH)_2$.

The numerical values of the solubility products of $Cu(OH)_2$ and $Pd(OH)_2$ are given in the table below.

hydroxide	**solubility product, K_{sp}**
$Cu(OH)_2$	2.20×10^{-20}
$Pd(OH)_2$	1.00×10^{-31}

Maximum separation of the two ions is achieved when $Cu(OH)_2$ is just about to precipitate out from solution.

(i) Determine the hydroxide ion concentration at maximum separation. [1]

The two ions are said to be *selectively* separated when a maximum of 0.01% of the precipitated compound still remains as the aqueous ions.

(ii) By calculating the concentration of Pd^{2+} remaining in solution at maximum separation, determine whether Pd^{2+} can be selectively separated from Cu^{2+}. [2]

[Total: 20]

Section B

Answer **one** question from this section.

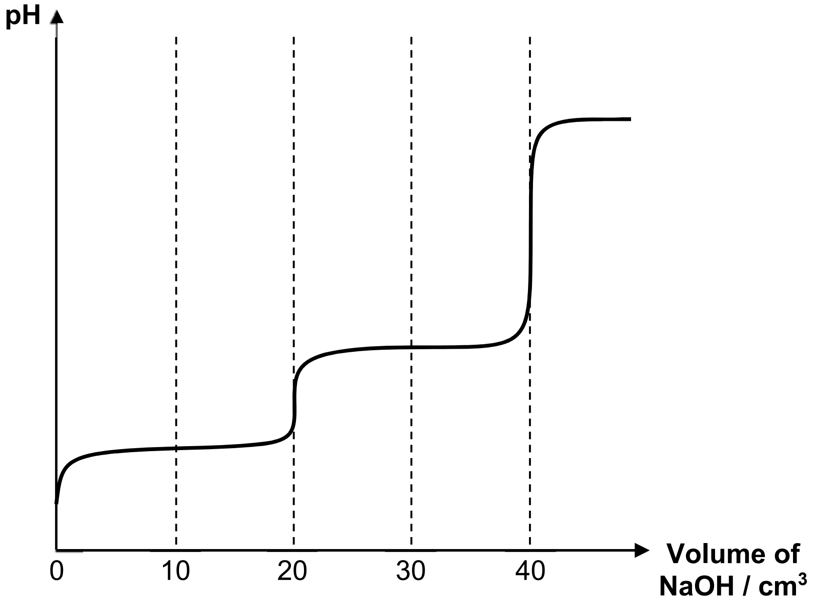
4 **(a)** The pK_a values of some weak acids are given below.

acid	**formula**	**pK_{a1}**	**pK_{a2}**
peroxyethanoic acid		y	–
ethanoic acid		4.76	–
malonic acid		2.83	5.69

(i) Suggest, with reasoning, whether the pK_{a1} of peroxyethanoic acid, y, is larger or smaller than the pK_{a1} of ethanoic acid. [2]

(ii) Explain why pK_{a2} of malonic acid is higher than pK_{a1} of ethanoic acid. [1]

(iii) 25.0 cm^3 of a sample containing malonic acid was titrated with 0.800 mol dm^{-3} of a solution of NaOH. The following titration curve was obtained.



You may represent malonic acid as H_2A.
Calculate the concentration of malonic acid in the sample. [1]

(iv) Calculate the initial pH of malonic acid, explaining any assumptions made. [2]

(v) From the list of indicators below, state a suitable indicator that can be used to detect the first equivalence point for the titration of malonic acid with NaOH, giving a reason for your choice.

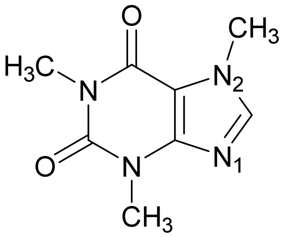
indicator	**pH at which colour changes**
methyl violet	0−1.6
bromocresol green	3.8−5.4
cresol purple	7.6−9.2

[1]

(vi) The experiment in **(a)(iii)** was repeated with ethanoic acid of the same concentration as malonic acid. Explain whether the pH at equivalence point would be higher or lower than the first equivalence point of the titration with malonic acid. [1]

(b) Describe and explain how the ease of hydrolysis of CH_3CH_2Cl differs from that of CH_3COCl. [2]

(c) Caffeine is a component of many over the counter analgesics.



caffeine

(i) Predict the products when caffeine undergoes prolonged heating with aqueous sodium hydroxide. [3]

(ii) Caffeine is monobasic. Given that both N_1 and N_2 are sp^2-hybridised, suggest why N_1 is basic while N_2 is neutral. [2]

(d) A zinc-air electrochemical cell is operated by the reaction of zinc with the oxygen in air under an alkaline condition. At the anode, zinc is converted to aqueous zincate ions, $Zn(OH)_4^{2-}$, by air.

(i) Construct an equation for the anode reaction. [1]

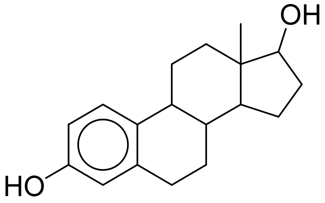
(ii) At 298 K, the standard e.m.f. of a zinc-air electrochemical cell is +1.65 V. By using suitable data from the *Data Booklet*, suggest the standard electrode potential of the $Zn(OH)_4^{2-}(aq)|Zn(s)$ half-cell at 298 K. [2]

(iii) Determine the effect of using pure oxygen instead of air on the e.m.f. of the zinc-air electrochemical cell at 298 K. [2]

[Total: 20]

5 Many hormones in the human body contain hydroxy or carbonyl compounds.

(a) Estradiol, an estrogenic hormone, can be synthesized from *Testosterone*. The structure of estradiol is shown below.



estradiol

Draw the structure of the organic product formed when estradiol is reacted with each of the following under suitable conditions:

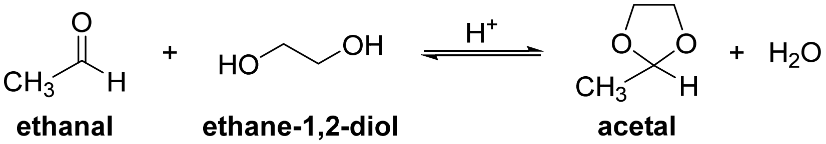
(i) Cl_2(aq) [1]

(ii) $SOCl_2$ [1]

(iii) Sodium metal [1]

When aldehydes or ketones are reacted with an alcohol and an acid catalyst, acetals are formed.

The reaction between ethanal and ethane-1,2-diol was studied in the inert solvent dioxane.



(b) When the initial rate of this reaction was measured at various concentrations of the two reactants with H^+ concentration of 0.05 mol dm^{-3}, the following results were obtained.

experiment	$[CH_3CHO]$ / mol dm^{-3}	$[HOCH_2CH_2OH]$ / mol dm^{-3}	relative rate
1	0.20	0.10	1.00
2	0.25	0.10	1.25
3	0.25	0.16	2.00

(i) Determine the order of reaction with respect to the following reactants, explaining how you arrive at your answer.

- CH_3CHO
- $HOCH_2CH_2OH$ [2]

(ii) Hence, write the rate equation for the reaction, including units of the rate constant. [2]

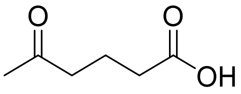
(iii) When the H^+ concentration used in experiment 2 was increased to 0.10 mol dm^{-3}, the relative rate had a value of 2.50.

State the value of the relative rate when the concentrations of CH_3CHO, $HOCH_2CH_2OH$ and H^+ used are 0.20 mol dm^{-3} each. [1]

(c) The acetal group does not react with bases or reducing agents, which the carbonyl group is susceptible to. For instance, both $NaBH_4$ and $LiA\mathit{l}H_4$ do not react with the acetal group.

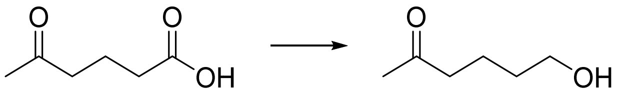
Hence it is possible to use the formation of acetals from carbonyl compounds as a way to protect the carbonyl groups from these reagents. Subsequently one can restore the carbonyl functional group by acidic hydrolysis since the formation of acetals is a reversible reaction.

(i) Draw the structure of the product formed when the following compound is reacted with $NaBH_4$ and $LiA\mathit{l}H_4$ respectively.



[1]

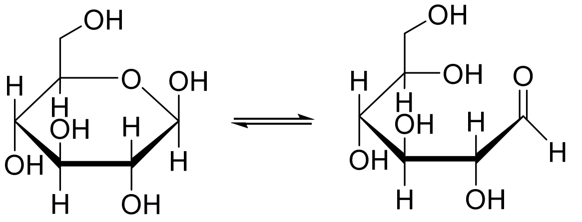
(ii) By using ethane-1,2-diol, $HOCH_2CH_2OH$, as the alcohol to form an acetal group in the inert solvent dioxane as a first step, suggest a suitable synthesis route for the following conversion.



[2]

Copper is used widely in electrical equipment, the minting of coins and for decorative purposes such as in jewellery. Pure copper could be obtained from the electrolysis of a solution containing Cu^{2+} ions, or from electrolysis involving impure copper.

(d) Copper ions are present in Fehling's solution and can be used to test for "reducing sugars". Glucose, a basic form of sugar, has the following structure.



cyclic form of glucose

open-chain form of glucose

Glucose gives a positive test with Fehling's solution.

(i) Identify the functional group involved in the reaction and describe what is observed when Fehling's solution is added to glucose with heating. [1]

(ii) Explain why glucose is classified as a "reducing sugar". [1]

(e) In an electrolytic cell, a current of 0.25 A is passed through solution of concentrated copper(II) chloride using platinum electrodes.

(i) Write the equation for the half-cell reaction taking place at the anode. [1]

(ii) When the cell operates for 2.00 hours, 0.496 g of copper is deposited at one electrode. Determine the percentage efficiency of the electrolytic cell. [2]

(f) A sample of impure copper was composed mainly of copper, but with silver and chromium as impurities.

Draw a fully labelled diagram and with reference to relevant $E^\ominus$ values, explain how pure copper could be obtained from the impure sample. [4]

[Total: 20]

BLANK PAGE

Suggested Answer

1 (a) (i) $\underset{\text{base}}{CH_3OH} + \underset{\text{acid}}{\mathbf{HZ}} \longrightarrow CH_3OH_2^+ + \mathbf{Z^-}$ **[1m]**

(ii) $\underset{\text{acid}}{NH_3} + \underset{\text{base}}{\mathbf{B^-}} \longrightarrow NH_2^- + \mathbf{BH}$ **[1m]**

(b)

	acid	**base**
I	$\mathbf{H_3O^+}$	H_2O
II	H_2	$\mathbf{H^-}$

[1m] for both correct

(c) (i) $HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

Midway between blue and yellow indicates that $[H^+] = [HA]$

Hence, $K_a = \dfrac{[H^+]\cancel{[A^-]}}{\cancel{[HA]}} = [H^+]$

$\therefore\ pH = pK_a = -\lg K_a = -\lg(1.0\times10^{-5}) = \underline{\mathbf{5.0}}$ **[1m]**

(ii) $HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$

Upon addition of NaA (a strong electrolyte) to the solution, it undergoes complete dissociation and **$[A^-]$ in the solution is thus momentarily increased**. In accordance to Le Chatelier's principle, the **equilibrium position of the above reaction would shift to the left** **[1m]** to remove the additional A^- ions added. Hence the **$[H^+]$ would decrease** **[1m]** and the pH of the solution would correspondingly **increase**. **Accept alternative explanation using HH equation**

(iii) Before addition of NaOH at pH = 5:

System: Acidic buffer

pH 5 is the point of maximum buffering capacity where pH = pK_a = 5

Thus $[HA] = [A^-] =$ 0.050 mol dm^{-3}

$$n_{HA} = n_{A^-} = \frac{50}{1000}\times0.10 = \underline{\mathbf{5.00\times10^{-3}\ mol}}$$

On addition of NaOH:

n_{OH^-} added $= 1.00\times10^{-3}$ mol

When small amount of OH^- is added to the buffer:

$$OH^- + HA \rightarrow A^- + H_2O$$

n_{A^-} after addition of $OH^- = 5.00\times10^{-3} + 1.00\times10^{-3} = \underline{\mathbf{6.00\times10^{-3}\ mol}}$

n_{HA} after addition of $OH^- = 5.00\times10^{-3} - 1.00\times10^{-3} = \underline{\mathbf{4.00\times10^{-3}\ mol}}$

$$\mathrm{pH} = \mathrm{p}K_a + \lg\frac{[\mathrm{A}^-]}{[\mathrm{HA}]}$$

$$= 5.00 + \lg\frac{\left(\frac{6.00\times10^{-3}}{V}\right)}{\left(\frac{4.00\times10^{-3}}{V}\right)}$$ **[1m] for correct substitution into formula**

$= \underline{\mathbf{5.18}}$ **[1m] for ans in 3 s.f., ecf**

(d) **(i)** Temperature of decomposition for CaO_2 is **lower than** that of BaO_2. **[1m]** **Charge density of Ba^{2+} < Ca^{2+}** thus **polarising power of Ba^{2+} < Ca^{2+}** because Ba^{2+} has a larger ionic size but both have the same charge. Since Ca^{2+} is more polarising, the **O–O bond in O_2^{2-} is weakened** to greater extent. **[1m]** Hence CaO_2 decomposes more readily into CaO and O_2 as compared to BaO_2.

(ii) Al_2O_3 has a **giant ionic structure** with **strong electrostatic forces of attraction** between the oppositely charged Al^{3+} and O^{2-} ions. Melting Al_2O_3 involves overcoming the **strong ionic bonding** in the lattice which requires a large amount of heat energy. **[1m]**

P_4O_{10} has a **simple molecular structure**. It consists of discrete molecules with **instantaneous dipole–induced dipole interactions** existing between the molecules. Melting P_4O_{10} involves overcoming these relatively **weak** intermolecular forces and requires less heat energy than in the case of melting Al_2O_3. Hence P_4O_{10} has a lower melting point than Al_2O_3. **[1m]**

SiO_2 has a **giant covalent structure** (or macromolecular structure) with each Si atom covalently bonded to four O atoms tetrahedrally. Melting SiO_2 involves breaking the **strong Si–O covalent bonds** and this requires more heat energy than in the case of melting Al_2O_3. Hence the melting point of SiO_2 is higher than that of Al_2O_3. **[1m]**

(e) **(i)** For Step I: $\mathbf{Cl_2(aq) + 2Br^-(aq) \rightarrow 2Cl^-(aq) + Br_2(aq)}$

$$E^\ominus_{\text{cell}} = E^\ominus_{\text{reduction}} - E^\ominus_{\text{oxidation}} = +1.36 - (+1.07) = \underline{\mathbf{+0.29\ V}}$$ **[1m]**

Since the $E^\ominus_{\text{cell}} > 0$, the oxidation of the Br^- ion by Cl_2 is a **thermodynamically / energetically spontaneous process under standard conditions**.

For Step II: $Br_2(aq) + SO_2(g) + 2H_2O(l) \rightarrow 2HBr(g) + H_2SO_4(g)$

$$E^\ominus_{\text{cell}} = E^\ominus_{\text{reduction}} - E^\ominus_{\text{oxidation}} = +1.07 - (+0.17) = \underline{\mathbf{+0.90\ V}}$$ **[1m]**

Since the $E^\ominus_{\text{cell}} > 0$, the oxidation of SO_2 by Br_2 is a **thermodynamically / energetically spontaneous process under standard conditions**.

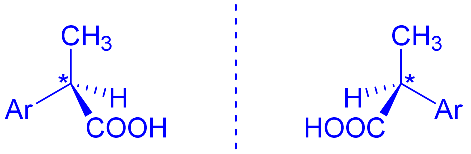
Both correct conclusions on energetically spontaneous reactions **[1m]**

(ii) SO_2 is a **bent** molecule, whereas Br_2 is a linear molecule **[1m]**. SO_2 is **polar** as it has a **net dipole moment**, whereas Br_2 is non-polar. **[1m]**

(iii) The sulfuric acid remains in the solution because it is significantly less volatile than bromine. This is so because it exists as an aqueous ionic mixture consisting of H^+, HSO_4^- and SO_4^{2-} ions solvated by water molecules (through **ion-dipole interactions**) **[1m]** and is hence not volatile.

2 (a) (i) A chiral carbon is an asymmetrical **carbon attached to four different substituents**. **[1m]**

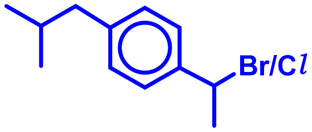
(ii)



[1m] for correct 3D configuration
[1m] for correct chiral carbon identification and pair of enantiomers

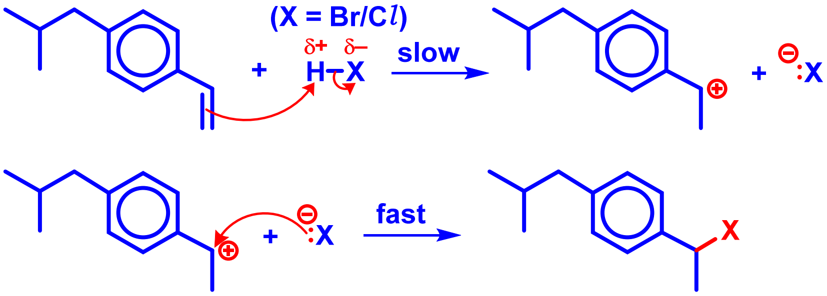
(iii) **Optical activity / Optical rotation** **[1m]** of the enantiomers can be used. Since the pair of enantiomers will **rotate plane-polarised light in different directions** **[1m]** this can be used to identify the pure enantiomer.

(iv)



[1m]

(v) Type of Reaction: **Electrophilic addition** **[1m]**



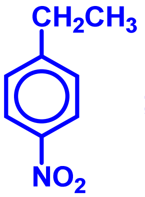
[1m] arrow pushing, balanced equation
[1m] partial charges, charges, carbocation intermediate

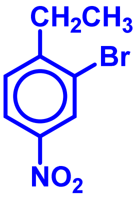
(vi) Step **II** – Reagent: **ethanolic KCN**
Condition: **heat with reflux**
[1m] for both reagent and conditions
Step **III** – Reagent: **dilute H_2SO_4**
Condition: **heat with reflux**
[1m] for both reagent and conditions

(b) (i)
$$\Delta G_r^\ominus = \Delta H_r^\ominus - T\Delta S_r^\ominus$$
$$\Delta S_r^\ominus = \frac{\Delta H_r^\ominus - \Delta G_r^\ominus}{T} = \frac{+211-(+110)}{300}$$ **[1m] for correct equation and sub**
$$= +0.3367\ \text{kJ mol}^{-1}\ \text{K}^{-1} = \underline{\mathbf{+337\ J\ mol^{-1}\ K^{-1}}}$$ **[1m] for answer and units**

(ii) $\Delta G_r^\ominus = \Delta H_r^\ominus - T\Delta S_r^\ominus = +211-(900\times 0.3367) = \underline{\mathbf{-92.0\ kJ\ mol^{-1}}}$ **[1m]**

(iii) As the temperature of the reaction increases, **$\Delta G_r^\ominus$ becomes more negative**. Therefore, reaction becomes **more spontaneous**. **[1m]** This will hold true if **$\Delta H_r^\ominus$ and $\Delta S_r^\ominus$ remains constant/are unaffected by temperature change**. **[1m]**

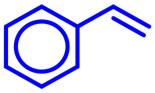
(c) **(i)** **Y** is 

; **Z** is 

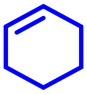
[1m] for each structure

(ii) Ethylbenzene **cannot be oxidised to benzoic acid first** as the benzoic acid has a **3-directing COOH group**. **[1m]**

Starting with ethylbenzene which has a **2,4-directing ethyl group**, nitration will occur at the 4-position, forming **Y**. **[1m]** Subsequently, **Y** has a 2-directing ethyl group and a 3-directing NO_2 group, bromination will be direct to the 2-position relative to ethyl, to form **Z**.

3 **(a)** **(i)** (I) 

[1m]

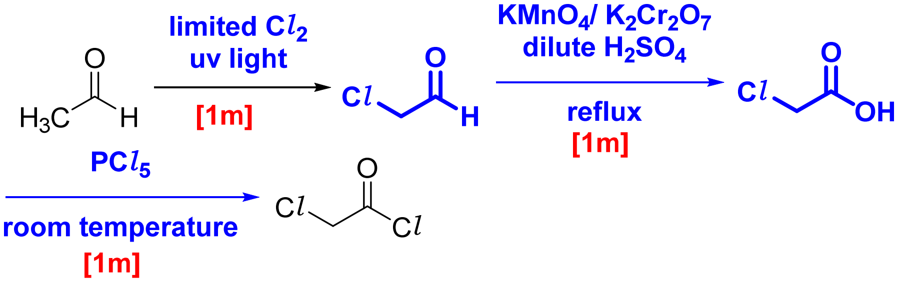
(**II**) 

[1m]

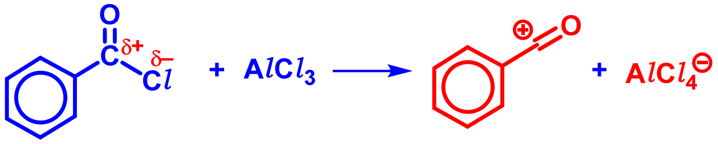
(ii) **Reagents and conditions:** Add aqueous iodine in sodium hydroxide to a solution of acetophenone and cyclohexanone separately. Heat the solution. **[1m]**

Observations: Pale yellow precipitate of triiodomethane (CHI_3) will be observed for acetophenone but not for cyclohexanone. **[1m]**

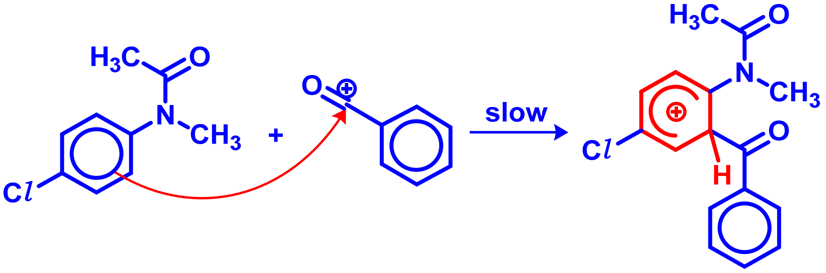
(b) **(i)**



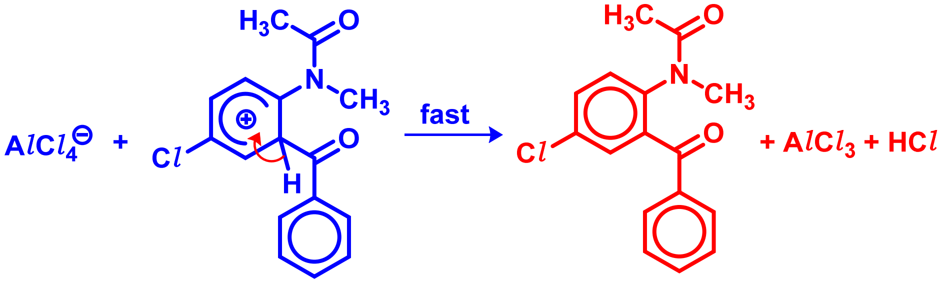
(ii) **Step 1:** Generation of electrophile



Step 2: Electrophilic attack

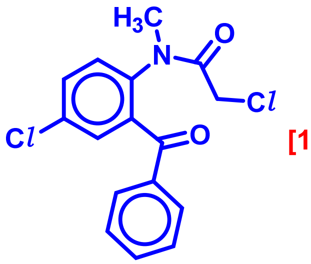


Step 3: $AlCl_4^{\ominus}$ abstracts $H^{\oplus}$ from arenium ion



[1m] curly arrows, charges and partial charges (for C–Cl bond)
[1m] slow step; correct arenium intermediate and balanced equations

(iii)

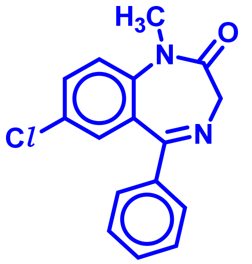


[1m]

W

Reagent for Step **V** : **Ethanolic NH_3** **[1m]**

(iv)



[1m]

diazepam

(c) **(i)** A *ligand* is a neutral **molecule or an anion** which possesses **at least one lone pair of electrons** which can be used to form **dative bonds** with the central atom or ion. **[1m]**

(ii) The Pd^{2+} cation forms a complex with ethene, **decreasing the electron density** in the double bond of ethene, making the molecule prone to nucleophilic attack. **[1m]**

(iii) $CuCl_2$(aq) contains the $[Cu(H_2O)_6]^{2+}$ ion. Cu^{2+} has a **d^9 configuration/partially unfilled d orbitals** so **electron transition between d orbitals** is possible. **(✓$_1$)**
In an octahedral Cu(II) complex ion, the presence of **ligands causes the d orbitals to split into 2 (different) energy levels** **(✓$_2$)**.
Energy gap/ΔE corresponds to the radiation in the visible light spectrum **(✓$_3$)**.
When radiation from the visible light spectrum is absorbed, **an electron transits from a d orbital of LOWER energy to a d orbital of HIGHER energy**. **(✓$_4$)**
Hence, the **colour seen is the complement of the colours absorbed** **OR the colour seen is the colours that are not absorbed**. **(✓$_5$)**
5(✓): [3m] ; 4–3(✓): [2m] ; 1–2(✓): [1m]

(d) **(i)** When $Cu(OH)_2$ is about to precipitate out, $IP(Cu(OH)_2) = K_{sp}(Cu(OH)_2)$

$[OH^-]$ at maximum separation $= \sqrt{\dfrac{2.20\times10^{-20}}{0.200}} = \underline{\mathbf{3.32\times10^{-10}\ mol\ dm^{-3}}}$ **[1m]**

(ii) $[Pd^{2+}]$ at maximum separation $= \dfrac{1.00\times10^{-31}}{\left(3.32\times10^{-10}\right)^2} = \underline{\mathbf{9.07\times10^{-13}\ mol\ dm^{-3}}}$ **[1m]**

$\%[Pd^{2+}]$ remaining $= \dfrac{9.07\times10^{-13}}{0.200}\times100\% = 4.54\times10^{-10}\% < 0.01\%$ **[1m]**

Therefore Pd^{2+} **can** be selectively precipitated from Cu^{2+}.

4 **(a)** **(i)** The pK_{a1} of peroxyethanoic acid, *y*, is **larger** **[1m]** than pK_{a1} of ethanoic acid. The negative charge on the oxygen of the peroxyethanoate ion is stabilised by the **electron-withdrawing** inductive effect of the **neighbouring electronegative oxygen**, while the negative charge on the oxygen of the ethanoate ion is much more stabilised by **effective delocalisation over the C=O**. Since the ethanoate ion is **resonance stabilised** and is more stable than the peroxyethanoate ion, ethanoic acid is more acidic than peroxyethanoic acid. **[1m]**

(ii) The pK_{a2} of malonic acid is higher because it is **more difficult to remove an H^+ ion from an already negatively charged species than from a neutral ethanoic acid molecule**. **[1m]**

(iii) Concentration of $H_2A = \dfrac{\frac{20.00}{1000}\times0.800}{\frac{25.00}{1000}} = \underline{\mathbf{0.640\ mol\ dm^{-3}}}$

(iv) Assumption: Since $K_{a1} >> K_{a2}$, it can be assumed that the H_3O^+ from the second dissociation is negligible and can be ignored, and all the H_3O^+ in the solution comes from the first dissociation. **[1m]**

$$K_{a1} = \frac{\left[H^+\right]^2}{\left[H_2A\right]-\left[H^+\right]} = 10^{-2.83}$$

$$\frac{\left[H^+\right]^2}{0.640-\left[H^+\right]} = 1.479\times10^{-3}$$

$$\frac{\left[H^+\right]^2}{0.640} \approx 1.479\times10^{-3}\left(\text{since } 0.640 \gg \left[H^+\right]\right)$$

$$\left[H^+\right] = 0.03077\ \text{mol dm}^{-3}$$

initial pH = **1.51** **[1m]**

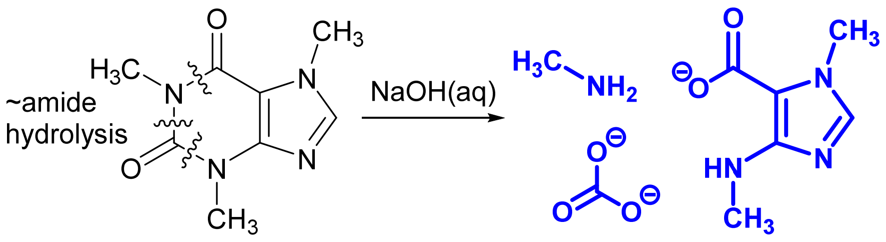
(v) **Bromocresol green** because the **pH at equivalence point falls within the region of rapid pH change**. **[1m]**

(vi) Since ethanoic acid has a larger pK_{a1} than malonic acid, its **conjugate base has a higher K_b (or is a stronger base)** than that of the monoanion of malonic acid. Hence, conjugate base of ethanoic acid hydrolyses to a greater extent, **resulting in pH at equivalence point being higher**. **[1m]**

(b) CH_3COCl **hydrolyses more readily** than CH_3CH_2Cl as the acyl carbon is **more electron-deficient** (or has a larger δ+ charge) compared to the α-carbon, as it is **bonded to another electronegative atom O** besides Cl **[1m]**, hence more susceptible to nucleophilic attack by water or HO^-.

In addition, the acyl carbon is **trigonal planar** (sp^2-hybridised) while the α-carbon is **tetrahedral** (sp^3-hybridised), hence CH_3COCl experiences **less steric hindrance** **[1m]** compared to CH_3CH_2Cl for approach of the nucleophile.

(c) **(i)**



[1m] for each structure

(ii) The **lone pair of electrons on N_1 is located in one of the sp^2-hybridised orbital which is perpendicular to the unhybridised p orbitals of the neighbouring sp^2-hybridised carbon atoms**, thus **this lone pair is not delocalised into the neighbouring C=C bond** and available for protonation. **[1m]**
On the other hand, the **lone pair of electrons on N_2 is located in the remaining unhybridised p orbital which is parallel to the unhybridised p orbitals of the neighbouring sp^2-hybridised carbon atoms**, thus **this lone pair is delocalised into the neighbouring C=C bonds** and unavailable for protonation. **[1m]**

(d) **(i)** $\mathbf{Zn(s) + 4OH^-(aq) \rightarrow Zn(OH)_4^{2-}(aq) + 2e^-}$ **[1m]**

(ii) From *Data Booklet*, cathode equation is

$$O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq) \qquad E^\ominus = +0.40\text{ V} \text{ [1m]}$$

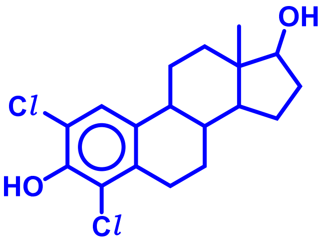
$$E^\ominus_{\text{cell}} = E^\ominus_{\text{reduction}} - E^\ominus_{\text{oxidation}} = E^\ominus\left(O_2|OH^-\right) - E^\ominus\left(Zn(OH)_4^{2-}\middle|Zn\right)$$

$$+1.65 = +0.40 - E^\ominus\left(Zn(OH)_4^{2-}\middle|Zn\right)$$

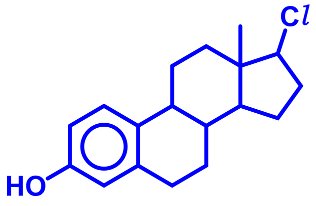
$$E^\ominus\left(Zn(OH)_4^{2-}\middle|Zn\right) = +0.40 - (+1.65) = \underline{\mathbf{-1.25\text{ V}}} \text{ [1m]}$$

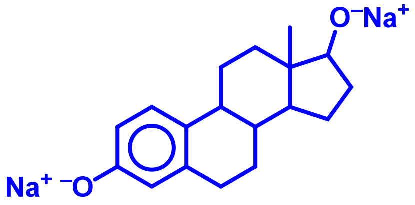
(iii) The use of pure air increases partial pressure of oxygen gas, thus equilibrium position of $O_2(g) + 2H_2O(l) + 4e^- \rightleftharpoons 4OH^-(aq)$ shifts to the **right** **[1m]**, causing cell **e.m.f. to increase** **[1m]** **(Since e.m.f. = $E^\ominus\left(O_2|OH^-\right) - E^\ominus\left(Zn(OH)_4^{2-}\middle|Zn\right)$)**.

5 **(a)** **(i)**



[1m]

(ii)  **[1m]**

(iii)  **[1m]**

(b) **(i)** **CH_3CHO**

Comparing **expt 1 & 2**,
when **concentration of CH_3CHO was increased 1.25 times**, keeping the concentration of CH_3OH constant, the **relative rate was 1.25 times the original value**.
Hence **order of reaction w.r.t. CH_3CHO is 1**. **[1m]**

$HOCH_2CH_2OH$

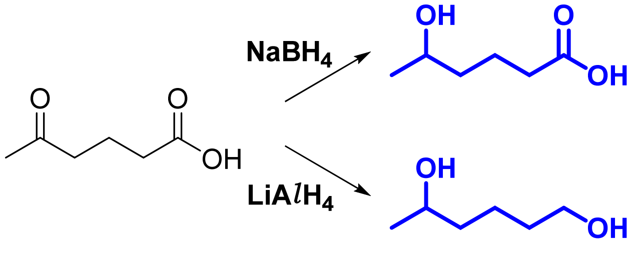
Comparing **expt 2 & 3**,
when **concentration of $HOCH_2CH_2OH$ was increased 1.6 times**, keeping the concentration of CH_3CHO constant, the **relative rate was 1.6 times the original value**.
Hence **order of reaction w.r.t. $HOCH_2CH_2OH$ is 1**. **[1m]**

(ii) **Rate = $k[CH_3CHO][HOCH_2CH_2OH]$ [1m]**
Units of k: **$mol^{-1}\ dm^{3}\ time^{-1}$** **[1m] units for time can be s, min, h**

(iii) rate = $k'[H^+]^n[CH_3CHO][HOCH_2CH_2OH]$, where n is the order of reaction w.r.t. H^+.
When $[H^+]$ doubles from 0.05 mol dm^{-3} to 0.10 mol dm^{-3},
relative rate doubles from that in expt 2.
Hence, order of reaction w.r.t. H^+ is 1.

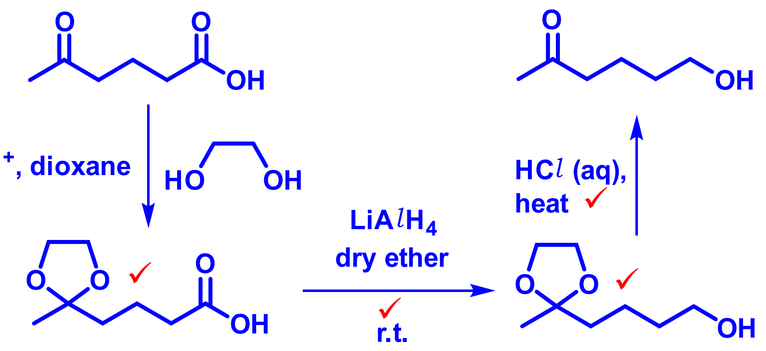
rate = $k'[H^+][CH_3CHO][HOCH_2CH_2OH]$
If $[H^+] = [CH_3CHO] = [HOCH_2CH_2OH] = 0.20$ mol dm^{-3}, compared to expt 1,
i.e. $[H^+]$ is 4× Expt 1, $[HOCH_2CH_2OH]$ is 2× Expt 1,
relative rate should be 8 times that of Expt 1,
i.e. **relative rate = 8** **[1m, accept 1 to 3 sf]**

(c) **(i)**



[1m] for both

(ii)



4✓ : [2m] ; 2–3✓ : [1m]

(d) (i) (Aliphatic) **Aldehyde**
Brick-red ppt of Cu_2O formed **[1m] for both**

(ii) **Cu^{2+}** (Cu in oxidation state +2) in Fehling's solution is **reduced** by glucose to **Cu(I) oxide** (Cu in oxidation state +1). **[1m]**

(e) (i) **$2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$** **[1m] including state symbols**

(ii) $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

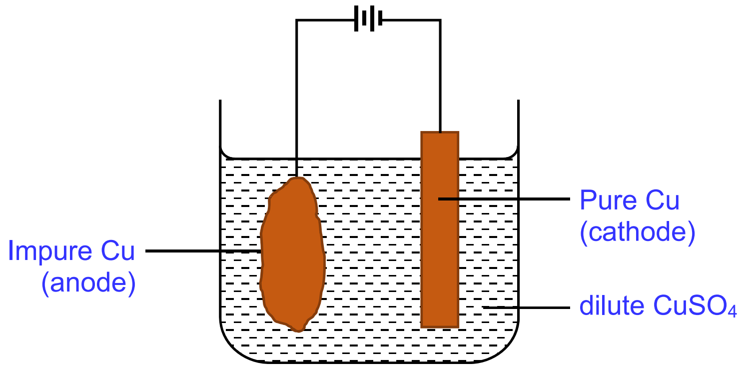
Assuming 100% efficiency,

$$n_{Cu} \text{ expected} = \frac{q}{n \times F} = \frac{I \times t}{n \times F} = \frac{0.25 \times (2 \times 60 \times 60)}{2 \times 96500} \textbf{ [1m]} = 9.326 \times 10^{-3} \text{ mol}$$

$$n_{Cu} \text{ deposited} = \frac{0.496}{63.5} = 7.811 \times 10^{-3} \text{ mol}$$

$$\text{Percentage efficiency} = \frac{7.811 \times 10^{-3}}{9.326 \times 10^{-3}} \times 100\% = 83.76\% \approx \underline{\mathbf{83.8\%}} \textbf{ [1m]}$$

(f)



[1m]

$Ag^+ + e^- \rightleftharpoons Ag$ $\quad E^\ominus = +0.80$ V

$Cu^{2+} + 2e^- \rightleftharpoons Cu$ $\quad E^\ominus = +0.34$ V

Since the $\underline{\boldsymbol{E^\ominus}\left(\mathbf{Cu^{2+}|Cu}\right)}$ **<u>is less positive</u>**, Cu is preferentially oxidised at the anode.

Thus **<u>Ag impurities will not be oxidised</u>** **[1m]** and they fall to the bottom as 'sludge'.

$Cr^{3+} + 2e^- \rightleftharpoons Cr$ $\quad E^\ominus = -0.74$ V

$Cu^{2+} + 2e^- \rightleftharpoons Cu$ $\quad E^\ominus = +0.34$ V **[1m] for quoting all 3 $E^\ominus$ values**

Since the $E^{\ominus}\left(\mathrm{Cr}^{3+}\middle|\mathrm{Cr}\right)$ is less positive, Cr is preferentially oxidised at the anode and goes into the solution (as Cr^{3+} ions) first, followed by Cu. At the cathode, however, since the **$\boldsymbol{E^{\ominus}\left(\mathrm{Cu}^{2+}\middle|\mathrm{Cu}\right)}$ is more positive, Cu^{2+} is preferentially reduced** and deposited on the pure Cu rod. **Cr^{3+} ions remain in the electrolyte** **[1m]** and are not plated onto the cathode.

EUNOIA JUNIOR COLLEGE
JC2 Preliminary Examination 2018
General Certificate of Education Advanced Level
Higher 2

CANDIDATE NAME	

CIVICS GROUP	1	7	–			INDEX NUMBER		

CHEMISTRY

9729/04

Paper 4 Practical

28 August 2018

2 hours 30 minutes

Candidates answer on the Question Paper.

Additional Materials: As listed in the Confidental Instructions

READ THESE INSTRUCTIONS FIRST

Write your name, civics group and registration number on 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 paper clips, highlighters, 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 19 and 20.

Shift
Laboratory

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	
2	
3	
4	
Total	

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

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

For Examiner's Use

1 Analysis of a solution containing both sodium hydroxide and sodium carbonate by Warder titration (double indicator method)

Aqueous sodium hydroxide easily reacts with atmospheric carbon dioxide. This results in the sodium hydroxide being contaminated with sodium carbonate Na_2CO_3.

The Warder titration (double indicator method) can be used to analyse a mixture containing both sodium hydroxide and sodium carbonate.

FA 1 is 0.125 mol dm^{-3} hydrochloric acid, HCl.
FA 2 is an aqueous solution containing sodium hydroxide, NaOH, and sodium carbonate, Na_2CO_3.

(a) Titration of FA 2 against FA 1 using methyl orange or screened methyl orange indicator

In this titration, **FA 1** is run from the burette into the conical flask containing **FA 2** with methyl orange or screened methyl orange indicator.

The end-point is reached when the yellow colour changes to orange for methyl orange, or the green colour changes to grey for screened methyl orange.

(i) 1. Fill the burette with **FA 1**.

2. Using a pipette, transfer 25.0 cm^3 of **FA 2** into a conical flask.

3. Add a few drops of methyl orange or screened methyl orange indicator.

4. Run **FA 1** from the burette into the conical flask until the colour of the solution changes.

5. Record your titration results in the space provided below. Make certain that your recorded results show the precision of your working.

6. Repeat points **1** to **5** as necessary until consistent results are obtained.

Results

[5]

(ii) From your titrations, obtain a suitable volume of **FA 1** to be used in your calculations. Show clearly how you obtained this volume.

Volume of **FA 1** = ... [1]

(b) Titration of FA 2 against FA 1 using thymolphthalein indicator

When the titration in **(a)** was repeated using thymolphthalein as the indicator, 25.0 cm^3 of **FA 2** required 23.35 cm^3 of **FA 1**.

The following explains why different results were obtained using two different indicators.

- When **thymolphthalein** is used as the indicator, the following reactions would have taken place at the end-point of the titration.

  1. $NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l)$
  2. $Na_2CO_3(aq) + HCl(aq) \rightarrow NaCl(aq) + NaHCO_3(aq)$

- When **methyl orange** is used as the indicator in **(a)**, the following reactions would have taken place at the end-point of the titration.

  1. $NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l)$
  2. $Na_2CO_3(aq) + HCl(aq) \rightarrow NaCl(aq) + NaHCO_3(aq)$
  3. $NaHCO_3(aq) + HCl(aq) \rightarrow NaCl(aq) + CO_2(g) + H_2O(l)$

(i) Calculate the amount of hydrochloric acid present in the volume of **FA 1** calculated in **(a)(ii)**.

amount of HC*l* in volume in **(a)(ii)** = ... [1]

(ii) Calculate the amount of hydrochloric acid in 23.35 cm^3 of **FA 1**.

amount of HC*l* in 23.35 cm^3 of **FA 1** = ... [1]

(iii) Using your answer to **(b)(i)** and **(b)(ii)**, calculate the amount of hydrochloric acid that reacts with the Na_2CO_3 in the titration using thymolphthalein indicator.

amount of HCl that react with Na_2CO_3 = ... [1]

(iv) Hence, calculate the mass of sodium carbonate present in 25.0 cm^3 of **FA 2**.

[A_r: C, 12.0; O, 16.0; Na, 23.0]

mass of Na_2CO_3 in 25.0 cm^3 of **FA 2** = ... [1]

(v) The **overall** equation for the reaction of Na_2CO_3 with HCl when methyl orange is used as indicator is given below.

$$Na_2CO_3(aq) + 2HCl(aq) \rightarrow 2NaCl(aq) + CO_2(g) + H_2O(l)$$

Calculate the amount of HCl that reacted with the Na_2CO_3 in the above equation in 25.0 cm^3 of **FA 2**.

amount of HCl = ... [1]

(vi) Use your answers to **(b)(i)** and **(b)(v)** to calculate the mass of sodium hydroxide in 25.0 cm^3 of **FA 2**.

[A_r: H, 1.0; O, 16.0; Na, 23.0]

mass of NaOH = ... [1]

(vii) Calculate the percentage by mass of sodium carbonate in the mixture of sodium hydroxide and sodium carbonate in **FA 2**.

percentage by mass of Na_2CO_3 in **FA 2** = ... [1]

(c) The error (uncertainty) associated with **each reading** is given as follows:

50.00 cm^3 burette: ±0.05 cm^3

25.0 cm^3 pipette: ±0.04 cm^3

Using the above data, calculate the percentage error (uncertainty) when a

(I) 50.00 cm^3 burette

(II) 25.0 cm^3 pipette

is used to measure 25 cm^3 of **FA 2** into the conical flask.

Hence state whether a 50.00 cm^3 burette or 25.0 cm^3 pipette will be more suitable to measure 25.0 cm^3 of **FA 2** accurately.

....

....

....

....

....

....

.... [2]

[Total: 15]

2 To determine the percentage by mass of sodium hydrogencarbonate in the unknown sample based on gravimetric method

Sodium hydrogencarbonate decomposes on heating to give sodium carbonate, carbon dioxide and water vapour.

$$2NaHCO_3(s) \xrightarrow{\Delta} Na_2CO_3(s) + CO_2(g) + H_2O(g)$$

Sodium chloride on the other hand is unaffected by heat.

FA 3 is a mixture of anhydrous sodium hydrogencarbonate, $NaHCO_3$, and sodium chloride, $NaCl$.

In this question, you will heat to decompose the sodium hydrogencarbonate in **FA 3** and determine the mass of carbon dioxide and water lost. The data will be used to determine

- the mass of $NaHCO_3$ in **FA 3**,
- the percentage composition by mass of $NaHCO_3$ in **FA 3**.

(a) Thermal decomposition of $NaHCO_3$

In this experiment, solid **FA 3** is heated strongly in a boiling tube, over a non-luminous Bunsen flame, until there is no further change in the mass.

1. Weigh accurately about 4.5 g of **FA 3** in the boiling tube provided. Record your weighings in the space provided below.
2. Heat the tube gently first, then strongly.
3. Place the boiling tube into a **dry** 250 cm^3 beaker to cool.

You may wish to proceed with other experiments while waiting for the boiling tube to cool.

4. Weigh and record the mass of the cooled boiling tube containing the residue.
5. Repeat points **2** to **4** as necessary until a constant mass is obtained.
6. **Turn off your Bunsen burner**.

(i) In an appropriate format in the space below, record all weighings measurements.

[3]

(ii) Using your results, calculate the mass of carbon dioxide and water vapour evolved.

mass of CO_2 and H_2O evolved = ... [1]

(iii) Using your answer to **(a)(ii)**, calculate the amount of carbon dioxide evolved.

[A_r: H, 1.0; C, 12.0; O, 16.0]

amount of CO_2 evolved = ... [1]

(iv) Calculate the mass of sodium hydrogencarbonate in the sample of **FA 3**.

[A_r: H, 1.0; C, 12.0; O, 16.0; Na, 23.0]

mass of $NaHCO_3$ in sample of **FA 3** = ... [1]

(v) Determine the percentage by mass of sodium hydrogencarbonate in **FA 3**.

percentage by mass of $NaHCO_3$ in **FA 3** = ... [1]

(b) Suggest one possible source of error in this experiment. How would this error affect the calculated results in **(a)(iv)**?

....

....

....

....

.... [2]

(c) **Planning**

Plan an experiment to determine the percentage by mass of sodium hydrogencarbonate in the unknown sample based on volumetric analysis method.

In this experiment, you will titrate a **solution of FA 3** against **FA 1**, using a suitable indicator.

You can assume you are provided with the following reagent:

FA 4 is a solution containing 30.00 g dm^{-3} of **FA 3**.

In your plan, you should include details of

- the amount of reagents you would use,
- the apparatus you would use and the procedure you would follow,
- the measurements you would take,
- appropriate calculations to show how the percentage by mass of sodium hydrogencarbonate in **FA 3** can be determined, assuming the average titre is ***y*** cm^3.

....

....

....

....

....

....

....

....

....

....

For Examiner's Use

[6]

[Total : 15]

3 Investigation of the kinetics of the reaction between calcium carbonate and hydrochloric acid

Calcium carbonate that reacts with hydrochloric acid in an acid-carbonate reaction as shown below.

$$CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$$

FA 5 is powdered $CaCO_3$.

In this question, you will measure the volume of CO_2 gas produced at timed intervals until the reaction is complete, using an excess of dilute hydrochloric acid.

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

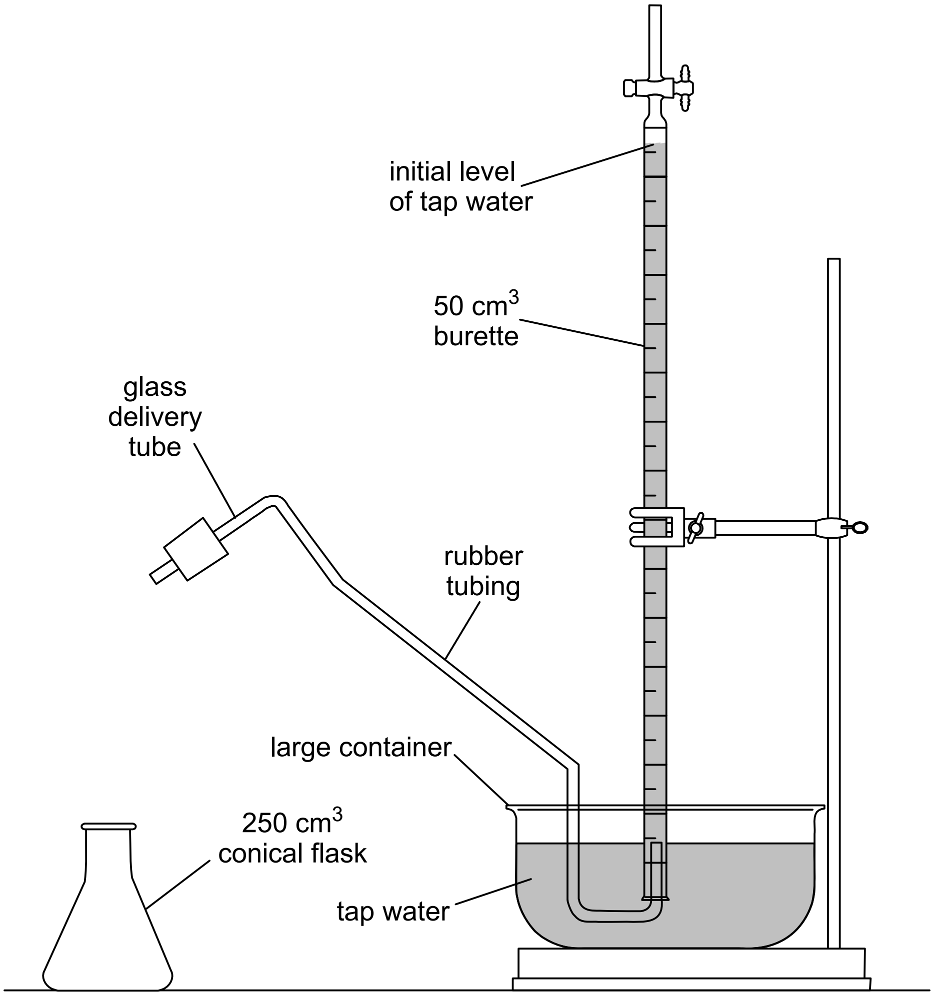


Fig 3.1

You will measure the level of water in the burette at timed intervals.

In an appropriate format in the space provided on page **11**, prepare a table in which you may record each burette reading and the time it was taken. The time taken should be recorded to one decimal place.

In addition, your table will need to show the volume of CO_2 collected up to that time, recorded to one decimal place.

1. Set up the apparatus as shown in the Fig. 3.1. You should insert the rubber tubing to a sufficient depth in the burette so that it will not subsequently shake loose.

2. Adjust the water level in the burette until it is between 48.0 cm^3 and 50.0 cm^3. You may find it helpful to use an empty dropping pipette to introduce small amounts of air from the bottom of the burette tube.

3. Transfer all the solid **FA 5** provided in the weighing bottle into a dry and clean 250 cm^3 conical flask.

4. Use an appropriate measuring cylinder, measure 40 cm^3 of **FA 1**.

5. Transfer the **FA 1** into the conical flask containing **FA 5** and insert the bung into the conical flask.

6. Allow any bubbles created in the burette when the bung was inserted in the conical flask to rise to the top. Start the stopwatch, read and record the initial water level in the burette.

   Note: Once you have started the stopwatch, allow it to continue running for the duration of the experiment. You **must not stop** the stopwatch until the reaction is complete.

7. Check that the rubber tubing is securely positioned in the burette.

8. Hold the flask by its neck and **gently swirl** it continuously.

9. At t = 0.5 min, read and record the water level in the burette, to 1 decimal place, together with the time it was measured, in your table.

10. Continue to gently swirl the flask. Read and record the water level in the burette every half minute, until the reaction is complete.

(a) (i) Experimental Results

[3]

(ii) Plot on the grid below, a graph of the volume of CO_2 on the *y*-axis, against time, *t*, on the x-axis.

Draw the most appropriate best-fit curve, taking into account all of your points.

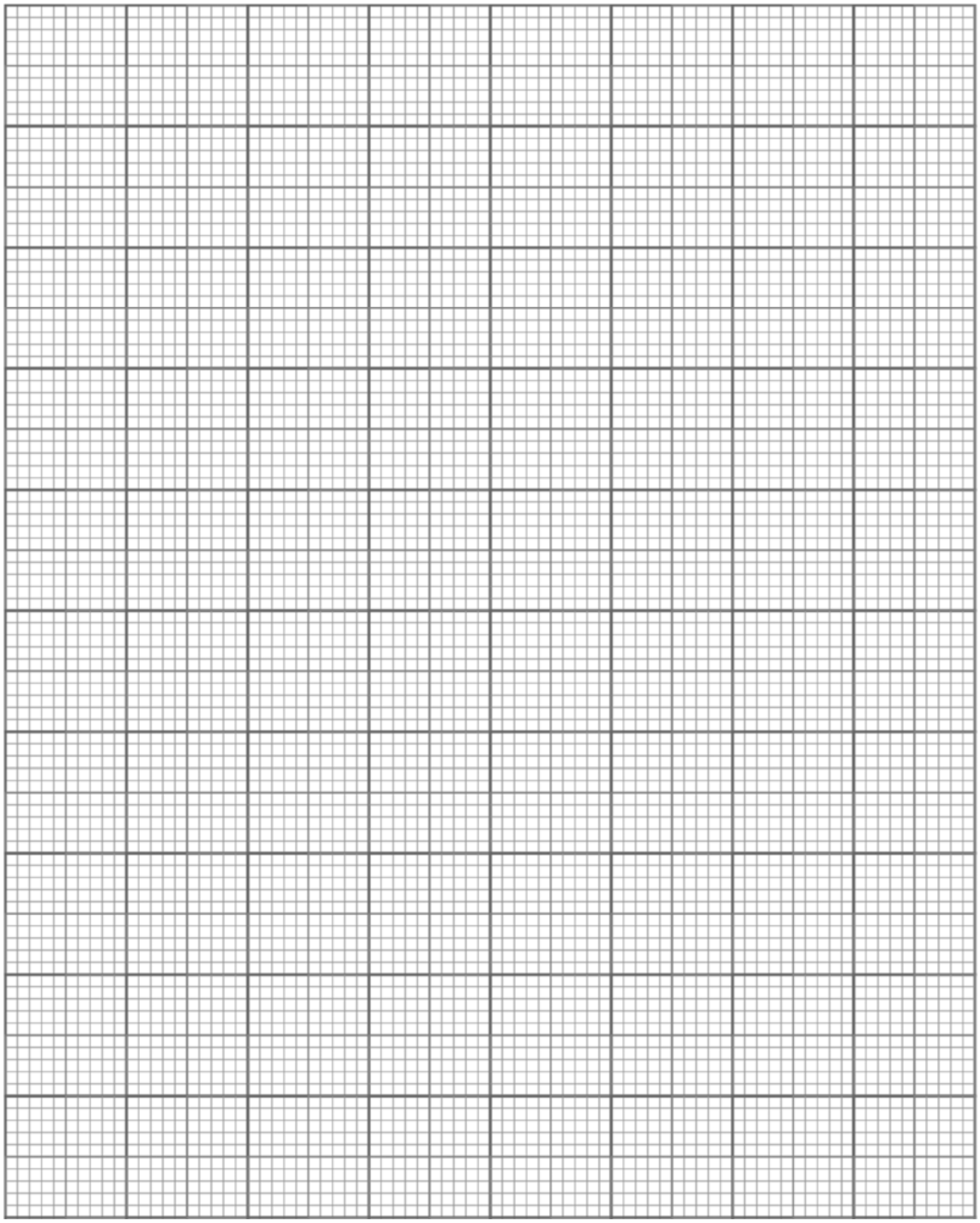


Fig. 3.2 [3]

(iii) It has been claimed that the reaction between calcium carbonate and hydrochloric acid is pseudo-first order with respect to calcium carbonate.

State whether you agree or disagree with this claim. Use evidence from your graph in Fig. 3.2 to support your answer.

....

....

....

....

....

.... [2]

(b) Planning

Besides using the continuous measurement method in **3(a)** to determine the order of reaction of a reactant, the initial rates method can also be used.

Plan an investigation, which **does not** involve graph plotting, to determine the order of reaction with respect to hydrochloric acid, HCl, using the initial rates method.

You are provided the following chemicals and apparatus:

- same apparatus used in the experimental setup in **3(a)**,
- 2.00 mol dm^{-3} HCl solution
- **FA 5** powdered $CaCO_3$
- stopwatch

In your plan, you should include details of:

- the different concentrations of the reactants used and the conditions of the experiment,
- the procedure you would follow, including the end-point of the experiment
- the measurements you would take,
- an outline of how you would use your results to determine the order of reaction with respect to HCl.

You may use the space below to draw a table indicating the headers of the measurements and calculations you would be performing.

For Examiner's Use

[6]

[Total: 14]

For Examiner's Use

4 Carry out the following experiments with **FA 6**.

In all tests the reagents should be added gradually until no further change is observed unless you are instructed otherwise.

Observations should include:

(i) descriptions of colour changes and precipitates;

(ii) names of gases evolved and details of the test used to identify each one.

You should indicate clearly at which stage in a test a change occurs, writing any deductions that you make alongside the observations upon which they are based.

Marks will be given *only* for the prescribed tests and will *not* be given for chemical equations.

TEST	OBSERVATION	CONCLUSION
Tests of FA 6 **(a)** Heat **FA 6** in a test-tube until no further change is observed. **Allow the residue to cool** and retain it for **(b)**. You may wish to proceed with the tests in **4(c)** while waiting for the residue to cool.		
(b) Dissolve the residue from test **(a)** in deionised water and use separate portions of the solution for tests **(i)** to **(iii)**		
(i) Add aqueous silver nitrate to a portion of the solution. Then add aqueous ammonia.		

TEST	OBSERVATION	CONCLUSION
(ii) Add a few drops of aqueous potassium manganate(VII) followed by dilute sulfuric acid.		
(iii) Add a few crystals of **FA 6**, shake to dissolve and then add dilute sulfuric acid.		
(c) Dissolve **FA 6** in water and use separate portions of the solution for tests **(i)** and **(ii)**.		
(i) Add a few drops of aqueous potassium manganate(VII) followed by dilute sulfuric acid.		
(ii) Add aqueous potassium bromide followed by dilute sulfuric acid. Add hexane and shake the mixture.		

You are *not* required to identify **FA 6**. [7]

(d) **(i)** **FA 6** and the residue from **(a)** contains element **X** in two different oxidation states. Using your observations from the tests in **(b)** and **(c)**, explain which compound, **FA 6** or the residue, contains **X** in the higher oxidation state.

....

....

....

....

....

.... [2]

(ii) The reaction in test **(b)(iii)** is said to be a **comproportionation** reaction. In light of your observations to test **(b)(i)** and **(b)(iii)**, together with your answer to **(d)(i)**, suggest what the term comproportionation may refer to.

....

....

....

....

....

....

.... [2]

[Total: 11]

BLANK PAGE

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) 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

EUNOIA JUNIOR COLLEGE
JC2 Preliminary Examination 2018
General Certificate of Education Advanced Level
Higher 2

CANDIDATE NAME	

CIVICS GROUP	1	7	–			INDEX NUMBER		

CHEMISTRY

9729/04

Paper 4 Practical

28 August 2018

2 hours 30 minutes

Candidates answer on the Question Paper.

Additional Materials: As listed in the Confidental Instructions

READ THESE INSTRUCTIONS FIRST

Write your name, civics group and registration number on 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 paper clips, highlighters, 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 19 and 20.

Shift
Laboratory

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	
2	
3	
4	
Total	

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

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

For Examiner's Use

1 Analysis of a solution containing both sodium hydroxide and sodium carbonate by Warder titration (double indicator method)

Aqueous sodium hydroxide easily reacts with atmospheric carbon dioxide. This results in the sodium hydroxide being contaminated with sodium carbonate Na_2CO_3.

The Warder titration (double indicator method) can be used to analyse a mixture containing both sodium hydroxide and sodium carbonate.

FA 1 is 0.125 mol dm^{-3} hydrochloric acid, HCl.
FA 2 is an aqueous solution containing sodium hydroxide, NaOH, and sodium carbonate, Na_2CO_3.

(a) Titration of FA 2 against FA 1 using methyl orange or screened methyl orange indicator

In this titration, **FA 1** is run from the burette into the conical flask containing **FA 2** with methyl orange or screened methyl orange indicator.

The end-point is reached when the yellow colour changes to orange for methyl orange, or the green colour changes to grey for screened methyl orange.

(i) 1. Fill the burette with **FA 1**.

2. Using a pipette, transfer 25.0 cm^3 of **FA 2** into a conical flask.

3. Add a few drops of methyl orange or screened methyl orange indicator.

4. Run **FA 1** from the burette into the conical flask until the colour of the solution changes.

5. Record your titration results in the space provided below. Make certain that your recorded results show the precision of your working.

6. Repeat points **1** to **5** as necessary until consistent results are obtained.

Results

Titration number	1	2
Final burette reading / cm^3	33.70	35.80
Initial burette reading / cm^3	0.00	2.00
Volume of **FA 1** used / cm^3	33.70	33.80
	✓	✓

[1] **<u>table</u> with <u>correct headings</u> *('burette' must be stated)* <u>and units</u>. (*Do not award if any final and initial burette readings are inverted/ if 50 is used as initial burette reading/ burette reading is >50)***

[1] **<u>All burette readings</u> recorded to the nearest 0.05 cm^3 + correct computation of titres**

[1] **Has two <u>uncorrected</u> titres for end-point within 0.10 cm^3 + <u>place ✓ under</u> two <u>selected titres within 0.10</u> cm^3. *(Do not award if additional titration is performed after consistent titres are obtained.)***

[2] **Accuracy (Teacher's reading ±0.20 cm^3: 2m; ±0.40 cm^3: 1m)**

[5]

(ii) From your titrations, obtain a suitable volume of **FA 1** to be used in your calculations. Show clearly how you obtained this volume.

Average volume of **FA 1** $= \frac{33.70 + 33.80}{2}$

$= 33.75\ \text{cm}^3$

- **state correct term "Average volume"**
- **quote the selected titres in the average working**
- **give correct final value to 2 d.p.**

Volume of **FA 1** = ...**$33.75\ \text{cm}^3$**...... [1]

(b) **Titration of FA 2 against FA 1 using thymolphthalein indicator**

When the titration in **(a)** was repeated using thymolphthalein as the indicator, 25.0 cm^3 of **FA 2** required 23.35 cm^3 of **FA 1**.

The following explains why different results were obtained using two different indicators.

- When **thymolphthalein** is used as the indicator, the following reactions would have taken place at the end-point of the titration.

  1. $NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l)$
  2. $Na_2CO_3(aq) + HCl(aq) \rightarrow NaCl(aq) + NaHCO_3(aq)$

- When **methyl orange** is used as the indicator in **(a)**, the following reactions would have taken place at the end-point of the titration.

  1. $NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l)$
  2. $Na_2CO_3(aq) + HCl(aq) \rightarrow NaCl(aq) + NaHCO_3(aq)$
  3. $NaHCO_3(aq) + HCl(aq) \rightarrow NaCl(aq) + CO_2(g) + H_2O(l)$

(i) Calculate the amount of hydrochloric acid present in the volume of **FA 1** calculated in **(a)(ii)**.

Amount of HC*l* in 33.75 cm^3 of **FA 1** $= 0.125 \times \frac{33.75}{1000} = \underline{\mathbf{0.00422}}$ mol

amount of HC*l* in volume in **(a)(ii)** = ...**0.00422 mol**...... [1]

(ii) Calculate the amount of hydrochloric acid in 23.35 cm^3 of **FA 1**.

Amount of HC*l* in 23.35 cm^3 of **FA 1** $= 0.125 \times \frac{23.35}{1000} = \underline{\mathbf{0.00292}}$ mol

amount of HC*l* in 23.35 cm^3 of **FA 1** = ...**0.00292 mol**...... [1]

(iii) Using your answer to **(b)(i)** and **(b)(ii)**, calculate the amount of hydrochloric acid that reacts with the Na_2CO_3 in the titration using thymolphthalein indicator.

Amount of HC*l* that react with Na_2CO_3 = 0.00422 – 0.00292 = **<u>0.00130</u>** mol

amount of HC*l* that react with Na_2CO_3 = ...**0.00130 mol**.......... [1]

(iv) Hence, calculate the mass of sodium carbonate present in 25.0 cm^3 of **FA 2**.

[A_r: C, 12.0; O, 16.0; Na, 23.0]

Mass of Na_2CO_3 in 25.0 cm^3 of **FA 2** = 0.00130 × 106.0 = **<u>0.138</u>** g

mass of Na_2CO_3 in 25.0 cm^3 of **FA 2** = ...**0.138 g**.......... [1]

(v) The **overall** equation for the reaction of Na_2CO_3 with HC*l* when methyl orange is used as indicator is given below.

$$Na_2CO_3(aq) + 2HCl(aq) \rightarrow 2NaCl(aq) + CO_2(g) + H_2O(l)$$

Calculate the amount of HC*l* that reacted with the Na_2CO_3 in the above equation in 25.0 cm^3 of **FA 2**.

Amount of HC*l* that react with Na_2CO_3 = 2 × 0.00130 = **<u>0.00260</u>** mol

amount of HC*l* = ...**0.00260 mol**.......... [1]

(vi) Use your answers to **(b)(i)** and **(b)(v)** to calculate the mass of sodium hydroxide in 25.0 cm^3 of **FA 2**.

[A_r: H, 1.0; O, 16.0; Na, 23.0]

Mass of NaOH in 25.0 cm^3 of **FA 2** = (0.00422 – 0.00260) × 40.0 = **<u>0.0648</u>** g

mass of NaOH = ...**0.0648 g**.......... [1]

(vii) Calculate the percentage by mass of sodium carbonate in the mixture of sodium hydroxide and sodium carbonate in **FA 2**.

$$\% \text{ by mass of } Na_2CO_3 \text{ in } \mathbf{FA\ 2} = \frac{0.138}{0.138 + 0.0648} \times 100 = \underline{\mathbf{68.0\%}}$$

percentage by mass of Na_2CO_3 in **FA 2** = **68.0%** [1]

(c) The error (uncertainty) associated with **each reading** is given as follows:

50.00 cm³ burette: ±0.05 cm³

25.0 cm³ pipette: ±0.04 cm³

Using the above data, calculate the percentage error (uncertainty) when a

(I) 50.00 cm³ burette

(II) 25.0 cm³ pipette

is used to measure 25 cm³ of **FA 2** into the conical flask.

Hence state whether a 50.00 cm³ burette or 25.0 cm³ pipette will be more suitable to measure 25.0 cm³ of **FA 2** accurately.

Error when burette is used = 2 × ±0.05 = ±0.10 cm³

Note: This is because when using the burette, 2 readings are made- initial and final; hence the error has to be added up.

% error when using burette = 0.10/25 × 100% = **0.4%**

Error when 25 cm³ pipette is used = ±0.04 cm³

% error when using 25 cm³ pipette = 0.04/25 × 100% = **0.16%**

[1]

The use of a burette to measure 25 cm³ of **FA 2** will result in greater % error.

Hence a **25.0 cm³ pipette is more suitable** to measure 25 cm³ of **FA 2**. **[1]**

(from correct % calculations, allow ecf from % error)

[2]

[Total: 15]

2 To determine the percentage by mass of sodium hydrogencarbonate in the unknown sample based on gravimetric method

Sodium hydrogencarbonate decomposes on heating to give sodium carbonate, carbon dioxide and water vapour.

$$2NaHCO_3(s) \xrightarrow{\Delta} Na_2CO_3(s) + CO_2(g) + H_2O(g)$$

Sodium chloride on the other hand is unaffected by heat.

FA 3 is a mixture of anhydrous sodium hydrogencarbonate, $NaHCO_3$, and sodium chloride, NaC*l*.

In this question, you will heat to decompose the sodium hydrogencarbonate in **FA 3** and determine the mass of carbon dioxide and water lost. The data will be used to determine

- the mass of $NaHCO_3$ in **FA 3**,
- the percentage composition by mass of $NaHCO_3$ in **FA 3**.

(a) Thermal decomposition of $NaHCO_3$

In this experiment, solid **FA 3** is heated strongly in a boiling tube, over a non-luminous Bunsen flame, until there is no further change in the mass.

1. Weigh accurately about 4.5 g of **FA 3** in the boiling tube provided. Record your weighings in the space provided below.
2. Heat the tube gently first, then strongly.
3. Place the boiling tube into a **dry** 250 cm^3 beaker to cool.

You may wish to proceed with other experiments while waiting for the boiling tube to cool.

4. Weigh and record the mass of the cooled boiling tube containing the residue.
5. Repeat points **2** to **4** as necessary until a constant mass is obtained.
6. **Turn off your Bunsen burner**.

(i) In an appropriate format in the space below, record all weighing measurements.

Mass of empty boiling tube / g	29.410
Mass of boiling tube and **FA 3** / g	33.891
Mass of **FA 3** used / g	4.481
Mass of boiling tube and residue after first heating /g	33.218
Mass of boiling tube and residue after second heating /g	33.065
Mass of boiling tube and residue after third heating /g	33.065

[1] Record "total mass of boiling tube + FA 3" + "mass of boiling tube + residue after 1st heating" + "mass of boiling tube + residue after 2nd heating"

[1] Record two constant masses (within 0.01g) of boiling tube + residue after heating

[1] All mass readings are recorded to 3 d.p. and mass of FA 3 used is within ±0.05 g, with appropriate units stated

[3]

(ii) Using your results, calculate the mass of carbon dioxide and water vapour evolved.

Mass of CO_2 and H_2O evolved = 4.481 g – 3.655 g = 0.826 g

mass of CO_2 and H_2O evolved = ...**0.826 g**............ [1]

(iii) Using your answer to **(a)(ii)**, calculate the amount of carbon dioxide evolved.

[A_r: H, 1.0; C, 12.0; O, 16.0]

Let the amount of carbon dioxide evolved by *x* mol.

$n_{CO_2} = n_{H_2O} = x$ mol

$$x(44.0) + x(18.0) = 0.826$$

$$x = \frac{0.826}{44.0 + 18.0} = 0.01332$$

amount of CO_2 evolved = ...**0.0133 mol**............ [1]

(iv) Calculate the mass of sodium hydrogencarbonate in the sample of **FA 3**.

[A_r: H, 1.0; C, 12.0; O, 16.0; Na, 23.0]

$$n_{NaHCO_3} = 2n_{CO_2} = 2 \times 0.01332 = 0.02665 \text{ mol}$$

$$\begin{aligned}\text{Mass of NaHCO}_3 &= 0.02665 \times (23.0 + 1.0 + 12.0 + 3 \times 16.0) \\ &= 0.02665 \times 84.0 \\ &= 2.238 \text{ g} \approx 2.24 \text{ g}\end{aligned}$$

mass of $NaHCO_3$ in sample of **FA 3** = ...**2.24 g**............ [1]

(v) Determine the percentage by mass of sodium hydrogencarbonate in **FA 3**.

% by mass of $NaHCO_3$ in FA1 = $\frac{2.238}{4.481} \times 100\% = 49.9\%$

percentage by mass of $NaHCO_3$ in **FA 3** = ...**49.9%**............ [1]

(b) Suggest one possible source of error in this experiment. How would this error affect the calculated results in **(a)(iii)**?

Incomplete decomposition [1] may occur and therefore the mass lost recorded or mass of CO_2 and H_2O evolved is lower than actual. The calculated mass of $NaHCO_3$ is lower than actual. [1]

[2]

(c) Planning

Plan an experiment to determine the percentage by mass of sodium hydrogencarbonate in the unknown sample based on volumetric analysis method.

In this experiment, you will titrate a **solution of FA 3** against **FA 1**, using a suitable indicator.

You can assume you are provided with the following reagent:

FA 4 is a solution containing 30.00 g dm^{-3} of **FA 3**.

In your plan, you should include details of

- the amount of reagents you would use,
- the apparatus you would use and the procedure you would follow,
- the measurements you would take,
- appropriate calculations to show how the percentage by mass of sodium hydrogencarbonate in **FA 3** can be determined, assuming the average titre is ***y*** cm^3.

Procedure

Step 1: Pipette 25.0 cm^3 of **FA 4** into a 250 cm^3 conical flask and add 1–2 drops of methyl orange indicator.
Step 2: Fill a burette with **FA 1**.
Step 3: Titrate the contents of the conical flask with **FA 4** from the burette until the solution changes from yellow to orange at the end point.
Step 4: Tabulate your titration values in the table below.

Titration number	**Accurate**		
	1	**2**	
Final burette reading / cm^3			
Initial burette reading / cm^3			
Volume of **FA 1** used / cm^3			

Step 5: Obtain from your titration results a suitable average titre. Show clearly the titres you used in calculating this average.

- Suitable volume of reagents used, apparatus used [1]
- Suitable indicator and colour change at the end point [1]
- Logical flow of procedure and Data collection [1]

Calculations

Average titre = y cm^3

Calculate the mass of $NaHCO_3$ per dm^3 of **FA 4**

$HCO_3^- + H^+ \longrightarrow CO_2 + H_2O$

n_{HCl} used in titration = $\frac{\mathbf{y} \times 0.200}{1000} = 2\mathbf{y} \times 10^{-4}$ mol $= n_{NaHCO_3}$ in 25.0 cm^3 of **FA 4** **[1]**

n_{NaHCO_3} per dm^3 = $\frac{2\mathbf{y} \times 10^{-4} \times 1000}{25} = 8\mathbf{y} \times 10^{-3}$ mol

mass of $NaHCO_3$ per dm^3 = 8$\mathbf{y}$ × 10^{-3} × 84.0 = 0.672$\mathbf{y}$ g **[1]**

% mass of $NaHCO_3$ in **FA 3**= $\frac{0.672\mathbf{y}}{30.0} \times 100\% = 2.24\mathbf{y}$ % **[1]**

[6]

[Total : 15]

3 Investigation of the kinetics of the reaction between calcium carbonate and hydrochloric acid

Calcium carbonate that reacts with hydrochloric acid in an acid-carbonate reaction as shown below.

$$CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$$

FA 5 is powdered $CaCO_3$.

In this question, you will measure the volume of CO_2 gas produced at timed intervals until the reaction is complete, using an excess of dilute hydrochloric acid.

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

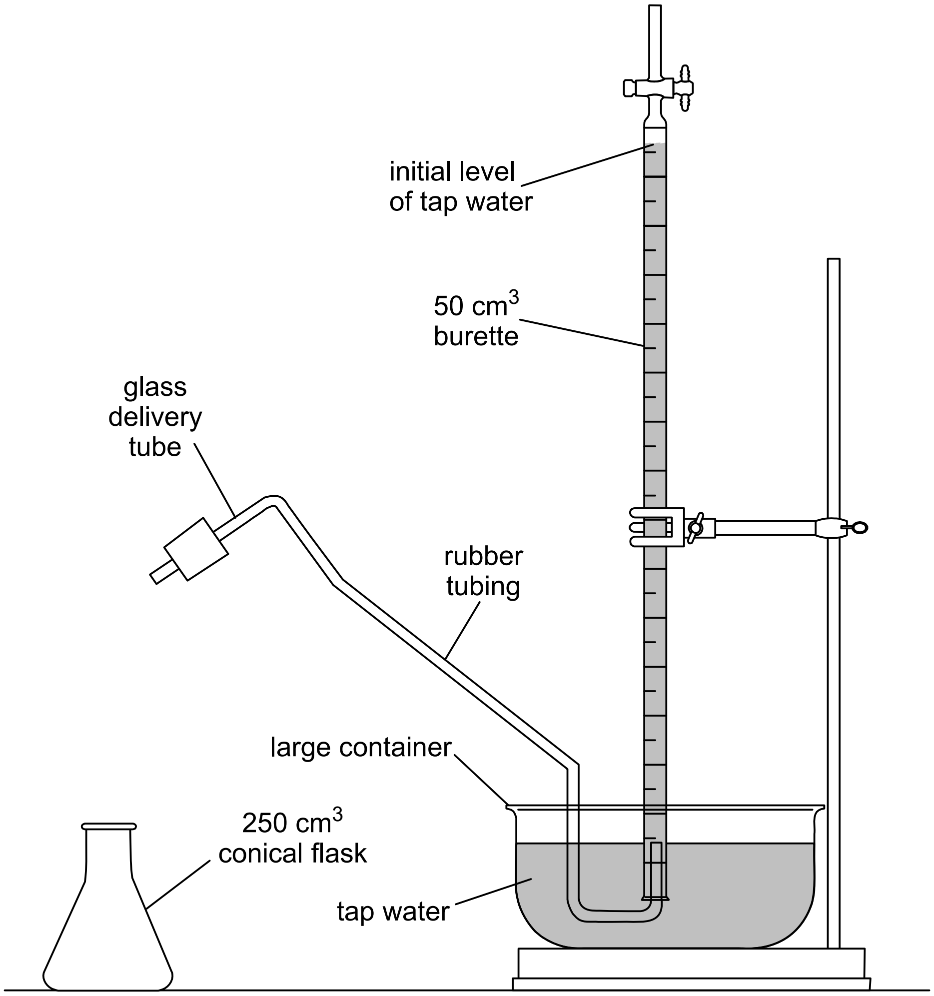


Fig 3.1

You will measure the level of water in the burette at timed intervals.

In an appropriate format in the space provided on page **11**, prepare a table in which you may record each burette reading and the time it was taken. The time taken should be recorded to one decimal place.

In addition, your table will need to show the volume of CO_2 collected up to that time, recorded to one decimal place.

1. Set up the apparatus as shown in the Fig. 3.1. You should insert the plastic/rubber tubing to a sufficient depth in the burette so that it will not subsequently shake loose.

2. Adjust the water level in the burette until it is between 48.0 cm^3 and 50.0 cm^3. You may find it helpful to use an empty dropping pipette to introduce small amounts of air from the bottom of the burette tube.

3. Transfer all the solid **FA 5** provided in the weighing bottle into a dry and clean 250 cm^3 conical flask.

4. Use an appropriate measuring cylinder, measure 40 cm^3 of **FA 1**.

5. Transfer the **FA 1** into the conical flask containing **FA 5** and insert the bung into the conical flask.

6. Allow any bubbles created in the burette when the bung was inserted in the conical flask to rise to the top. Start the stopwatch, read and record the initial water level in the burette.

   Note: Once you have started the stopwatch, allow it to continue running for the duration of the experiment. You **must not stop** the stopwatch until the reaction is complete.

7. Check that the plastic/rubber tubing is securely positioned in the burette.

8. Hold the flask by its neck and **gently swirl** it continuously.

9. At *t* = 0.5 min, read and record the water level in the burette, to 1 decimal place, together with the time it was measured, in your table.

10. Continue to gently swirl the flask. Read and record the water level in the burette every half minute, until the reaction is complete.

(a) (i) Experimental Results

Time / min	**Burette Reading / cm^3**	**Volume of CO_2 / cm^3**
0.0	48.0	0.0
0.5		
1.0		

[1] Tabulates burette readings at t = 0 until the end of the experiment, time/min and volume of CO_2/cm^3.
Tables have correct headers and units.
Tabulation may be vertical or horizontal; lines are not essential but there should be no absence of headers. Where units have not been included in the header, there should be the appropriate unit for each entry in the table
[1] All burette readings and CO_2 volumes to 0.1 cm^3, and times to 0.5 min.
[1] Full set of results with final readings that have at least 3 values that are the same

[3]

For Examiner's Use

(ii) Plot on the grid below, a graph of the volume of CO_2 on the *y*-axis, against time, *t*, on the x-axis.

Draw the most appropriate best-fit curve, taking into account all of your points.

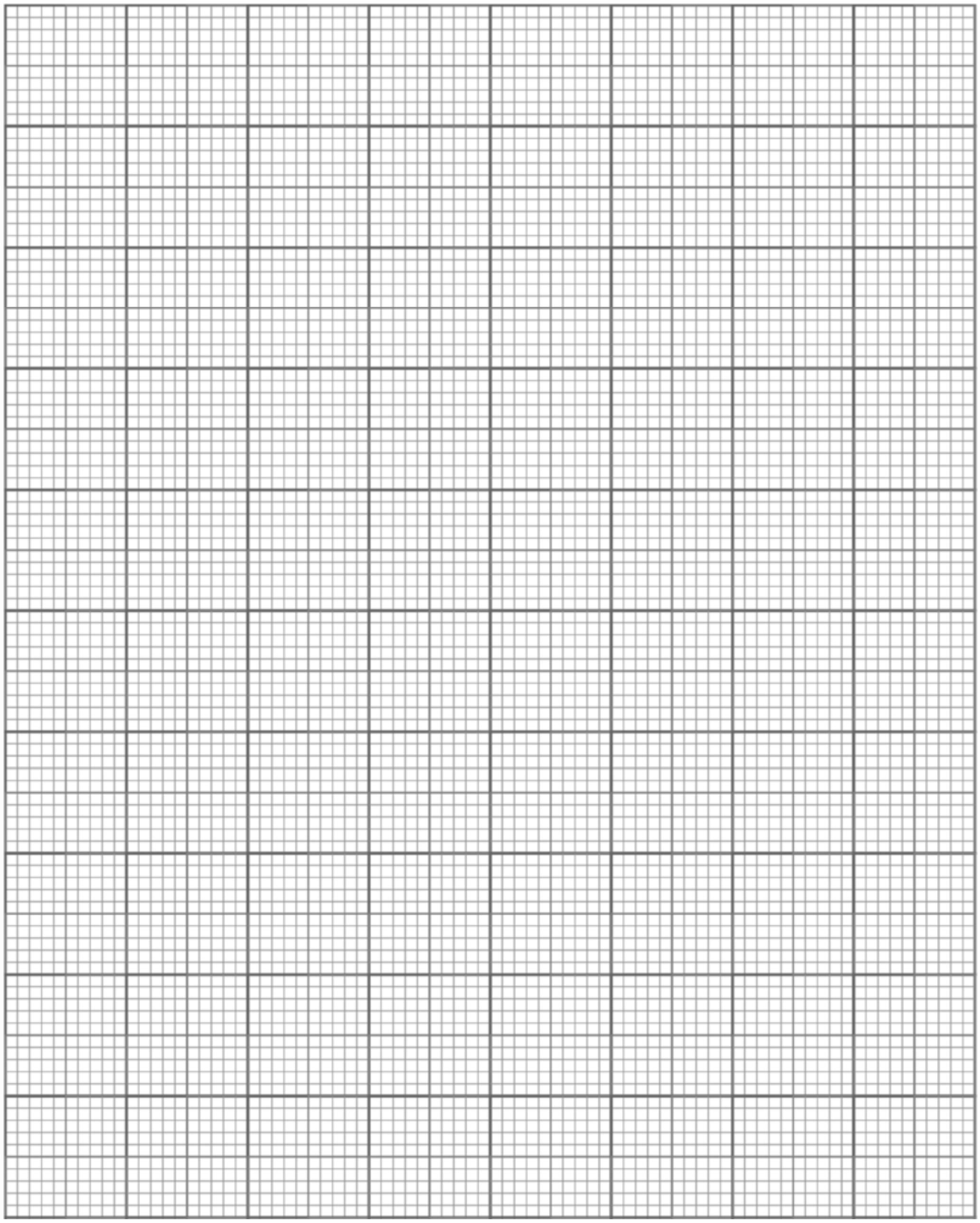


Fig. 3.2 [3]

[1] Axes correct way round + correct labels + units + scale
Sensible linear scale must be chosen so that plotted points occupy at least half the graph grid in both x and y directions

[1] All points correctly plotted to within ±½ small square. Check all points and put ticks if correct

[1] Graph line must be best-fit line (*Do not allow mark if clearly anomalous points are included*)

(iii) It has been claimed that the reaction between calcium carbonate and hydrochloric acid is pseudo-first order with respect to calcium carbonate.

State whether you agree or disagree with this claim. Use evidence from your graph in Fig. 3.2 to support your answer.

[1] Determine at least 2 half-lives ....

[1] Conclude correctly on claim based on half-lives obtained ....

....

....

....

.... [2]

(b) Planning

Besides using the continuous measurement method in **3(a)** to determine the order of reaction of a reactant, the initial rates method can also be used.

Plan an investigation, which **does not** involve graph plotting, to determine the order of reaction with respect to hydrochloric acid, HC*l*, using the initial rates method.

You are provided the following chemicals and apparatus:

- same apparatus used in the experimental setup in **3(a)**,
- 2.00 mol dm^{-3} HC*l* solution
- **FA 5** powdered $CaCO_3$
- stopwatch

In your plan, you should include details of:

- the different concentrations of the reactants used and the conditions of the experiment,
- the procedure you would follow, including the end-point of the experiment
- the measurements you would take,
- an outline of how you would use your results to determine the order of reaction with respect to HC*l*.

You may use the space below to draw a table indicating the headers of the measurements and calculations you would be performing.

[1] Controls concentrations, volumes and total volume to be used for the experiment. States that temperature should be done at constant T (room temperature)

[2] Describe a suitable "stop-time"; *i.e.* the time required to produce at most 10% of the expected total volume of CO_2

[3] Propose to use the same procedure as 3(a) but modified to include the collection of CO_2 for two different concentrations of HC*l* that can be used to determine order of reaction.

[4] Describe the appropriate measurements needed to be taken and describing the calculations of 1/*t*

[5] Describe the use of 1/*t* as the initial rate of the experiment.

[6] Using inspection method or mathematically, describe how the deduction of the order of reaction of HC*l* can be done.

[6]

[Total: 14]

4 Carry out the following experiments with **FA 6**.

In all tests the reagents should be added gradually until no further change is observed unless you are instructed otherwise.

Observations should include:

(i) descriptions of colour changes and precipitates;

(ii) names of gases evolved and details of the test used to identify each one.

You should indicate clearly at which stage in a test a change occurs, writing any deductions that you make alongside the observations upon which they are based.

Marks will be given *only* for the prescribed tests and will *not* be given for chemical equations.

TEST	OBSERVATION	CONCLUSION
Tests of FA 6 **(a)** Heat **FA 6** in a test-tube until no further change is observed. **Allow the residue to cool** and retain it for **(b)**. You may wish to proceed with the tests in **4(c)** while waiting for the residue to cool.	• Violet gas evolved which bleaches litmus. **[1] with identity of gas** • Colourless gas evolved which relights glowing splint. **[1] with identity of gas** • White residue, same colour as original	• Gas is I_2 • Gas is O_2 • IO_3^- present • K^+, Na^+, Ca^{2+}, Ba^{2+} or Mg^{2+} may be present
(b) Dissolve the residue from test **(a)** in deionised water and use separate portions of the solution for tests **(i)** to **(iii)**	• Colourless solution	
(i) Add aqueous silver nitrate to a portion of the solution.	• Yellow ppt	
Then add aqueous ammonia.	• Ppt insoluble in aqueous ammonia **[1] for both**	• I^- present in residue **[1]**

For Examiner's Use

TEST	OBSERVATION	CONCLUSION
(ii) Add a few drops of aqueous potassium manganate(VII) followed by dilute sulfuric acid.	• Brown solution / black ppt [1] • Purple $KMnO_4$ decolourised	• I_2 produced [1] • I^- present in residue • Reducing agent present [1]
(iii) Add a few crystals of **FA 6**, shake to dissolve and then add dilute sulfuric acid.	• Brown solution obtained [1] **with identification of I_2**	• I_2 produced • **FA 6** is an oxidising agent [1] • I^- present in residue
(c) Dissolve **FA 6** in water and use separate portions of the solution for tests **(i)** and **(ii)**.	• Colourless solution	
(i) Add a few drops of aqueous potassium manganate(VII) followed by dilute sulfuric acid.	• Purple colour of $KMnO_4$ remains [1]	• Reducing agent absent [1]
(ii) Add aqueous potassium bromide followed by dilute sulfuric acid.	• Orange solution formed	**[1] either** • Br_2 produced [1] • Oxidising agent present [1]
Add hexane and shake the mixture.	• Dark red top organic layer and yellow/orange bottom aqueous layer	

You are *not* required to identify **FA 6**. **[14 max 7]** [7]

(d) **(i)** **FA 6** and the residue from **(a)** contains element **X** in two different oxidation states. Using your observations from the tests in **(b)** and **(c)**, explain which compound, **FA 6** or the residue, contains **X** in the higher oxidation state.

FA 6 **[1, with correct reasoning]** contains **X** in the higher oxidation state. From test **(c)(i)**, **FA 6** does not react with the strong oxidising agent, $KMnO_4$, whereas in test **(b)(ii)**, the residue decolourises $KMnO_4$. [1] Hence, **FA 6** cannot be oxidised, while the residue can be oxidised, meaning that **FA 6** must have contained **X** in the higher oxidation state

[2]

(ii) The reaction in test **(b)(iii)** is said to be a **comproportionation** reaction. In light of your observations to test **(b)(i)** and **(b)(iii)**, together with your answer to **(d)(i)**, suggest what the term comproportionation may refer to.

Test **(b)(i)** confirms the presence of I^- in the residue, which is oxidised to I_2 by **FA 6**, which contains I (**X**) in a higher oxidation state, in test **(b)(iii)**. [1]

Comproportionation refers to a reaction in which **two reactants**, each containing the **same element** but with a **different oxidation state**, form **a product** in which the element involved has the **same intermediate oxidation state**. [1]

[2]

[Total: 11]

BLANK PAGE

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) 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