Candidate Name: ____________________

Class	Adm No

H

millennia institute

2018 Preliminary Exams
Pre-University 3

H2 CHEMISTRY **9729/01**

Paper 1 Multiple Choice **21 Sept 2018**

1 hour

Additional materials: Multiple Choice Answer Sheet
Data Booklet

READ THESE INSTRUCTIONS FIRST

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Write your name, class and admission number in the spaces provided at the top of this page and on the Multiple Choice Answer Sheet provided.

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FOR EXAMINER'S USE	
TOTAL (30 marks)	

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

Which sample of gas below contains the same number of particles as 19.0 g of fluorine gas?

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

. Arsenic in the form of arsenic trioxide, As_2O_3, was used in the past as rat poison. To test for the presence of As_2O_3, 1.0 g sample containing some As_2O_3 is dissolved and excess H_2S is then added to the solution. 0.492 g of As_2S_3 is precipitated as a result. The equation for the reaction is given below:

$$As_2O_3 + 3H_2S \longrightarrow As_2S_3 + 3H_2O$$

What is the percentage by mass of arsenic in the original sample?

A 15.9%
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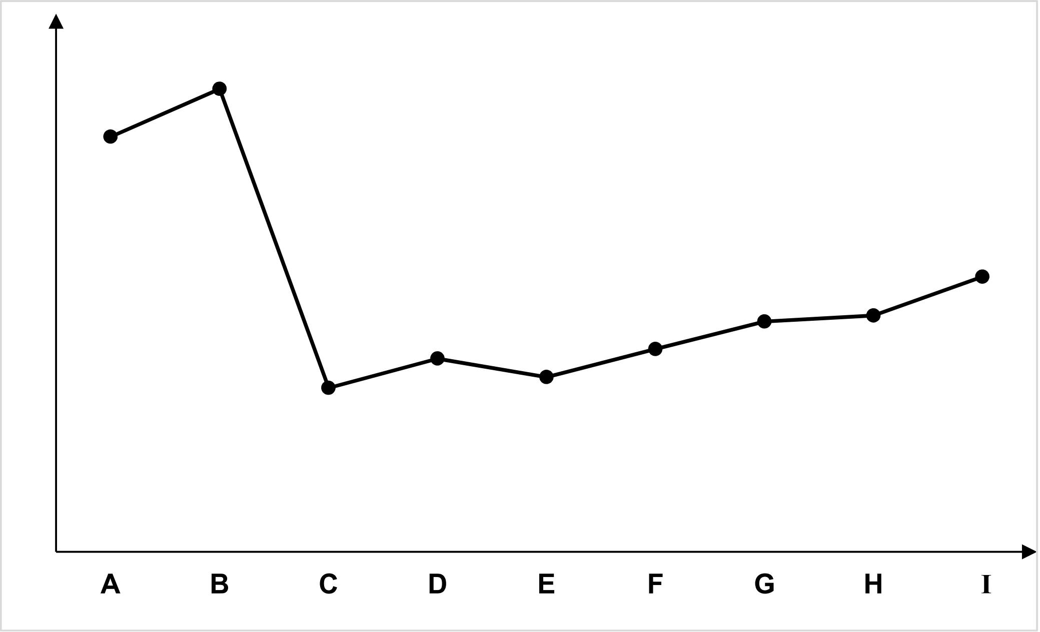
Tin(II) ions can be used as a reducing agent. What volume of 0.025 mol dm^{-3} of tin(II) ions is needed to completely reduce 5×10^{-4} mol of potassium manganate(VII)?

A 8.00 cm^3 **B** 16.0 cm^3
C 25.0 cm^3 **D** 50.0 cm^3

. The graph below shows the 3rd ionisation energy of elements **A** to **I**, which are consecutive elements with atomic number less than 20.

Third ionisation energy



elements

Which of the following statements is correct?

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C Element **E** has a lower 3rd ionisation energy than element **D** because of inter-electronic repulsion from the paired 2p electrons.

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. A sample of $^{9}Be^{2+}$ ions are passed through some charged electrical plates. The angle of deflection of the $^{9}Be^{2+}$ ions is 12.0°.
Another sample of doubly charged **X** ions are also passed through the same electrical plates and deflected at an angle of -6.75°. What is the mass number of **X**?

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A CO_2, NO_2, SO_2
B BF_3, $AlCl_3$, PBr_3
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A helium　　**B** sulfur dioxide

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. Which of the following is a conjugate acid-base pair?

A CO_2/CO_3^{2-}

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. **X**, **Y** and **Z** react together to give some products as shown.

$$\mathbf{X} + \mathbf{Y} + \mathbf{Z} \longrightarrow \text{products}$$

The rate equation of the reaction above can be written as rate = k[**X**][**Y**].

Which of the following graphs is correct of the reaction above?

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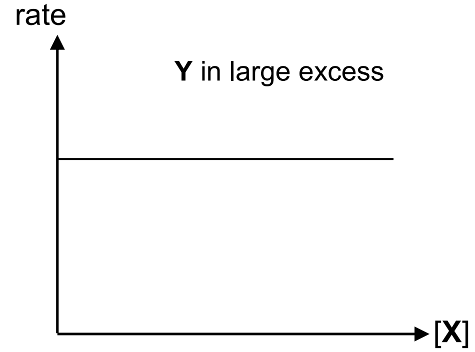

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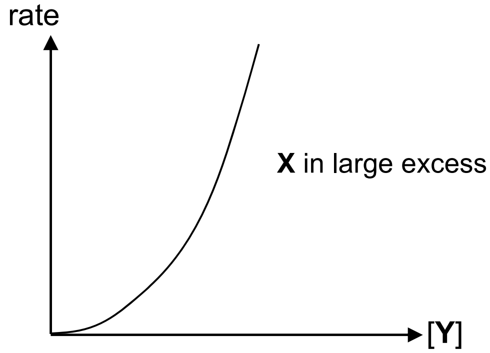

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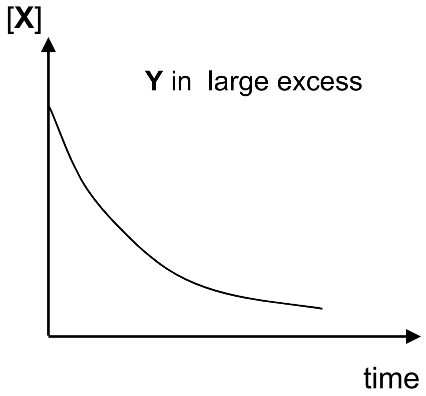

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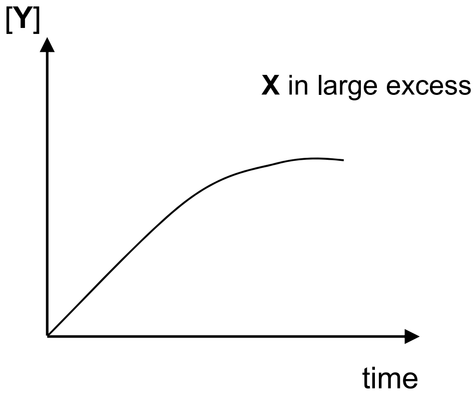

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$$Ag_2SO_4(s) \rightleftharpoons 2Ag^+(aq) + SO_4^{2-}(aq)$$

Given that the solubility product of Ag_2SO_4 is ***S***, what is the concentration of Ag^+ in a saturated solution of Ag_2SO_4?

A $\left(\frac{\boldsymbol{S}}{4}\right)^{\frac{1}{3}}$ **B** $\sqrt{\boldsymbol{S}}$

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1 It forms an acidic solution in water.
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Which factor best explains this trend?

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B stability of group 2 oxides
C ionic radii of group 2 metal ions
D lattice energy of group 2 nitrates

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. American pennies are made of copper-coated zinc. Each penny is coated with 0.0625 g of copper metal. How much time is needed to plate one uncoated zinc penny when the penny is placed in a 0.5 mol dm^{-3} solution of $CuSO_4$ with a current of 0.25 A?

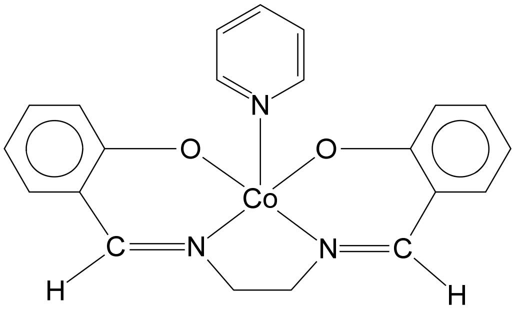
A 380 seconds **B** 760 seconds

C 380 hours **D** 760 hours

. Which of the following **cannot** act as a ligand to form complexes?

A H_2O **B** OH^- **C** AlH_3 **D** HCl

. The following cobalt complex is known to be the functional model for biological oxygen carrier.



What is the electronic configuration of the cobalt cation in the above complex?

A [Ar]$3d^4$ **B** [Ar]$3d^7$ **C** [Ar]$3d^5 4s^2$ **D** [Ar]$3d^7 4s^2$

. A solution containing copper(II) sulfate was subjected to a few chemicals as shown in the reaction scheme below.

$$CuSO_4 \xrightarrow[\text{excess } NH_3(aq)]{\textbf{I}} \textbf{P} \xrightarrow[KCN(aq)]{\textbf{II}} [Cu(CN)_6]^{4-}$$

Which of the following statements are correct about the reaction scheme?

1 CN^- is a stronger ligand than NH_3.
2 The copper in $CuSO_4$ is reduced.
3 Ligand exchange took place in both steps **I** and **II**.

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

. What is the number of non-cyclic constitutional isomers that can be exhibited by $C_3H_4Br_2$?

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

. Which of the following is a propagation step in the reaction of ethane with bromine in the presence of ultraviolet light?

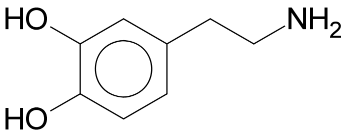
A $CH_2BrCH_2\bullet + Br_2 \longrightarrow CH_2BrCH_2Br + Br\bullet$

B $\bullet CHBrCH_3 + HBr \longrightarrow \bullet CBr_2CH_3 + H_2$

C $CH_3CH_2\bullet + \bullet Br \longrightarrow CH_3CH_2Br$

D $CH_3CH_3 + Br\bullet \longrightarrow CH_3CH_2Br + H\bullet$

. Dopamine is a neurotransmitter that is involved in addiction.



Dopamine

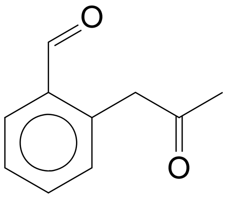
Which of the following statements is true about dopamine?

1 It will react with hot sodium hydroxide to produce ammonia.
2 One mole of dopamine will react with excess Na(s) to produce 2 moles of $H_2(g)$.
3 It can decolourise aqueous bromine.

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

. Which of the following will give a positive reaction with both Tollens' reagent and aqueous alkaline iodine?

A



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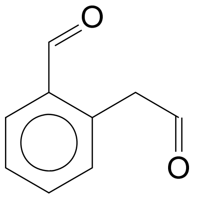

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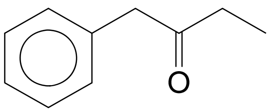

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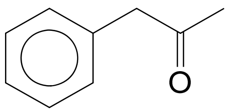

. Phenol is weakly acidic and has a pK_a of 9.95. Which of the following substances, in the presence of water, has a higher pK_a than phenol?

A chloroethanoic acid
B ethanoyl chloride
C 4-chlorophenol
D ethanol

. The following fragments were obtained when a polypeptide is hydrolysed.

phe-ser
ala-ala
ser-phe-gly
lys-asp
ala-lys
gly-ala

Given that the polypeptide chain is known to have 8 amino acids residues, which of the following could be the polypeptide?

A ser-phe-ala-ala-gly-ser-lys-asp
B phe-ser-phe-gly-ala-ala-lys-asp
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END OF PAPER

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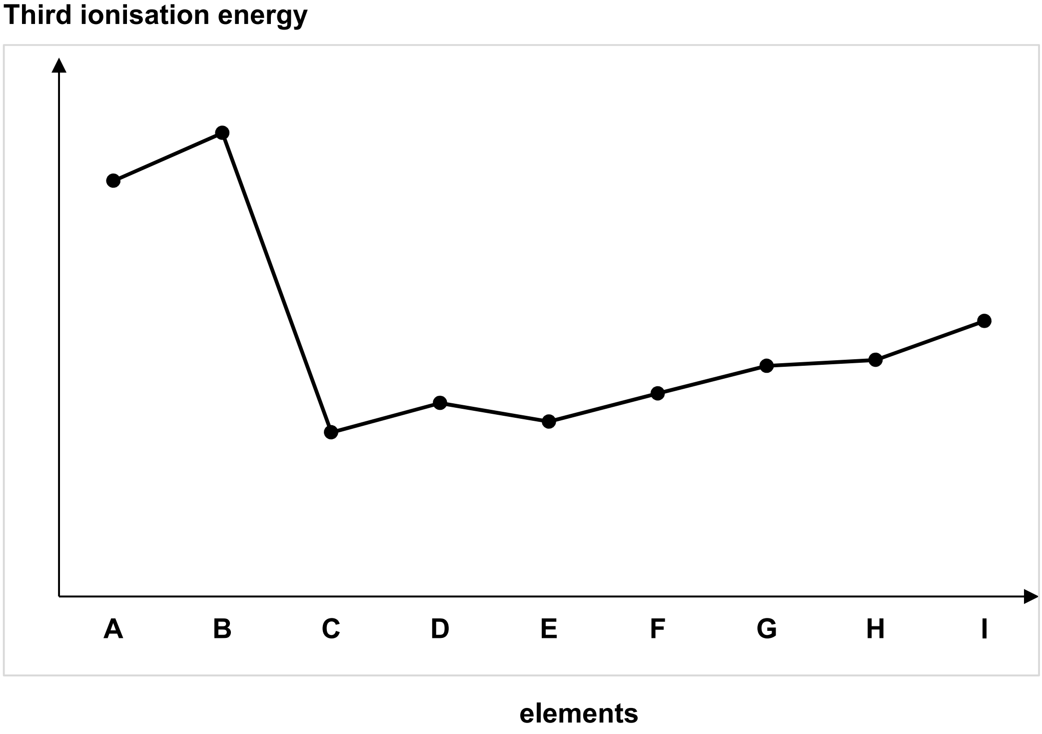

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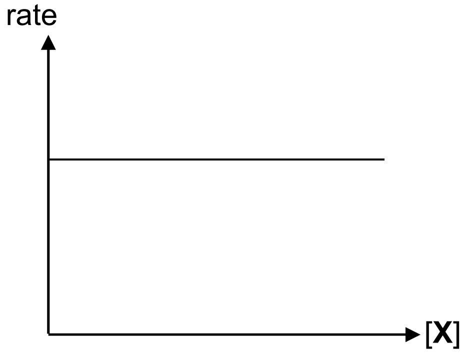

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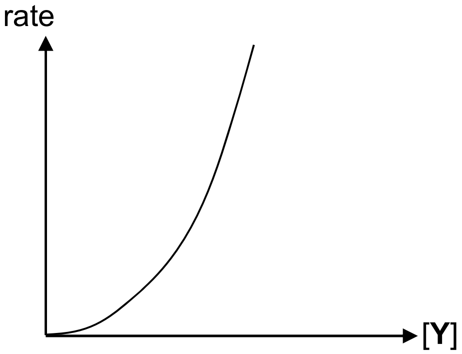

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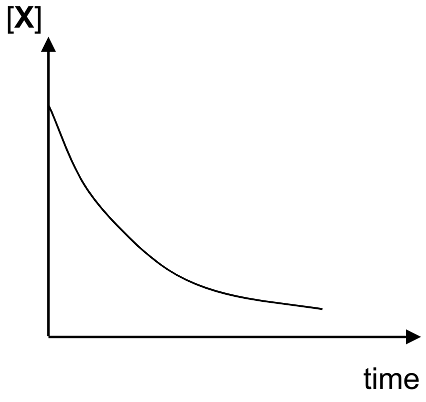

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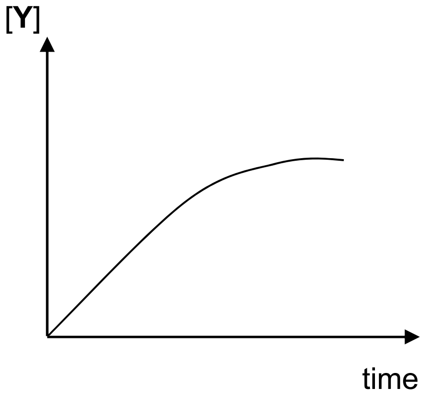

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$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g) \qquad \Delta H = -92\ kJ\ mol^{-1}$$

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. Which of the following statements is true about aluminium chloride?

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2 It conducts electricity in the solid state.
3 It can dimerise through dative bonding.

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

. Group 2 nitrates decompose in this manner: $\mathbf{M}(NO_3)_2 \longrightarrow \mathbf{M}O(s) + 2NO_2(g) + \frac{1}{2}O_2(g)$ and require more energy for decomposition down the group. Which factor best explains this trend?

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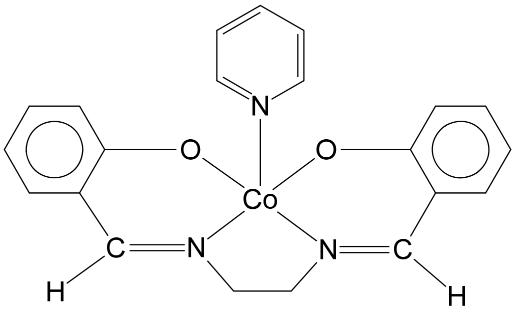

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A 1 only **B** 3 only

C 1 and 2 only **D** 1 and 3 only

. What is the number of non-cyclic constitutional isomers that can be exhibited by $C_3H_4Br_2$?

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

. Which of the following is a propagation step in the reaction of ethane with bromine in the presence of ultraviolet light?

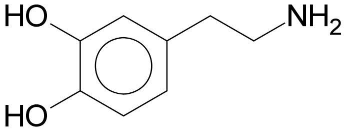
A $CH_2BrCH_2\bullet + Br_2 \longrightarrow CH_2BrCH_2Br + Br\bullet$

B $\bullet CHBrCH_3 + HBr \longrightarrow \bullet CBr_2CH_3 + H_2$

C $CH_3CH_2\bullet + \bullet Br \longrightarrow CH_3CH_2Br$

D $CH_3CH_3 + Br\bullet \longrightarrow CH_3CH_2Br + H\bullet$

. Dopamine is a neurotransmitter that is involved in addiction.



Dopamine

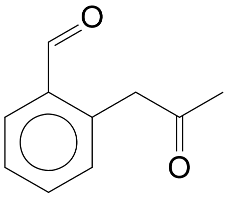
Which of the following statements is true about dopamine?

1 It will react with hot sodium hydroxide to produce ammonia.
2 One mole of dopamine will react with excess Na(s) to produce 2 moles of $H_2(g)$.
3 It can decolourise aqueous bromine.

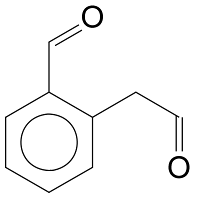
A 2 only
B 3 only
C 1 and 2 only
D 2 and 3 only

. Which of the following will give a positive reaction with both Tollens' reagent and aqueous alkaline iodine?

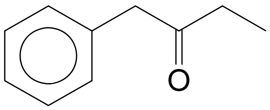
A



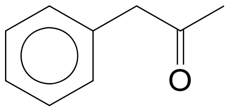
B



C



D



. Phenol is weakly acidic and has a pK_a of 9.95. Which of the following substances, in the presence of water, has a higher pK_a than phenol?

A chloroethanoic acid **B** ethanoyl chloride
C 4-chlorophenol **D** ethanol

. The following fragments were obtained when a polypeptide is hydrolysed.

phe-ser
ala-ala
ser-phe-gly
lys-asp
ala-lys
gly-ala

Given that the polypeptide chain is known to have 8 amino acids residues, which of the following could be the polypeptide?

A ser-phe-ala-ala-gly-ser-lys-asp
B phe-ser-phe-gly-ala-ala-lys-asp
C phe-ser-ala-gly-ala-ala-lys-asp
D ser-phe-phe-gly-ala-ala-lys-asp

END OF PAPER

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	Class	Adm No
Candidate Name: ____________________		

H

millennia institute

2018 Preliminary Exams
Pre-University 3

H2 CHEMISTRY **9729/02**

Paper 2 Structured Questions **12th Sept 2018**

2 hours

Candidates answer on the Question paper.

Additional materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Do not turn over this question paper until you are told to do so

Write your name, class and admission number on all the work you hand in.

Write in dark blue or black pen.

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

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

Answer **all** questions.

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.

Question	**1**	**2**	**3**	**4**	**5**	Total
Marks	**20**	**15**	**12**	**12**	**16**	**75**

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

1 Ruthenium, Ru, is a Period 5 d-block element. Its ions have the ability to form complexes with both organic and inorganic ligands.

One such organic ligand is 2,2-bipyridine which can be represented by bpy.

(a) Define the term *ligand* and suggest why bpy can act as a bidentate ligand.

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

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

(b) In an experiment, varying volumes of solutions of 0.1 mol dm^{-3} Ru^{2+} and 0.1 mol dm^{-3} bpy are mixed to produce a coloured complex.

$$x\mathrm{Ru}^{2+} + y\mathrm{bpy} \rightarrow [\mathrm{Ru}_x(\mathrm{bpy})_y]^{2+}$$

The concentration of the coloured complex formed is proportional to the absorbance of the solution which is measured using a colorimeter. **Fig 1.1** shows the results experiment.

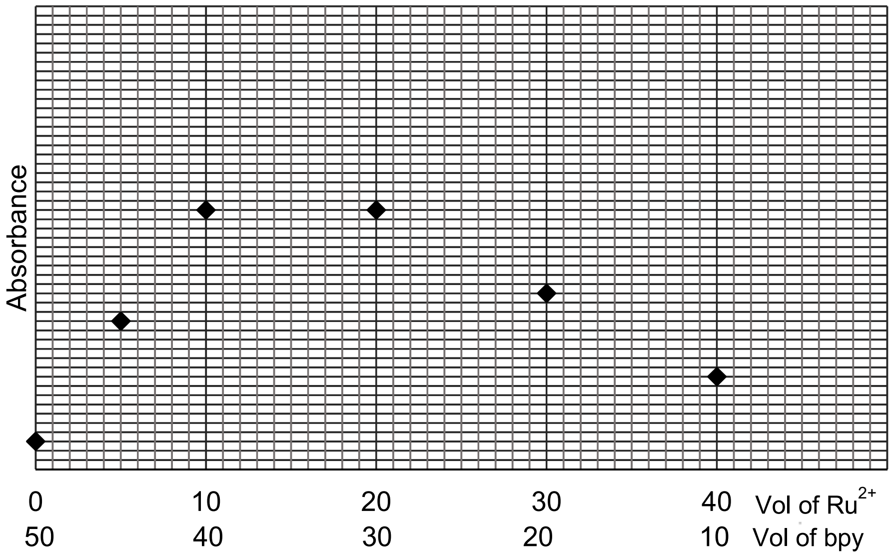


Fig 1.1

By drawing two best-fit lines in **Fig 1.1**, deduce the formula of the complex ion formed between Ru^{2+} and bpy and hence draw the structure of the complex ion.

For Examiners' Use

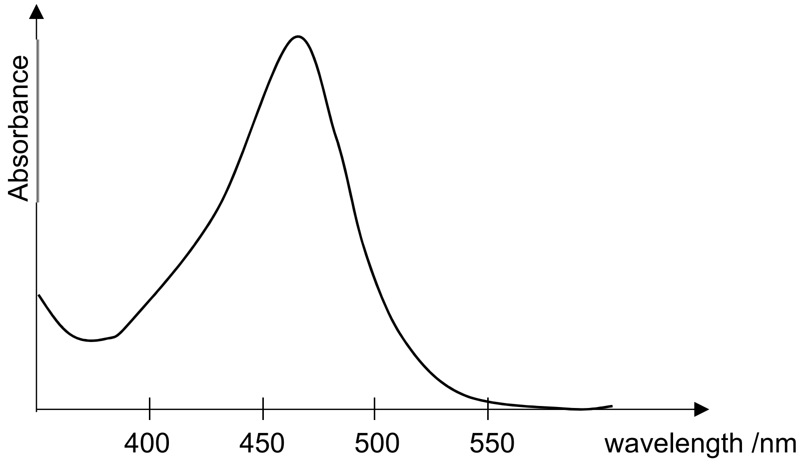
Formula of complex ion: …………………………..
Structure of complex ion:

[3]

(c) The table below shows the colour of the radiation of the electromagnetic spectrum and the corresponding wavelength range.

Wavelength range (nm)	**Colour**	**Complementary colour**
400 – 450	violet	yellow
450 – 490	blue	orange
490 – 550	green	red
550 – 580	yellow	violet
580 – 650	orange	blue
650 – 700	red	green

The diagram below shows the UV-Visible spectrum of the complex formed between Ru^{2+} and bpy.



Using the data provided, suggest the colour of the complex formed between Ru^{2+} and bpy.

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

(d) Ru^{2+} also forms an octahedral aqua complex with the formula $[Ru(H_2O)_6]^{2+}$. Typically, the colour of the complex changes when the ligands are different. This is due to different ligands causing the five d-orbitals to be split to different extent. **Fig 1.2** shows how the five d-orbitals are split in an octahedral environment.

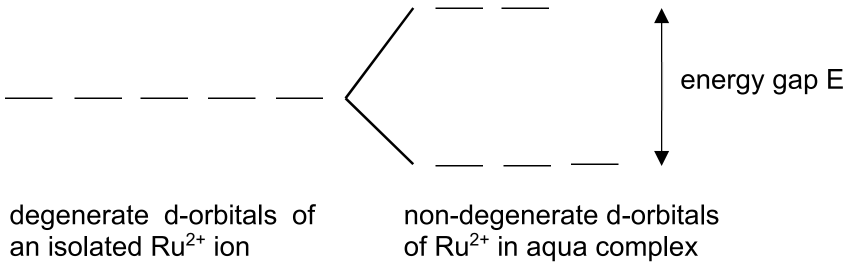


Fig 1.2

(i) With reference **Fig 1.2**, outline why $[Ru(H_2O)_6]^{2+}$ is coloured.

....

....

.... [2]

The electrons of transition metal ions in complexes can fill the non-degenerate d-orbitals in two different ways, namely the 'high spin' state and the 'low spin' state. This is dependent on the magnitude of the energy gap, E, and the pairing energy, P. Electrons usually prefer to occupy orbitals singly, rather than in pairs. Pairing energy, P, is the energy needed for an electron to fill an orbital that is already occupied by another electron.

In the 'high spin' state, the electrons occupy all the d-orbitals singly, before starting to pair up in the lower energy d-orbitals. This occurs because the magnitude of the energy gap, E, is smaller than the pairing energy, P.

In the 'low spin' state, the lower energy d-orbitals are filled first, by pairing up if necessary, before the higher energy d-orbitals are used. This occurs because the pairing energy, P, is smaller than the magnitude of the energy gap, E.

For Period 4 d-block elements, the electronic configuration of the 3d electrons can be either 'high spin' or 'low spin'. However, for Period 5 d-block elements, the 4d electrons are always in the 'low spin' state.

(ii) Suggest why electrons usually prefer to occupy orbitals singly, rather than in pairs.

……………………………………………………………………………………….

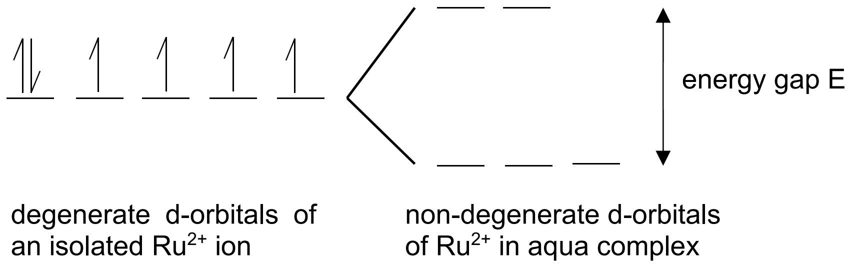
………………………………………………………………………………………[1]

(iii) With reference to the relative sizes of 3d and 4d orbitals, suggest a reason why 4d electrons prefer to pair up in the lower energy d-orbital before filling the higher energy d-orbitals.

……………………………………………………………………………………….

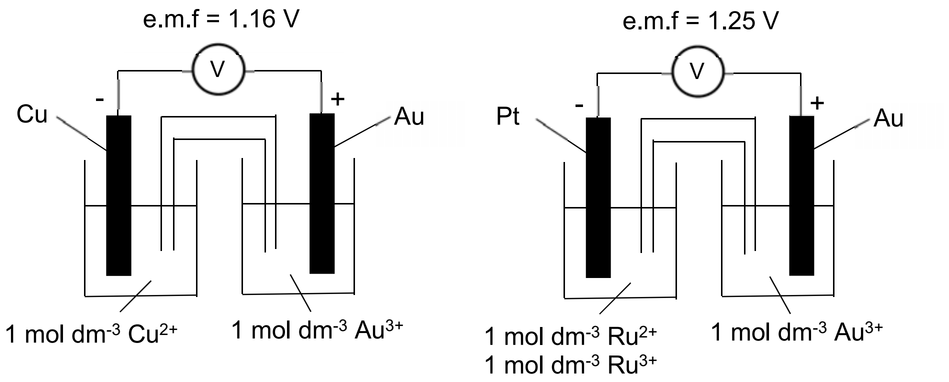
……………………………………………………………………………………… [1]

(iv) In the diagram below, show the electronic distribution of a Ru^{2+} ion in the 'low spin' state, given that the electronic configuration of Ru^{2+} is [Kr] $4d^6$.



[1]

(e) Two galvanic cells were set up under standard conditions to determine the standard electrode potential of Ru^{3+}/Ru^{2+}.



cell A

cell B

Fig 1.3

(i) Define the term *standard electrode potential*.

……………………………………………………………………………………………

……………………………………………………………………………………………

…………………………………………………………………………………………[1]

(ii) Using the data given in **Fig 1.3** and relevant data from the Data Booklet, determine the standard electrode potentials of Au^{3+}/Au and that of Ru^{3+}/Ru^{2+} respectively.

$E^{\ominus}(Au^{3+}/Au)$ = …………………………………

$E^{\ominus}(Ru^{3+}/Ru^{2+})$ = ………………………………… [3]

(iii) Hence using your answer in **(e)(ii)** and relevant data from the Data Booklet, state and explain whether Ru^{3+} is able to act as a homogenous catalyst for the reaction between $S_2O_8^{2-}$ and I^-.

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

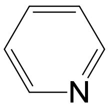
……………………………………………………………………………………….

……………………………………………………………………………………….

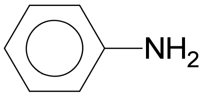
……………………………………………………………………………………….

………………………………………………………………………………… [3]

(f) Pyridine and phenylamine are two nitrogen-containing compounds.



pyridine
$pK_b = 8.75$



phenylamine
$pK_b = 9.33$

Pyridine has a resonance structure with six p electrons delocalised over the ring. The molecule is planar, with all atoms forming the ring being sp^2 hybridised. The lone pair of electrons on nitrogen occupies one of its sp^2 hybrid orbitals.

With reference to the shape and orientation of the orbitals about the nitrogen atom in both compounds, suggest why pyridine has a lower pK_b value.

……………………………………………………………………………………………….

……………………………………………………………………………………………….

……………………………………………………………………………………………….

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

[Total: 20]

2 **(a)** Upon heating at 160 °C, magnesium ethanoate decomposes to give magnesium carbonate and propanone as the products.

$$(CH_3COO)_2Mg \rightarrow MgCO_3 + CH_3COCH_3$$

Upon further heating, $MgCO_3$ undergoes further decomposition.

(i) Write an equation for the decomposition of $MgCO_3$.

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

When barium propanoate, $(CH_3CH_2COO)_2Ba$ was heated until constant mass, it was found that $BaCO_3$ and an organic compound **X**, $C_5H_{10}O$, were obtained. Despite further heating, $BaCO_3$ did not undergo decomposition.

When 2,4-dinitrophenylhydrazine was added to compound **X**, an orange precipitate was observed. Compound **X** did not give yellow precipitate with warm aqueous alkaline iodine.

(ii) Explain why $MgCO_3$ undergoes thermal decomposition more readily than $BaCO_3$.

………………………………………………………………………………………...

………………………………………………………………………………………...

………………………………………………………………………………………...

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

(iii) Suggest the structure of **X**.

[1]

(iv) Write a balanced chemical equation for the decomposition of barium propanoate.

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

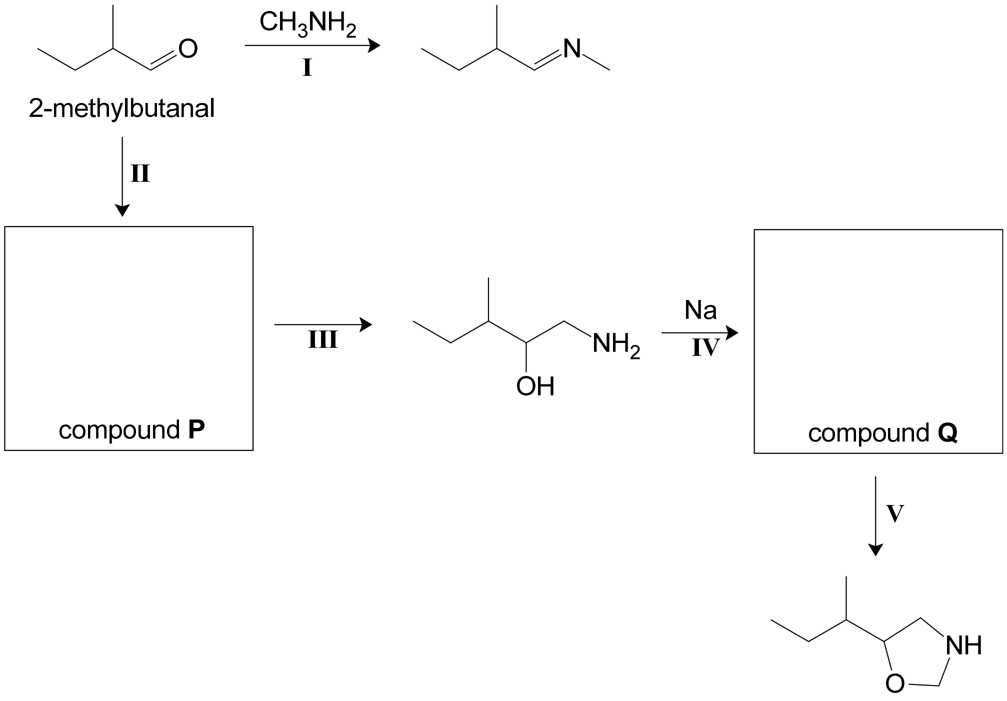
(v) Suggest why barium propanoate undergoes thermal decomposition more readily than barium carbonate.

………………………………………………………………………………………

………………………………………………………………………………………...

………………………………………………………………………………………[2]

(b) The scheme below shows the reactions of 2-methylbutanal.



(i) **R** is a constitutional isomer of 2-methylbutanal. **R** gives yellow precipitate when warmed with aqueous iodine in an alkaline medium. **R** does not decolourise aqueous bromine.
Draw the skeletal formulae of **two** possible structures of **R**.

[2]

(ii) Draw the structure of compounds **P** and **Q** in the boxes provided in the reaction scheme and state the reagents and conditions for steps **II**, **III** and **V**.

Step	**Reagents and Conditions**
II	
III	
V	

[5]

(iii) Suggest the type of reaction undergone by 2-methylbutanal in step **I**.

……………………………………………………………………………………[1]

[Total: 15]

3 **(a)** Cyanogen is a colourless yet extremely poisonous gas that is used in fumigation. Cyanogen is made up of carbon and nitrogen only, of which 46.2% is composed of carbon by mass.

At 30°C and 1 bar, 1.03 g of cyanogen occupies 0.500 dm^3. It dissolves readily in water.

Calculate the molecular formula of cyanogen.

[3]

(b) Draw the 'dot-and-cross' diagram of the cyanogen molecule and suggest the shape of the molecule with respect to the central atom.

Shape: ……………………………………… [2]

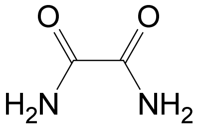
(c) Explain, in terms of bonding, why cyanogen dissolves readily in water.

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

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

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

(d) Oxamide is manufactured from cyanogen by hydrolysis that only involves water.



Oxamide

(i) Write the balanced equation for the production of oxamide from cyanogen and water. You may use the molecular formula of oxamide in your equation.

……………………………………………………………………………………..[1]

(ii) With the use of Data Booklet, calculate the enthalpy change of the reaction in **(d)(i)**.

[2]

(iii) The entropy change for the reaction in **(d)(i)** is +64.1 J mol^{-1} K^{-1}. Use your answer in **(d)(ii)** to calculate ΔG at 298 K. Hence predict if the reaction is spontaneous at 298 K.

[2]

[Total: 12]

4 **(a)** A bottle of supplement has the following nutritional information.

The serving size is 42.5g and each bottle contains 20 servings.

	Each serving contains	% of Recommended Daily Allowance
Total fat	3 g	5
Dietary Fibre	6 g	24
Protein	15 g	30
Calcium	546 mg	47
Iron	9 mg	43
Iodine	80 μg	48
Vitamin C	30 mg	52
Vitamin K	40 μg	51

Table 4.1

A student weighed out 75 g portion of this supplement and crushed it in a pestle and mortar to form a powder. She then added it to 100 cm^3, an excess, of 1.5 mol dm^{-3} sulfuric acid, stirred it and then filtered it.

She made the volume up to 250 cm^3 forming solution **A**. Finally, she titrated a 25.0 cm^3 portion of solution **A** with 1.8 x 10^{-4} mol dm^{-3} potassium dichromate(VI).

(i) Use the *Data Booklet* to construct an ionic equation for the reaction between Fe^{2+} in solution **A** and dichromate(VI) ions.

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

(ii) Calculate the volume of potassium dichromate(VI) solution that would be required to react with Fe^{2+} in 25.0 cm^3 of solution **A**.

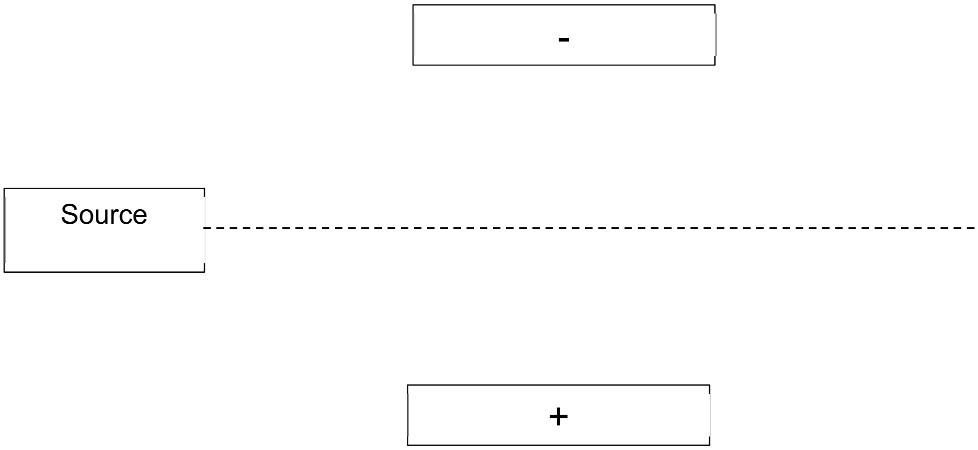
[3]

(b) Overdosage of iodine has many side-effects, including abdominal pain, delirium, fever, vomiting, and shortness of breath.

Assuming that a person does not consume any other food that contains iodine other than the supplement and a serving refers to 5 tablets, deduce if it is within the % daily recommended allowance for him to consume as many as 11 tablets in a single day. Justify with calculations.

[3]

(c) The iodine, calcium and iron content in the supplement is dissolved in water, forming ions. The ions are then isolated. Indicate on the diagram below how a beam of particles containing the three species, travelling at the same speed, behave in the same electric field. State your reasoning.



……………………………………………………………………………………………..

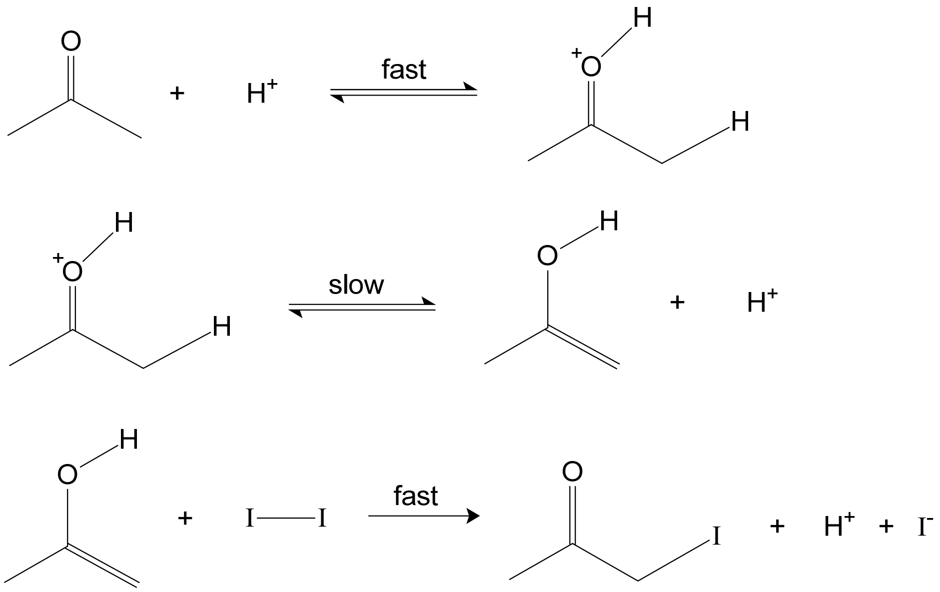
…………………………………………………………………………………………… [5]

[Total: 12]

5 **(a)** Propanone reacts with iodine in the presence of an acid catalyst.

$$CH_3COCH_3(aq) + I_2(aq) \rightarrow CH_3COCH_2I(aq) + H^+(aq) + I^-(aq)$$

The mechanism of this reaction is thought to be as follows:



(i) On the mechanism shown, draw curly arrows and lone pair of electrons to show the movement of electrons in each of the step. [3]

(ii) Based on the mechanism above, write the rate equation for this reaction.

……………………………………………………………………………………….[1]

(iii) Hence, sketch the graph of rate against $[I_2]$.

[1]

(b) 5.0 cm^3 of the reaction mixture was taken out when the reaction has proceeded for 30 seconds. The resultant solution was then made up to 100 cm^3 in a volumetric flask. 25.0 cm^3 portions of this solution were then titrated with 0.100 mol dm^{-3} of aqueous potassium thiosulfate, $K_2S_2O_3$, with the addition of starch solution. The results are shown in **Table 5.1**.

	1	2	3
Initial burette reading / cm^3	0.00	19.95	2.05
Final burette reading / cm^3	19.90	40.05	22.15
Volume of titre / cm^3	19.90	20.10	20.10

Table 5.1

(i) Write the ionic equation for the reaction between potassium thiosulfate and iodine in the solution.

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

(ii) Use the above results to determine the concentration of iodine in the original 5.0 cm^3 of the aliquot taken out at 30 seconds after the reaction has started.

[3]

(c) The iodine solution was then isolated and boiled to produce I_2(g).

A sketch of $\frac{pV}{RT}$ against p for 1 mole of H_2(g) at 473 K is shown in **Fig 5.1**. On the same axes, sketch the graph of $\frac{pV}{RT}$ against p for 1 mole of I_2(g) at 473 K and for 1 mole of H_2(g) at 500 K. Label your sketch clearly.

Justify the difference in behaviour.

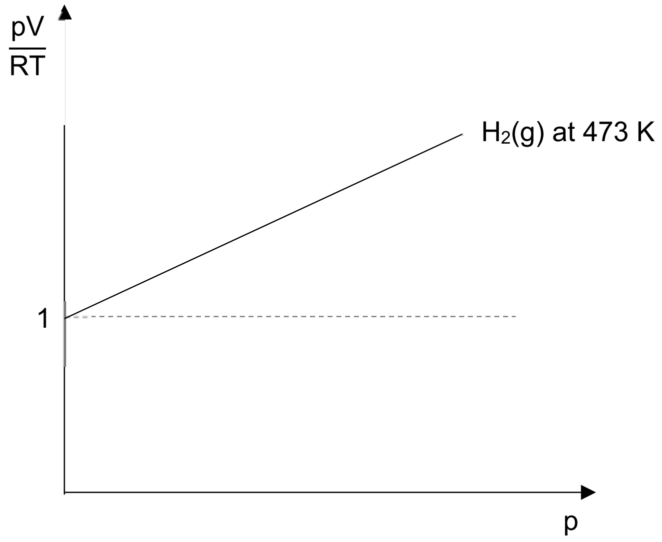


Fig 5.1

……………………………………………………………………………………………

……………………………………………………………………………………………

…………………………………………………………………………………………… [4]

(d) Describe all types of interactions found within the lattice structure of solid iodine fully.

……………………………………………………………………………………………

……………………………………………………………………………………………

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

[Total: 16]

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H

2018 Preliminary Exams

Pre-University 3

H2 CHEMISTRY **9729/02**

Paper 2 Structured Questions **12th Sept 2018**

2 hours

Candidates answer on the Question paper.

Additional materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Do not turn over this question paper until you are told to do so

Write your name, class and admission number on all the work you hand in.

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Answer **all** questions.

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

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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.

Question	1	2	3	4	5	Total
Marks	20	15	12	12	16	75

1 Ruthenium, Ru, is a Period 5 d-block element. Its ions have the ability to form complexes with both organic and inorganic ligands.

One such organic ligand is 2,2'-bipyridine which can be represented by bpy.

(a) Define the term *ligand* and suggest why bpy can act as a bidentate ligand.

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………[2]

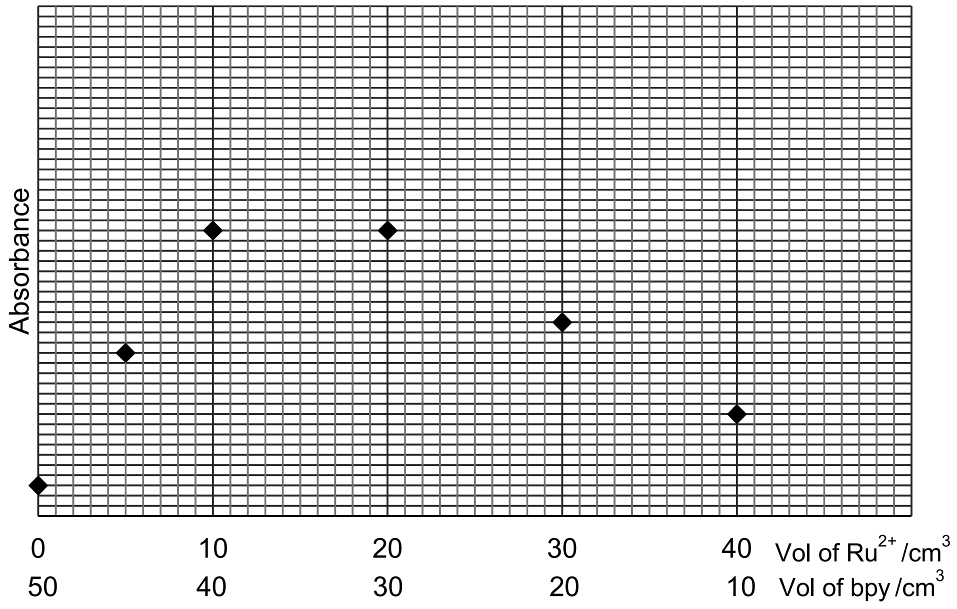
Ligand is a neutral molecule or anion which contain at least one atom bearing a lone pair of electrons which can form a dative bond to a central atom/ion, resulting in the formation of a complex.

Bpy has 2 nitrogen atoms with a lone pair of electrons each, so it can form two dative bonds with the central atom/ion.

(b) In an experiment, varying volumes of solutions of 0.1 mol dm^{-3} Ru^{2+} and 0.1 mol dm^{-3} bpy are mixed to produce a coloured complex.

$$x\mathrm{Ru}^{2+} + y\mathrm{bpy} \rightarrow [\mathrm{Ru}_x(\mathrm{bpy})_y]^{2+}$$

The concentration of the coloured complex formed is proportional to the absorbance of the solution which is measured using a colorimeter. The following graph is plotted using the results of the experiment.



By drawing two best-fit lines on the graph, deduce the formula of the complex ion formed between Ru^{2+} and bpy and hence draw the structure of the complex ion.

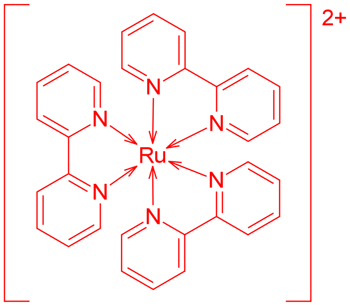
Formula of complex: …………………………..

Structure of complex ion:

[3]

Draw two straight lines that intersect one another.
Point of intersection shows $V_{Ru}{}^{2+}$ = 12.5 cm^3 and V_{bpy} = 37.5 cm^3
Ratio of Ru^{2+} to bpy = 1:3 ;

formula = $[Ru(bpy)_3]^{2+}$

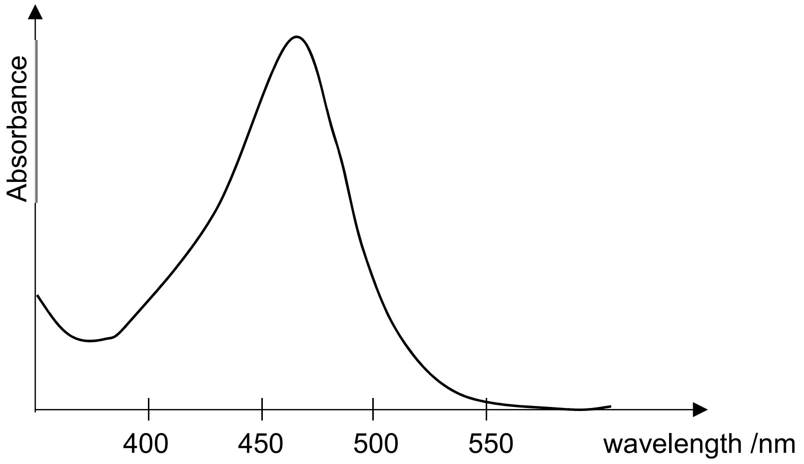


(c) The table below shows the colour of the radiation of the electromagnetic spectrum and the corresponding wavelength range.

Wavelength range (nm)	Colour	Complementary colour
400 – 450	violet	yellow
450 – 490	blue	orange
490 – 550	green	red
550 – 580	yellow	violet
580 – 650	orange	blue

650 – 700	red	green

The diagram below shows the UV-Visible spectrum of the complex formed between Ru^{2+} and bpy.



Use the data given to suggest the colour of the complex formed between Ru^{2+} and bpy.

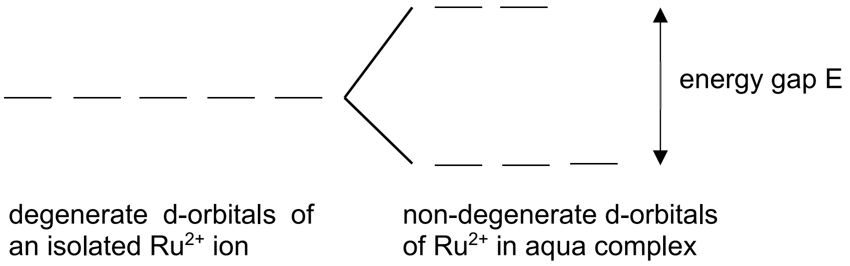
……………………………………………………………………………………….. [1]

Blue is absorbed hence the complex is orange ;

(d) Ru^{2+} also forms an octahedral aqua complex with the formula $[Ru(H_2O)_6]^{2+}$.

Typically, the colour of the complex changes when the ligands are different. This is due to different ligands causing the five d-orbitals to be split to different extent.

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



(i) With reference to this diagram, outline why $[Ru(H_2O)_6]^{2+}$ is coloured.

…………………………………………………………………………………………

…………………………………………………………………………………………

……………………………………………………………………………………… [2]

The electrons in the lower energy d-orbital absorbs radiation from the visible region of the electromagnetic spectrum and get promoted to the higher energy d-orbital.
The complementary colour of the light absorbed is shown as the colour of $[Ru(H_2O)_6]^{2+}$.

The electrons of transition metal ions in complexes can fill the non-degenerate d-orbitals in two different ways, namely the ‘high spin’ state and the ‘low spin’ state. This is dependent on the magnitude of the energy gap, E, and the pairing energy, P. Electrons usually prefer to occupy orbitals singly, rather than in pairs. Pairing energy, P, is the energy needed for an electron to fill an orbital that is already occupied by another electron.

In the ‘high spin’ state, the electrons occupy all the d-orbitals singly, before starting to pair up in the lower energy d-orbitals. This occurs because the magnitude of the energy gap, E, is smaller than the pairing energy, P.

In the ‘low spin’ state, the lower energy d-orbitals are filled first, by pairing up if necessary, before the higher energy d-orbitals are used. This occurs because the pairing energy, P, is smaller than the magnitude of the energy gap, E.

For Period 4 d-block elements, the electronic configuration of the 3d electrons can be either ‘high spin’ or ‘low spin’. However, for Period 5 d-block elements, the 4d electrons are always in the ‘low spin’ state.

(ii) Suggest why electrons usually prefer to occupy orbitals singly, rather than in pairs.

……………………………………………………………………………………………

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

Electrons are negatively charged and will exert repulsive force against each other.

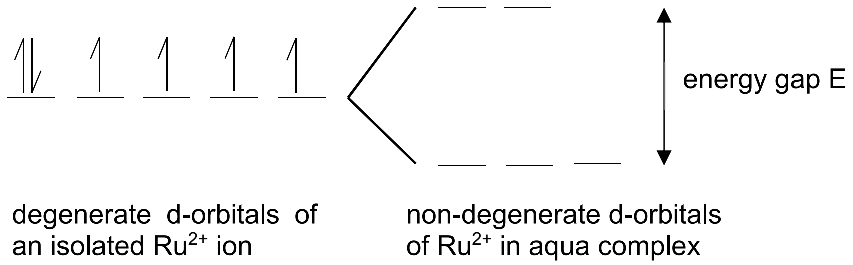
(iii) With reference to the relative sizes of 3d and 4d orbitals, suggest a reason why 4d electrons prefer to pair up in the lower energy d-orbital before filling the higher energy d-orbitals.

……………………………………………………………………………………………

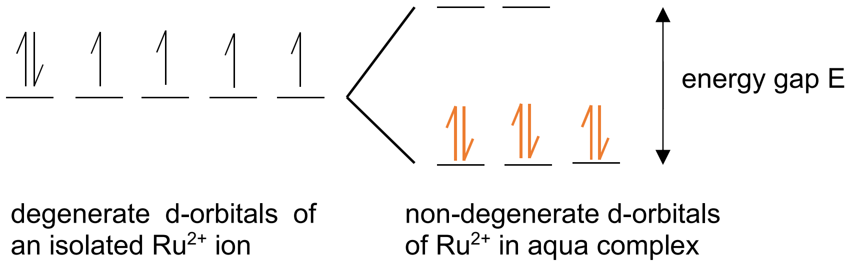
…………………………………………………………………………………………… [1]

4d is bigger in size compared to 3d orbitals. The bigger space causes the repulsion between electrons to be smaller hence the pairing energy becomes smaller than the magnitude of the energy gap.

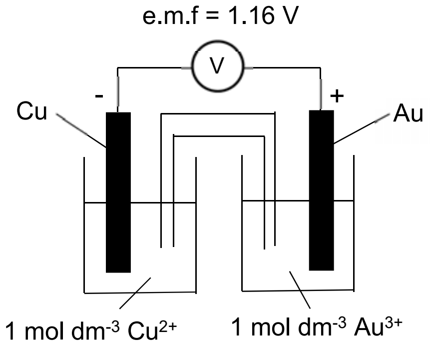
(iv) In the diagram below, show the electronic distribution of a Ru^{2+} ion in the ‘low spin’ state, given that the electronic configuration of Ru^{2+} is [Kr] $4d^6$.



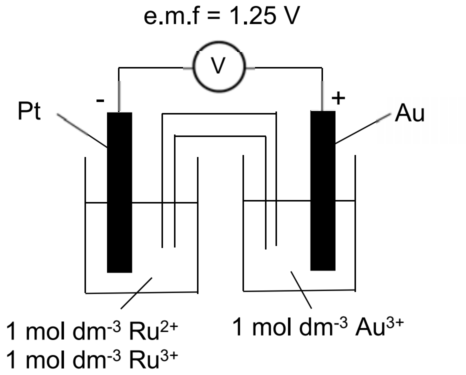
[1]



(e) Two galvanic cells were set up under standard conditions to determine the standard electrode potential of Ru^{3+}/Ru^{2+}.



cell A



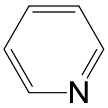
cell B

(i) Define the term *standard electrode potential*.

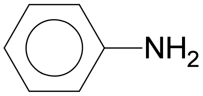
……………………………………………………………………………………………

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

			Standard electrode potential is the relative potential of the electrode under standard conditions compared with the standard hydrogen electrode whose electrode potential is assigned as zero.	
		(ii)	Using the data given and relevant data from the Data Booklet, determine the standard electrode potentials of Au^{3+}/Au and that of Ru^{3+}/Ru^{2+} respectively. $E^{\ominus}(Au^{3+}/Au)$ = …………………………………… $E^{\ominus}(Ru^{3+}/Ru^{2+})$ = …………………………………… [3]	
			$1.16 = E^{\ominus}(Au^{3+}/Au) - (+0.34)$ $E^{\ominus}(Au^{3+}/Au) = +1.50$ V ; $1.25 = +1.50 - E^{\ominus}(Ru^{3+}/Ru^{2+})$ $E^{\ominus}(Ru^{3+}/Ru^{2+}) = +0.25$ V ; working ;	
		(iii)	Hence using your answer in **(e)(ii)** and relevant data from the Data Booklet, state and explain whether Ru^{3+} is able to act as a homogenous catalyst for the reaction between $S_2O_8^{2-}$ and I^-. $S_2O_8^{2-}(aq) + 2I^-(aq) \rightarrow 2SO_4^{2-}(aq) + I_2(aq)$ ………………………………………………………………………………………… ………………………………………………………………………………………… ………………………………………………………………………………………… ………………………………………………………………………………………… [3]	
			$Ru^{3+} + e^- \rightleftharpoons Ru^{2+}$ +0.25 V $I_2 + 2e^- \rightleftharpoons 2I^-$ +0.54 V ; $2Ru^{3+} + 2I^- \rightarrow 2Ru^{2+} + I_2$ $E^{\ominus}_{cell} = +0.25 - 0.54 = -0.29$ V ; $E^{\ominus}_{cell} < 0$ hence reaction is not feasible and Ru^{3+} cannot be a catalyst;	
	(f)	Pyridine and phenylamine are two nitrogen-containing compounds.		



pyridine
pK_b = 8.75



phenylamine
pK_b = 9.33

Pyridine has a resonance structure with six p electrons delocalised over the ring. The molecule is planar, with all atoms forming the ring being sp^2 hybridised. The lone pair of electrons on nitrogen occupies one of its sp^2 hybrid orbitals.

With reference to the shape and orientation of the orbitals about the nitrogen atom in both compounds, suggest why pyridine has a lower pK_b value.

…………………………………………………………………………………………

…………………………………………………………………………………………

…………………………………………………………………………………………

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

The lone pair on N atom of phenylamine is in the p-orbital which lies perpendicular to the benzene plane hence able to delocalise into the ring.

The lone pair on N atom of pyridine is in the sp^2 hybrid orbital which lies on the same plane as the benzene ring hence unable to delocalise into the ring.

The lone pair on N atom of pyridine is more available for protonation hence it is a stronger base and therefore has a lower pK_b value.

2 **(a)** Upon heating at 160 °C, magnesium ethanoate decomposes to give magnesium carbonate and propanone as the products.

$$(CH_3COO)_2Mg \rightarrow MgCO_3 + CH_3COCH_3$$

Upon further heating, $MgCO_3$ undergoes further decomposition.

(i) Write an equation for the decomposition of $MgCO_3$.

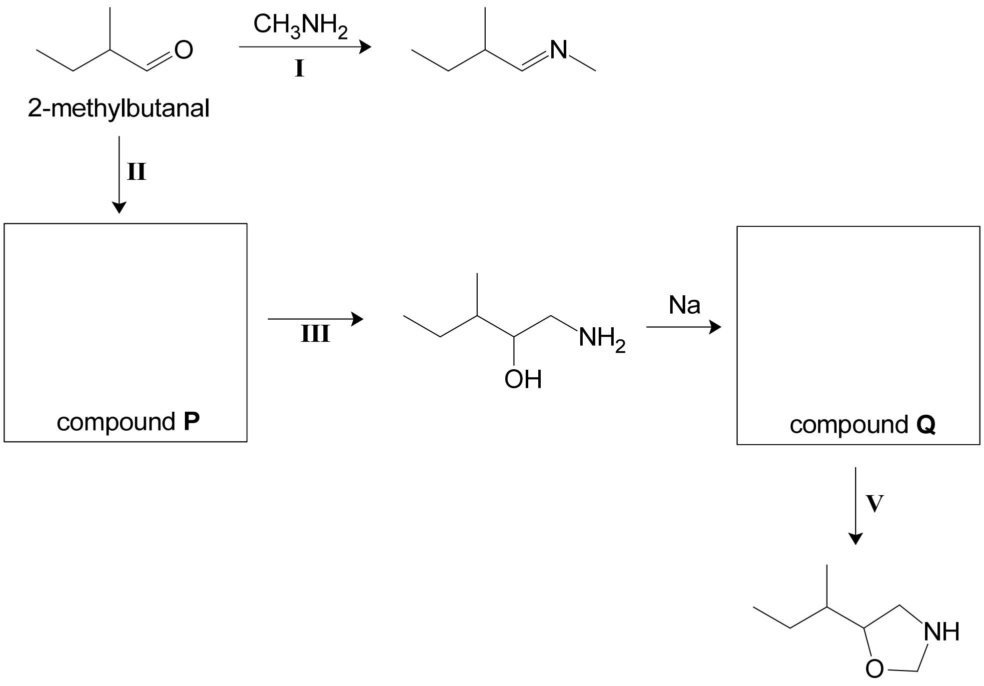
…………………………………………………………………………………[1]

$MgCO_3 \rightarrow MgO + CO_2$

When barium propanoate, $(CH_3CH_2COO)_2Ba$ was heated until constant mass, it was found that $BaCO_3$ and an organic compound **X**, $C_5H_{10}O$, were obtained. Despite further heating, $BaCO_3$ did not undergo decomposition.

When 2,4-dinitrophenylhydrazine was added to compound **X**, an orange precipitate was observed. Compound **X** did not give yellow precipitate with warm aqueous alkaline iodine.

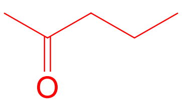
		(ii)	Explain why $MgCO_3$ undergoes thermal decomposition more readily than $BaCO_3$. ………………………………………………………………………………………... ………………………………………………………………………………………... …………………………………………………………………………………….. [2]	
			Mg^{2+} has a smaller ionic radius hence a higher charge density, its higher polarising power allows it to distort the electron cloud of carbonate to a greater extent. The C-O bond in $MgCO_3$ is weakened to a greater extent hence more easily decomposed.	
		(iii)	Suggest the structure of **X**. [1]	
			$CH_3CH_2COCH_2CH_3$	
		(iv)	Write a balanced chemical equation for the decomposition of barium propanoate. ……………………………………………………………………………………..[1]	
			$(CH_3CH_2COO)_2Ba \rightarrow BaCO_3 + CH_3CH_2COCH_2CH_3$	
		(v)	Suggest why barium propanoate undergoes thermal decomposition more readily than barium carbonate. ………………………………………………………………………………………. ………………………………………………………………………………………... ……………………………………………………………………………………….[2]	
			Propanoate ion has a larger electron cloud size ; hence it is more easily polarised ;	
	(b)	The scheme below shows the reactions of 2-methylbutanal.		

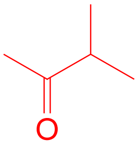


(i) **R** is a constitutional isomer of 2-methylbutanal. **R** gives yellow precipitate when warmed with aqueous iodine in an alkaline medium. **R** does not decolourise aqueous bromine.

Draw the skeletal formulae of **two** possible structures of **R**.

[2]





;;

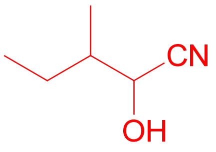
(ii) Draw the structure of compounds **P** and **Q** in the boxes provided in the reaction scheme and state the reagents and conditions for steps **II**, **III** and **V**.

Step	**Reagents and Conditions**
II	
III	

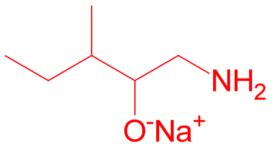
V	

[5]

Step	Reagents and Conditions
II	cold HCN, trace NaCN or NaOH
III	$LiAlH_4$ in dry ether
V	CH_2Cl_2



P



Q

(iii) Suggest the type of reaction undergone by 2-methylbutanal in step **I**.

……………………………………………………………………………………….[1]

condensation

3 **(a)** Cyanogen is a colourless yet extremely poisonous gas that is used in fumigation. Cyanogen is made up of carbon and nitrogen only, of which 46.2% is composed of carbon by mass.

At 30°C and 1 bar, 1.03 g of cyanogen occupies 0.500 dm^3. It dissolves readily in water.

Calculate the molecular formula of cyanogen.

[3]

	C	N
% by mass	46.2	53.8
A_r	12.0	14.0
Amount	3.85	3.84
Ratio	1	1

EF: CN (;)

pV=nRT

$10^5 \times 0.5 \times 10^{-3} = n(8.31)(303)$

n= 0.01986 mol

$n = \frac{mass}{Mr} = \frac{1.03}{Mr} = 0.01986$

$M_r = 51.87$ (;)

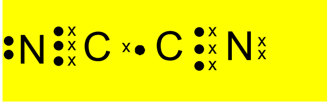
MF = $(CN)_y$

$y = \frac{51.87}{12+14} = 2$

MF: $(CN)_2$ (;)

(b) Draw the ‘dot-and-cross’ diagram of the cyanogen molecule and suggest the shape of the molecule with respect to the central atom.

Shape: ……………………………………… [2]



(;)

Shape: linear(;)

(c) Explain, in terms of bonding, why cyanogen dissolves readily in water.

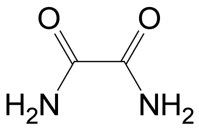
…………………………………………………………………………………………..…

……………………………………………………………………………………………..

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

Energy given out from the formation of hydrogen bonding between cyanogen and water (;) is sufficient to overcome the instantaneous dipole-induced dipole between cyanogen molecules(;) and hydrogen bonding between water molecules.

(d) Oxamide is manufactured from cyanogen by hydrolysis that only involves water.



Oxamide

(i) Write the balanced equation for the reaction of manufacturing oxamide from cyanogen and water. You may use the molecular formula of oxamide in your equation.

…………………………………………………………………………………….[1]

$(CN)_2 + 2\ H_2O \rightarrow H_2NC(O)C(O)NH_2$

(ii) With the use of Data Booklet, calculate the enthalpy change of the reaction in **(d)(i)**.

[2]

ΔH_{rxn} = 890x2+ 350 + 4(460) – [4(390) + 2(305) +2(740) +350](;)

= -30.0 kJ mol^{-1}(;)

(iii) The entropy change for the reaction in **(d)(i)** is +64.1 J mol^{-1} K^{-1}. Use your answer in **(d)(ii)** to calculate ΔG at 298 K. Hence predict if the reaction is spontaneous at 298 K.

[2]

ΔG_{rxn} = -30 – 298(+64.1x10^{-3}) = -49.1 kJ mol^{-1} (;)

$\Delta G_{rxn} < 0$ The reaction is spontaneous at 298 K (;)

4 **(a)** A bottle of supplement has the following nutritional information.

The serving size is 42.5g and each bottle contains 20 servings.

	Each serving contains	% of Recommended Daily Allowance
Total fat	3 g	5
Dietary Fibre	6 g	24
Protein	15 g	30
Calcium	546 mg	47
Iron	9 mg	43
Iodine	80 μg	48
Vitamin C	30 mg	52
Vitamin K	40 μg	51

A student weighed out 75 g portion of this supplement and crushed it in a pestle and mortar to form a powder. She then added it to 100 cm^3, an excess, of 1.5 mol dm^{-3} sulfuric acid, stirred it and then filtered it.

She made the volume up to 250 cm^3 forming solution **A**. Finally, she titrated a 25.0 cm^3 portion of solution **A** with 1.8 x 10^{-4} mol dm^{-3} potassium dichromate(VI).

(i) Use the *Data Booklet* to construct an ionic equation for the reaction between Fe^{2+} in solution **A** and dichromate(VI) ions.

…………………………………………………………………………………………[1]

$6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \rightarrow 2Cr^{3+} + 7H_2O + 6Fe^{3+}$

(ii) Calculate the volume of potassium dichromate(VI) solution that would be required to react with Fe^{2+} in 25.0 cm^3 of solution **A**.

[3]

Mass of Fe^{2+} in 75 g serving = $\frac{75}{42.5} \times 9$ = 15.88 mg

Amount of Fe^{2+} in 75 g serving = $\frac{15.88\times10^{-3}}{55.8}$ = 0.0002846 mol (;)

[Fe^{2+}] in solution **A** = $\frac{0.0002846}{\frac{250}{1000}}$ = 0.001138 mol dm^{-3}

Amount of Fe^{2+} in 25 cm^3 of solution **A** = $\frac{25}{1000} \times 0.001138$ = 0.00002846 mol (;)

Amount of $Cr_2O_7^{2-}$ to titrate with 25 cm^3 of solution **A** = $\frac{0.00002846}{6}$ = 0.000004744 mol

Volume of $Cr_2O_7^{2}$ = $\frac{0.000004744}{1.8\times10^{-4}}$ = 26.4 cm^3

(b) Overdosage of iodine has many side-effects, including abdominal pain, delirium, fever, vomiting, and shortness of breath.

Assuming that a person does not consume any other food that contains iodine other than the supplement and a serving refers to 5 tablets, deduce if it is within the % daily recommended allowance for him to consume as many as 11 tablets in a single day. Justify with calculations.

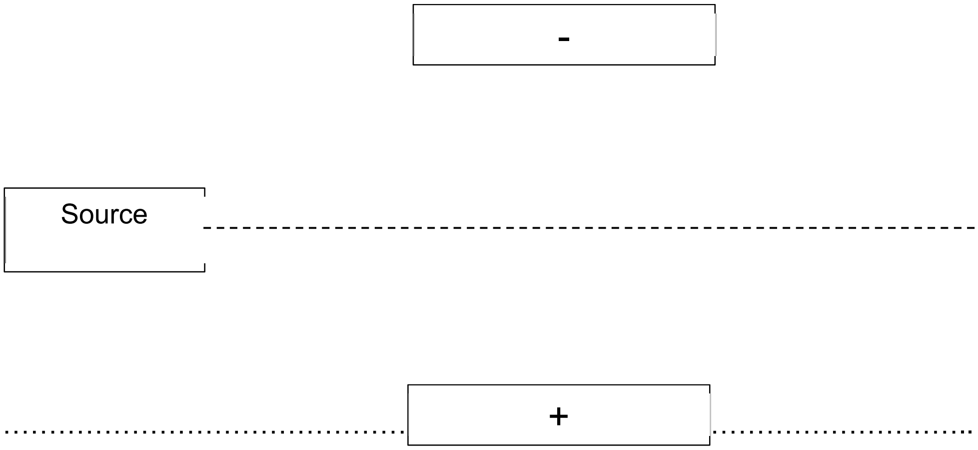
[3]

Daily recommended allowance of iodine= $80 \div \frac{48}{100}$ = 166.7 μg (;)

No of tablets within daily recommended allowance = $\frac{166.7}{80} \times 5$ = 10.4 (;)

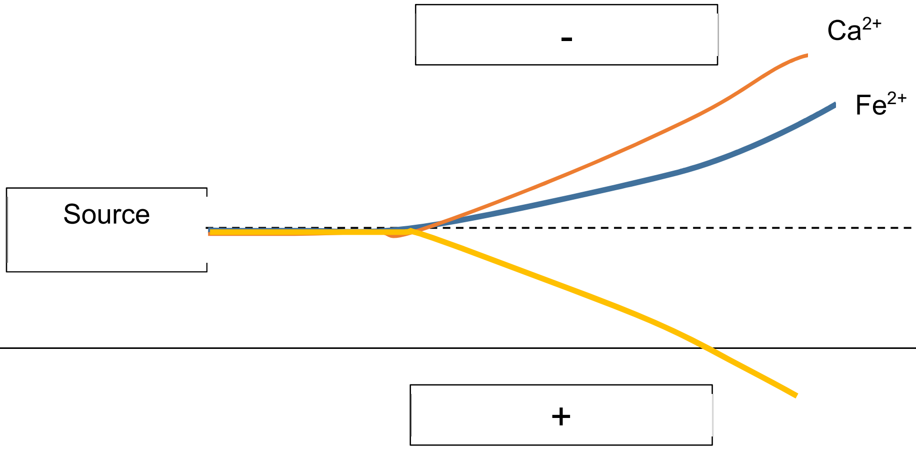
It is not within the % daily recommended allowance. (;)

(c) The iodine, calcium and iron content in the supplement is dissolved in water, forming ions. The ions are then isolated. Indicate on the diagram below how a beam of particles containing the three species, travelling at the same speed, behave in the same electric field. State your reasoning.

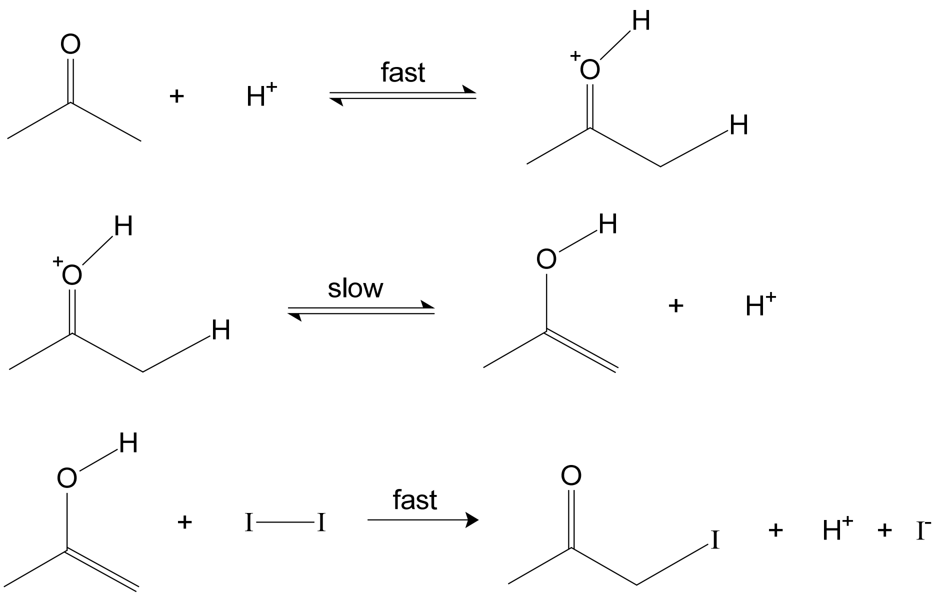


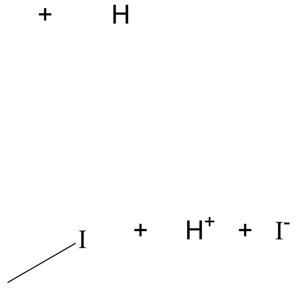
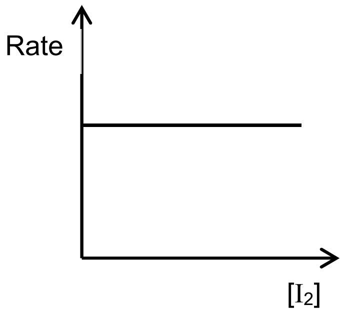
.... [5]

[Total: 12 marks]



		I^- Iodide is an anion while Ca^{2+} and Fe^{2+} are cations. Thus anion will be deflected towards the positively charged plate while the cations will be deflected towards the negatively charged plate(;) Based on charge/mass ratio, Fe^{2+} will have a smaller magnitude as it has a larger A_r, thus the angle of deflection will be smaller.(;)	

5	**(a)**	Propanone reacts with iodine in the presence of an acid catalyst. $CH_3COCH_3(aq) + I_2(aq) \rightarrow CH_3COCH_2I(aq) + H^+(aq) + I^-(aq)$ The mechanism of this reaction is thought to be as follows: 	
		(i) On the mechanism shown, draw curly arrows and lone pair of electrons to show the movement of electrons in each of the step. [3]	

			 [1] per step ;;;	
		(ii)	Based on the mechanism above, write the rate equation for this reaction. ……………………………………………………………………………………..[1]	
			Rate = k[CH_3COCH_3][H^+]	
		(iii)	Hence, sketch the graph of rate against [I_2] [1]	
				

(b) 5.0 cm^3 of the reaction mixture was taken out when the reaction has proceeded for 30 seconds. The resultant solution was then made up to 100 cm^3 in a volumetric flask. 25.0 cm^3 portions of this solution were then titrated with 0.100 mol dm^{-3} of aqueous potassium thiosulfate, $K_2S_2O_3$, with the addition of starch solution. The results are shown below.

	1	2	3
Initial burette reading / cm^3	0.00	19.95	2.05
Final burette reading / cm^3	19.90	40.05	22.15
Volume of titre / cm^3	19.90	20.10	20.10

(i) Write the ionic equation for the reaction between potassium thiosulfate and iodine in the solution.

……………………………………………………………………………………….[1]

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

(ii) Use the above results to determine the concentration of iodine in the original 5.0 cm^3 of the aliquot taken out at 30 seconds after the reaction has started.

[3]

Average titre volume = $\frac{20.10 + 20.10}{2}$ = 20.10 cm^3 (;)

Amount of $S_2O_3^{2-}$ = $\frac{20.10}{1000} \times 0.100$ = 0.00201 mol

Amount of I_2 in the 25.0 cm^3 solution= 0.00201 / 2 = 0.001005 mol(;)

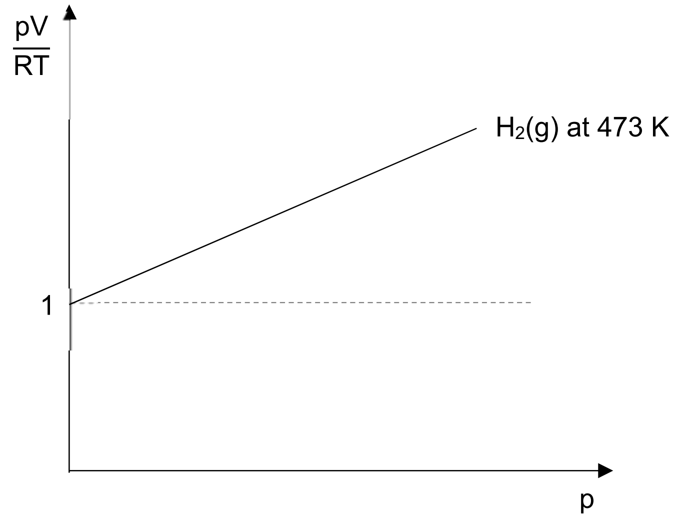
Amount of I_2 in the 100 cm^3 solution= 0.001005 x 4 = 0.00402 mol

$[I_2] = \frac{0.00402}{\frac{5}{1000}} = 0.804 \text{ mol dm}^{-3}$ (;)

(c) The iodine solution was then isolated and boiled to produce $I_2(g)$.

A sketch of $\frac{pV}{RT}$ against p for 1 mole of $H_2(g)$ at 473 K is shown below. On the same axes, sketch the graph of $\frac{pV}{RT}$ against p for 1 mole of $I_2(g)$ at 473 K and for 1 mole of $H_2(g)$ at 500 K. Label your sketch clearly.

Justify the difference in behaviour.



………………………………………………………………………………………………

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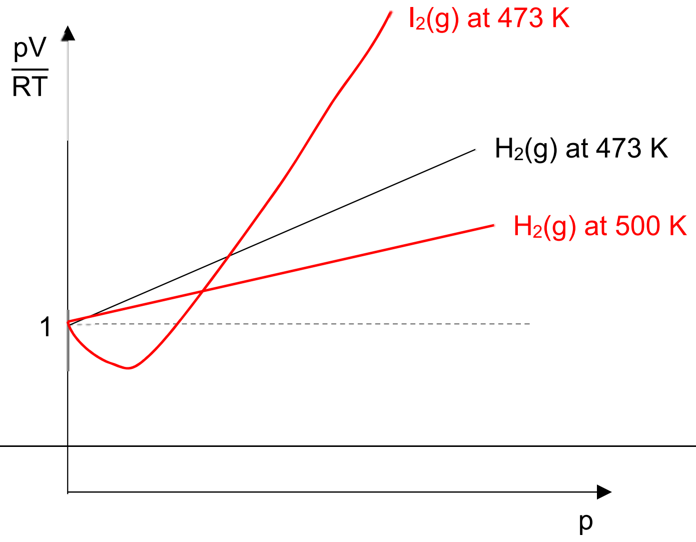
……………………………………………………………………………………………… [4]



		$H_2(g)$ behaves more ideally than $I_2(g)$ as it has a weaker instantaneous dipole-induced dipole forces of attraction between molecules due to smaller size of electron cloud. (;) At higher temperature, $H_2(g)$ has higher kinetic energy and moves more quickly. Thus, the molecules are further away and there will be weaker forces of attraction between them. (;)	
	(d)	Describe all types of interactions found within the lattice structure of solid iodine fully. …………………………………………………………………………………………… …………………………………………………………………………………………… ………………………………………………………………………………………….. [3] [Total: 16 marks]	
		Iodine molecules are held by instantaneous dipole-induced dipole forces of attraction between molecules(;) and strong covalent bonds between iodine atoms within the molecule(;). The covalent bond is the electrostatic forces of attraction between the bond pair and the nuclei of the iodine atoms.(;)	

Class	Adm No

Candidate Name: ____________________

millennia institute

2018 Preliminary Exams
Pre-University 3

H2 CHEMISTRY **9729/03**

Paper 3 Free Response **18th Sept 2018**

2 hours

Candidates answer on separate paper.

Additional materials: Answer Paper
Data Booklet

READ THESE INSTRUCTIONS FIRST

Do not turn over this question paper until you are told to do so

Write your name, class and admission number on all the work you hand in.

Write in dark blue or black pen.

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

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

Section A – Answer **all** questions.

Section B – Answer **one** question.

A Data Booklet is provided.

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

You are reminded of the need for good English and clear presentation in your answers.

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

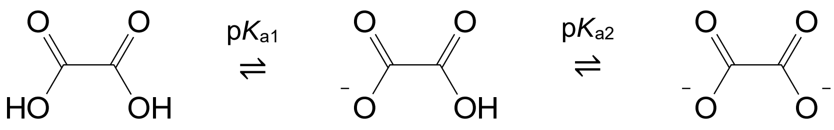
The number of marks is given in brackets [ ] at the end of each question or part question.

Question	Section A			Section B		Total
	1	**2**	**3**	**4**	**5**	
Marks	**23**	**20**	**17**	**20**	**20**	**80**

Section A

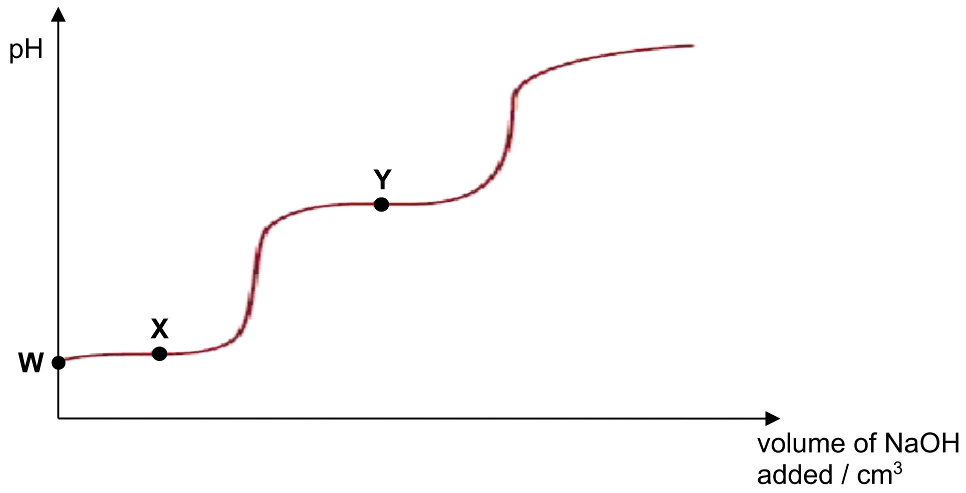
Answer **all** questions from this section.

. Oxalic acid is a weak diprotic Brønsted acid with pK_{a1} and pK_{a2} values of 1.25 and 4.14 respectively.



25 cm^3 of 0.50 mol dm^{-3} oxalic acid was titrated against a solution of 1 mol dm^{-3} of sodium hydroxide. Only 1 to 2 drops of phenolphthalein indicator was used in this titration. It was found that the first colour change occurred at 19.40 cm^3.

A sketch (not drawn to scale) of the pH titration curve is shown below.



(a) Suggest why the value of pK_{a2} is larger than pK_{a1}. [2]

(b) **(i)** Calculate the value of pH at point **W**. [1]

(ii) Given that the pH at point **X** is 1.25, calculate the volume of NaOH added at point **X**. [2]

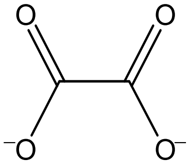
(c) **(i)** Define the term *buffer*. [1]

(ii) Write an equation to illustrate how the reaction mixture found at point **Y** can maintain the pH of a solution when a small amount of OH$^-$(aq) is added. [1]

(d) **(i)** Describe how you would recognise the end point of the titration described. [1]

(ii) Explain why only 1 or 2 drops of phenolphthalein indicator was used in the titration. [1]

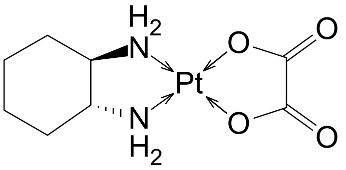
The oxalate ion, $C_2O_4^{2-}$, is known to form complexes with transition metal ions such as platinum(II). The structure of the oxalate ion is as follows.



(e) **(i)** It is observed that a solution of aqueous platinum(II) ions turns universal indicator orange.

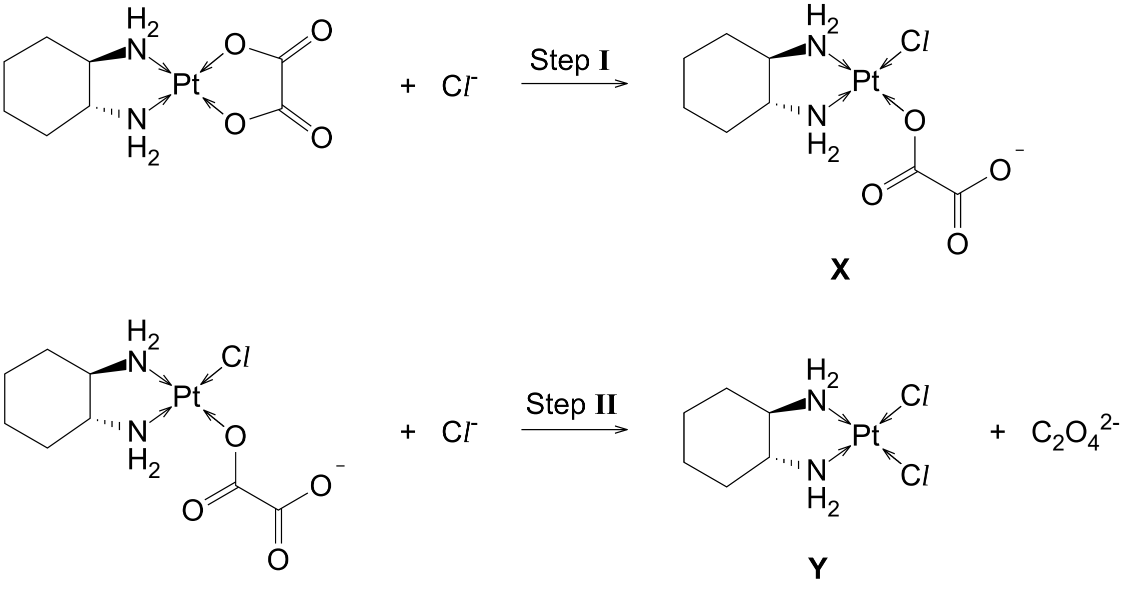
Given that platinum(II) is a transition metal ion known to form **square planar complexes**, explain the observation seen with the aid of a chemical equation. [3]

Oxaliplatin is a platinum(II) based anti-cancer drug used to treat colorectal cancer. It contains one $C_2O_4^{2-}$ ligand.



oxaliplatin

When a **concentrated** Cl^- solution is added to oxaliplatin, ligand exchange occurs and the Cl^- ligands take the place of $C_2O_4^{2-}$ in a two-step reaction.



(ii) By consideration of entropy changes, predict with explanation if Step I is likely to be **feasible** if diluted Cl^- solution was used instead. Assume that Cl^- and $C_2O_4^{2-}$ have the same ligand strength.

State the missing numerical data necessary to confirm your prediction. [2]

(iii) Determine if any the three complexes, oxaliplatin, **X** and/or **Y** can exhibit cis-trans isomerism. Explain your answer. [2]

(iv) Hydrated crystals of complex **Y** have the structural formula $[Pt(C_6H_{14}N_2)Cl_2].2H_2O$.

When excess $AgNO_3$ solution was added to an aqueous solution containing 0.0094 mol of an isomer of $[Pt(C_6H_{14}N_2)Cl_2].2H_2O$, 1.35 g of a white precipitate was obtained.

Determine the structural formula of this isomer. [3]

(f) **(i)** Determine the number of protons, neutrons and electrons in $^{52}Cr^{3+}$. [1]

(ii) State the full electronic configuration of $^{52}Cr^{3+}$. [1]

(iii) Draw and label the d orbitals in the valence shell of $^{52}Cr^{3+}$.

You are required to show the orientation of the orbitals with respect to the x, y and z axes. [2]

[Total: 23]

. **(a)** State the relationship between the Faraday constant, F, the charge on the electron, e, and the Avogadro number, L. [1]

(b) Copper metal containing impurities such as zinc, iron, and silver can be purified via electrolysis.

(i) Draw a **well-labelled** diagram of a suitable set-up for purifying impure copper and state the reaction occurring at the cathode. [3]

A fixed current was passed through the cell for a duration of time to determine the experimental values of F and L. The following are the results obtained.

current passed through the cell	= 0.500 A
duration of time	= 30.0 min
change in mass of cathode	= 0.299 g

(ii) Use the data above and relevant information from the *Data Booklet* to calculate a value of L. [3]

(c) Rechargeable lithium ion batteries have been developed in Japan.

The standard electromotive force of a rechargeable lithium ion battery is 3.70 V. During discharge, Li^+ ions flow from the anode to the cathode through the electrolyte.

During the **discharging** process, the ion-electron equation at the cathode is

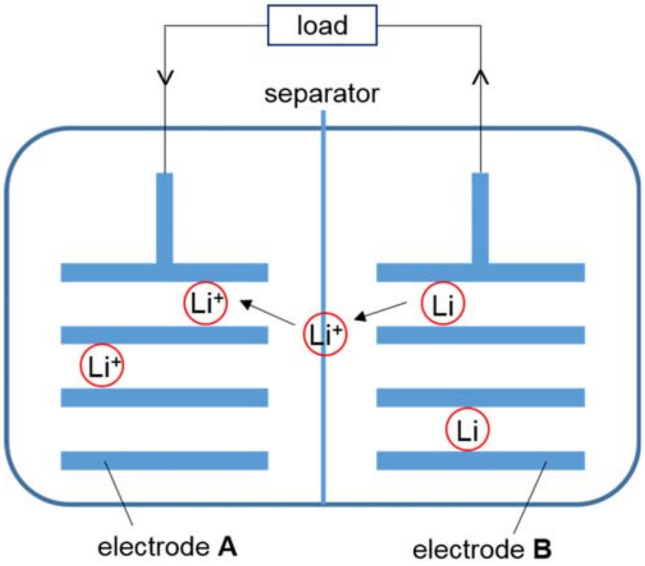
$$CoO_2 + Li^+ + e^- \rightarrow LiCoO_2,$$

and the ion-electron equation at the anode is

$$LiC_6 \rightarrow C_6 + Li^+ + e^-$$

where CoO_2 and graphite, C_6, are *layered* solid electrodes which can have Li^+ ions and Li atoms **embedded between their layers** respectively.

A schematic of the rechargeable lithium ion battery **during discharge** is shown below.



(i) By considering the overall equation of the battery during discharge, calculate a value for the standard Gibbs free energy of the reaction in kJ mol^{-1}. [1]

(ii) A fully charged battery cell starts with 10.0 g of CoO_2 and 10.0 g of LiC_6.

Calculate the mass of electrode **A** when this cell is fully **discharged**. [3]

(iii) The fully discharged cell is plugged into a power source to recharge it. During the charging process, the direction of electron-flow is reversed.

Determine the mass of electrode **B** when the cell is fully **charged**. [1]

(iv) Suggest **two** reasons why water cannot be used as the electrolyte solvent in rechargeable lithium ion batteries. [2]

(v) Rechargeable lithium ion batteries tend to perform poorly when used in cold countries. Suggest a reason for this. [1]

(d) Lithium oxide is a white solid that is used to lower the melting point of ceramic glazes.

(i) Write an equation, with state symbols, to represent the lattice energy of lithium oxide. [1]

(ii) Use the following data, together with appropriate data from the *Data Booklet*, to calculate a value for the lattice energy of lithium oxide.

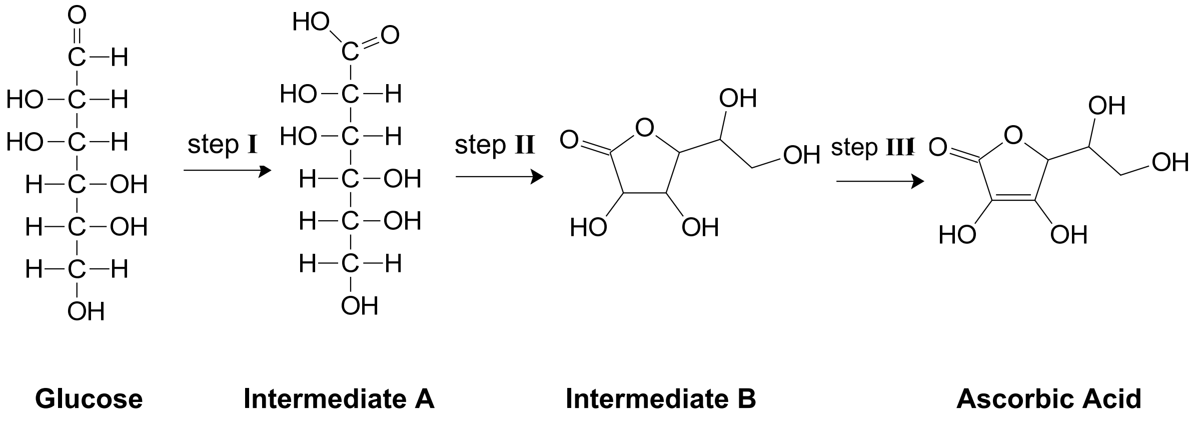
1st electron affinity of oxygen = -141.1 kJ mol^{-1}
2nd electron affinity of oxygen = +798 kJ mol^{-1}
enthalpy change of atomisation of lithium = +159.4 kJ mol^{-1}
enthalpy change of formation of lithium oxide = -597.9 kJ mol^{-1}

[4]

[Total: 20]

. Ascorbic acid, also known as Vitamin C is required for the synthesis of collagen in humans. A vitamin C deficient diet leads to a disease called scurvy. Ascorbic acid is known to be water soluble and is commonly used as a food additive.

The building block for ascorbic acid is the glucose molecule. The following synthetic pathway for the formation of ascorbic acid was proposed.



(a) State the functional groups present in intermediate **B**. [2]

(b) State the reagent and conditions required for step **II**. [1]

(c) State the type of reaction for steps **I** and **II**. [2]

(d) Identify the type(s) of stereoisomerism shown by ascorbic acid. State the total number of possible stereoisomers. [2]

(e) Explain why ascorbic acid is water soluble. [2]

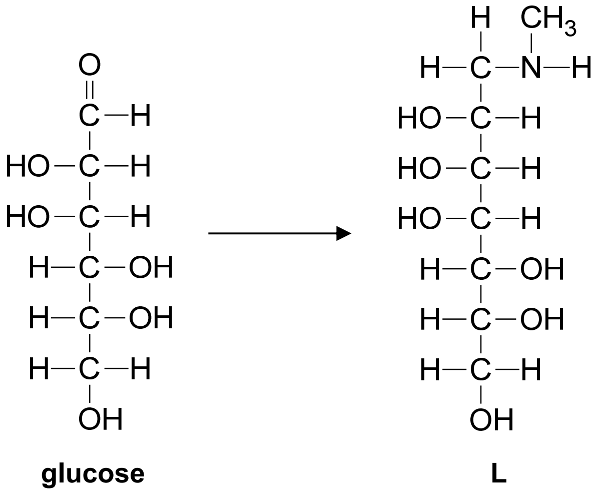
(f) Draw the structural formulae of all the organic products formed when ascorbic acid is treated with the following reagents. [3]

(i) PCl_5

(ii) excess hot acidified $K_2Cr_2O_7$

(iii) Na(s)

(g) Compound **L** can be formed from glucose.



Suggest a synthetic route, involving *not more than three steps*, from **glucose** to **L**.

In your answer, suggest the reagents and conditions involved in each step and draw the structural formulae of the intermediate organic products. You may use R to represent the side chain of the compound that is not involved in the reaction. [5]

[Total: 17]

Section B

Answer **one** question from this section.

. In the chlor-alkali industry, 19.8 g impure sample of NaC*l*(s) was dissolved in 150 cm^3 water to form sodium chloride solution. 50 cm^3 of the solution was electrolysed to produce chlorine, sodium hydroxide, and hydrogen.

$$2NaCl + 2H_2O \rightarrow Cl_2 + 2NaOH + H_2$$

The pure chlorine gas reacts with hydrogen gas to produce 1.8 g of hydrogen chloride gas in the presence of ultraviolet light.

(a) **(i)** Write an equation to show the production of hydrogen chloride gas. [1]

(ii) Explain why ultraviolet light is required in the production of hydrogen chloride. [1]

(iii) State the type of mechanism for the reaction between chlorine gas and hydrogen gas.[1]

(iv) Calculate the number of hydrogen chloride molecules produced at room temperature and pressure. [1]

(v) Calculate the percentage of sodium chloride present in the impure solid, assuming that all of the chlorine gas and hydrogen gas had reacted. [3]

(b) Hydrogen chloride gas can also be produced by the reaction between concentrated sulfuric acid and dilute hydrochloric acid.

State the role of concentrated sulfuric acid. [1]

(c) Explain why hydrogen chloride has a lower boiling point than hydrogen bromide. [2]

(d) When an equimolar mixture of gaseous ammonia and gaseous hydrogen chloride at an initial total pressure of 2.5 atm was injected into a chamber maintained at 400 °C, white crystals of ammonium chloride were formed as shown in the following dynamic equilibrium:

$$NH_3(g) + HCl(g) \rightleftharpoons NH_4Cl(s) \qquad \Delta H > 0$$

It was found that 84% of the gases had dissociated at equilibrium.

(i) Define the term *dynamic equilibrium*. [1]

(ii) Write an expression for the equilibrium constant, K_p, for this reaction. [1]

(iii) Calculate the value of K_p at 400 °C, giving its units. [2]

(iv) State and explain how the partial pressure of the gases and the value of K_p would change if the following changes were made separately:

I. the temperature of the chamber was halved to 200 °C
II. the volume of the chamber was increased (at constant temperature)
III. 2 atm of neon gas is inserted into the chamber [6]

[Total: 20]

. **(a)** The reaction between propanone, CH_3COCH_3, and bromine, Br_2, in the presence of acid, H^+, is found to have an overall order of reaction of 2.

(i) Given that rate is independent of the bromine concentration, write **three** possible rate expressions for this reaction. [3]

(ii) Three separate experiments were carried out. In each experiment, the concentration of one of the three different reactants was doubled respectively.

Predict the effect of doubling the concentration of each reactant on the rate of reaction for the **first** rate expression you have written in **(a)(i)**. [2]

(iii) The table below shows how the concentration of propanone changes with time in a reaction.

Time / min	[propanone] / mol dm^{-3}
5.0	1.6
7.0	1.4
9.0	1.2
12.0	1.0
15.0	0.8
18.5	0.6
21.5	0.5
25.0	0.4
28.0	0.3
35.0	0.2

Without plotting a graph, use the data given in the table to confirm that the reaction is first order with respect to propanone. Show your working clearly. [2]

(iv) The overall reaction described in **(a)** is:

$$CH_3COCH_3(aq) + Br_2(aq) \xrightarrow{H^+} CH_3COCH_2Br(aq) + HBr(aq)$$

State **one** dependent variable that you can readily measure in order to follow the progress of the reaction. [1]

(v) State and explain the role of acid in this overall reaction. [2]

(b) Similar to bromine, halogens like fluorine and chlorine are not naturally found in their elemental form due to their high reactivity.

(i) State and explain the trend in atomic radius down the halogen group. [2]

(ii) By citing relevant values from the *Data Booklet*, deduce and explain the relative reactivity of the halogens as oxidising agents. [2]

(iii) Describe **one** chemical test to illustrate the relative reactivity of any two halogens as oxidising agents. Clearly state any observations seen. [1]

(iv) Chlorine reacts explosively with hydrogen to form the hydride of chlorine, hydrogen chloride.

$$H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$$

Using your answer in **(b)(ii)** or otherwise, suggest a reason for the general reactivity of the halogens. [1]

(v) Describe and explain the trend in thermal stability of the halogen hydrides. [2]

(c) Chlorine is able to form an acidic oxide with the formula ClO_2. Another Period 3 element, magnesium, forms a basic oxide with the formula MgO.

(i) Write an equation to show how the oxide ion, O^{2-}, acts as a base in the reaction with water. [1]

(ii) Suggest why ClO_2 is not a basic oxide, unlike MgO. [1]

[Total: 20]

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	Class	Adm No
Candidate Name: ____________________		

2018 Preliminary Exams
Pre-University 3

H2 CHEMISTRY **9729/03**

Paper 3 Free Response

18th Sept 2018

2 hours

Candidates answer on separate paper.

Additional materials: Answer Paper
Data Booklet

READ THESE INSTRUCTIONS FIRST

Do not turn over this question paper until you are told to do so

Write your name, class and admission number on all the work you hand in.

Write in dark blue or black pen.

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

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

Section A – Answer **all** questions.

Section B – Answer **one** question.

A Data Booklet is provided.

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

You are reminded of the need for good English and clear presentation in your answers.

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

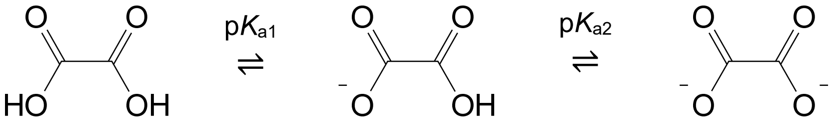
The number of marks is given in brackets [ ] at the end of each question or part question.

Question	**Section A**			**Section B**		Total
	1	**2**	**3**	**4**	**5**	
Marks	/ **23**	/ **20**	/ **17**	/ **20**	/ **20**	/ **80**

Section A

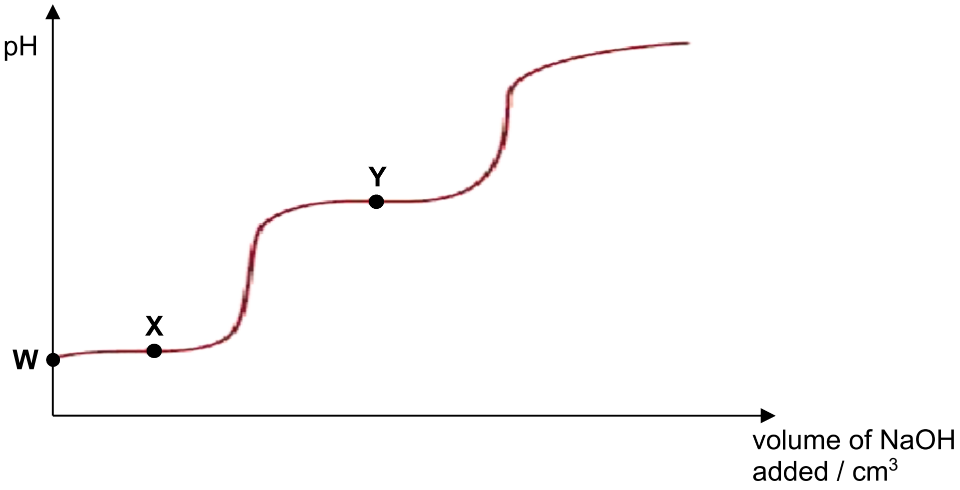
Answer **all** questions from this section.

. Oxalic acid is a weak diprotic Brønsted acid with pK_{a1} and pK_{a2} values of 1.25 and 4.14 respectively.



25 cm^3 of 0.50 mol dm^{-3} oxalic acid was titrated against a solution of 1 mol dm^{-3} of sodium hydroxide. Only 1 to 2 drops of phenolphthalein indicator was used in this titration. It was found that the first colour change occurred at 19.40 cm^3.

A sketch (not drawn to scale) of the pH titration curve is shown below.



(a) Suggest why the value of pK_{a2} is larger than pK_{a1}. [2]

Removal of H^+ for pK_{a2} is from a negatively charged species while that for pK_{a1} is from a neutral species, hence dissociation for pK_{a2} is more difficult / $(COOH)COO^-$ is less acidic than $(COOH)_2$ and the value of pK_{a1} is larger.

or

The first conjugate base of oxalic acid is stabilised by an intramolecular ion-dipole interaction with the OH group of $(COOH)COO^-$, hence dispersing the negative charge to a greater degree and increasing the acid strength. Thus the first pK_a value is smaller than the second pK_a as the second conjugate base formed does not have this extra stability.

(b) **(i)** Calculate the value of pH at point **W**. [1]

$[H^+] = \sqrt{(10^{-1.25})(0.50)}$

$= 0.1677$ mol dm^{-3}

pH = 0.776

(ii) Given that the pH at point **X** is 1.25, calculate the volume of NaOH added at point **X**. [2]

Amount of oxalic acid = 0.50 x $\frac{25}{1000}$
= 0.0125 mol

pH = pK_{a1} + log $\left(\frac{[\text{salt}]}{[\text{acid}]}\right)$

Let x be the amount of salt (COOH)COO⁻, which is also the amount of NaOH added.

1.25 = 1.25 + $\log\left(\frac{x/V}{(0.0125-x)/V}\right)$

$\frac{x}{0.0125-x}$ = 1

x = 0.00625 mol

vol. of NaOH added = $\frac{0.00625}{1}$
= 6.25 cm^3

or

pH = pK_{a1}, **X** is at MBC, which occurs at HEP(1).

Amount of oxalic acid reacted = 0.0125/2 = 0.00625 mol

= Amount of NaOH added

vol. of NaOH added = $\frac{0.00625}{1}$
= 6.25 cm^3

or

Since pH = pK_{a1}, **X** is at MBC, which occurs at HEP(1).

Since EP(1) vol. of NaOH = $\left(\frac{0.0125}{1}\right)$ = 0.0125 dm^3 = 12.5 cm^3

vol. of NaOH added at HEP(1) = 12.5/2 = 6.25 cm^3

(c) **(i)** Define the term *buffer*. [1]

A buffer is a solution which is able to resist pH changes when small quantities of acid or base are added.

(ii) Write an equation to illustrate how the reaction mixture found at point **Y** can maintain the pH of a solution when a small amount of $OH^-(aq)$ is added. [1]

$(COOH)COO^- + OH^- \rightarrow (COO^-)COO^- + H_2O$

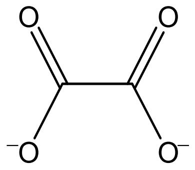
(d) **(i)** Describe how you would recognise the end point of the titration described. [1]

Colourless solution turns pale pink.

(ii) Explain why only 1 or 2 drops of phenolphthalein indicator was used in the titration. [1]

Indicators are weak acids/bases. Addition of more indicator could cause a significant change in the pH of the solution, affecting the accuracy of the titration.

The oxalate ion, $C_2O_4^{2-}$, is known to form complexes with transition metal ions such as platinum(II). The structure of the oxalate ion is as follows.



(e) **(i)** It is observed that a solution of aqueous platinum(II) ions turns universal indicator orange.

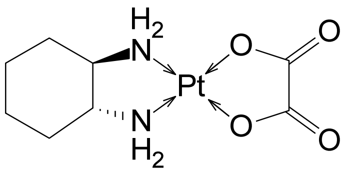
Given that platinum(II) is a transition metal ion known to form **square planar complexes**, explain the observation seen with the aid of a chemical equation. [3]

In water, Pt^{2+} exists as the tetraaqua complex $[Pt(H_2O)_4]^{2+}$

$[Pt(H_2O)_4]^{2+} \rightarrow [Pt(H_2O)_3(OH)]^{+} + H^{+}$

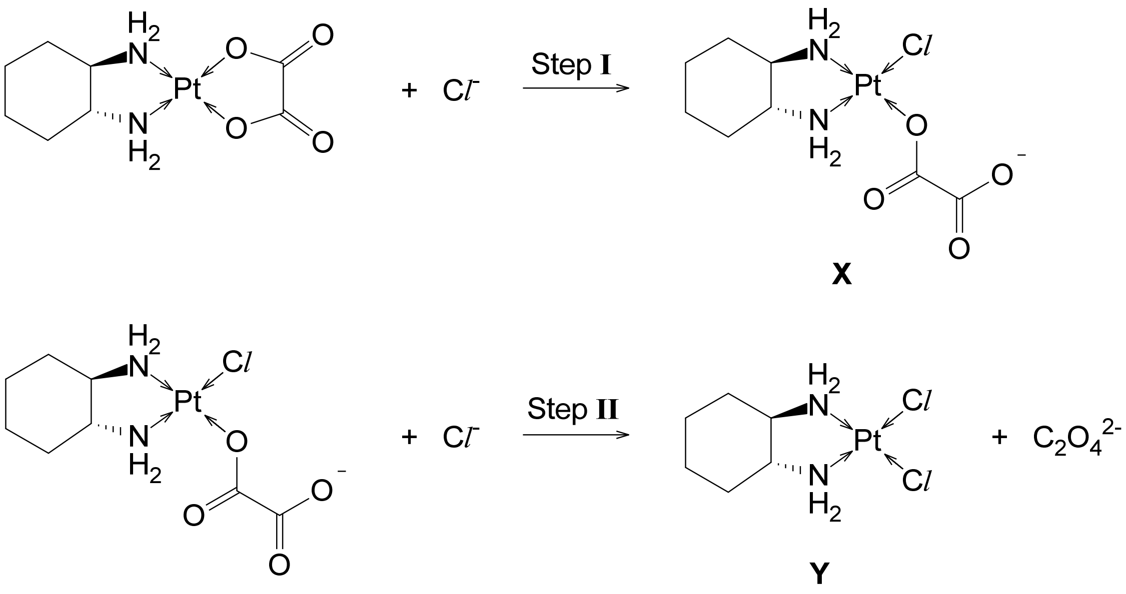
Transition metal ions such as Pt have a high charge density and can polarise the H_2O ligands to release H^+, making the solution acidic.

Oxaliplatin is a platinum(II) based anti-cancer drug used to treat colorectal cancer. It contains one $C_2O_4^{2-}$ ligand.



oxaliplatin

When a **concentrated** Cl^- solution is added to oxaliplatin, ligand exchange occurs and the Cl^- ligands take the place of $C_2O_4^{2-}$ in a two-step reaction.



(ii) By consideration of entropy changes, predict with explanation if Step **I** is likely to be **feasible** if diluted Cl^- solution was used instead. Assume that Cl^- and $C_2O_4^{2-}$ have the same ligand strength.

State the missing numerical data necessary to confirm your prediction. [2]

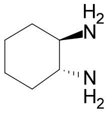
Not feasible, as entropy change of the ligand exchange reaction is negative / reaction is entropically disfavoured due to a decrease in the number of particles.

Enthalpy change of the ligand exchange reaction.

accept ΔG; BE(Pt-Cl) and BE(Pt-O)

(iii) Determine if any the three complexes, oxaliplatin, **X** and/or **Y** can exhibit cis-trans isomerism. Explain your answer. [2]

None of the three complexes can exhibit cis-trans isomerism.

The bidentate  ligand cannot be forced into a trans conformation. *OWTTE*

(iv) Hydrated crystals of complex **Y** have the structural formula $[Pt(C_6H_{14}N_2)Cl_2].2H_2O$.

When excess $AgNO_3$ solution was added to an aqueous solution containing 0.0094 mol of an isomer of $[Pt(C_6H_{14}N_2)Cl_2].2H_2O$, 1.35 g of a white precipitate was obtained.

Determine the structural formula of this isomer. [3]

Amount of AgCl = 1.35 / (107.9+35.5) = 0.009414 mol
= Amount of free Cl^-

∴ 1 mol of isomer contains 1 mol of free Cl^-.

$[Pt(C_6H_{14}N_2)(Cl)(H_2O)]^+Cl^-.H_2O$

(f) **(i)** Determine the number of protons, neutrons and electrons in $^{52}Cr^{3+}$. [1]

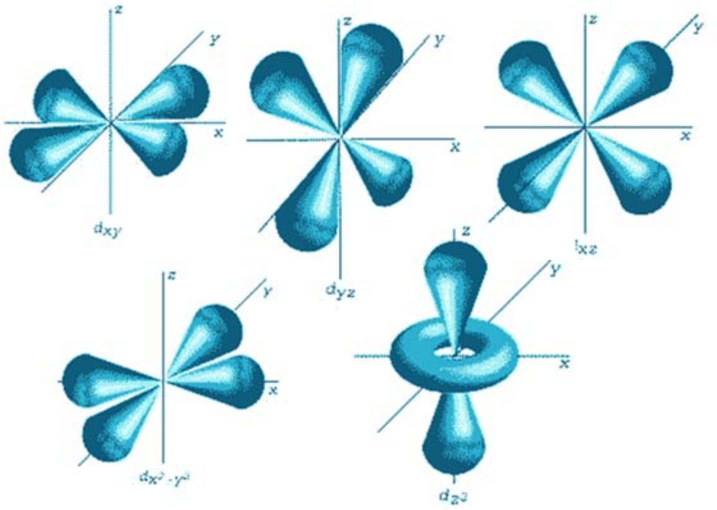
24 protons, 28 neutrons, 21 electrons

(ii) State the full electronic configuration of $^{52}Cr^{3+}$. [1]

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

(iii) Draw and label the d orbitals in the valence shell of $^{52}Cr^{3+}$.

You are required to show the orientation of the orbitals with respect to the x, y and z axes. [2]



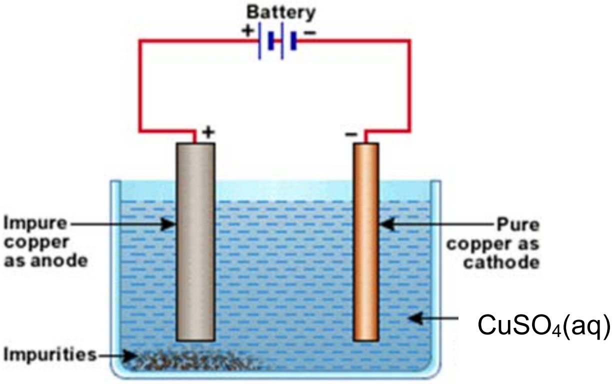
[Total: 23]

. **(a)** State the relationship between the Faraday constant, *F*, the charge on the electron, *e*, and the Avogadro number, *L*. [1]

F = Le

(b) Copper metal containing impurities such as zinc, iron, and silver can be purified via electrolysis.

(i) Draw a **well-labelled** diagram of a suitable set-up for purifying impure copper and state the reaction occurring at the cathode. [3]



Cathode reaction: $Cu^{2+}(aq) + 2e \rightarrow Cu(s)$

A fixed current was passed through the cell for a duration of time to determine the experimental values of *F* and *L*. The following are the results obtained.

current passed through the cell	= 0.500 A
duration of time	= 30.0 min
change in mass of cathode	= 0.299 g

(ii) Use the data above and relevant information from the *Data Booklet* to calculate a value of *L*. [3]

Q= It = 0.500 x 30.0 x 60 = 900C

Amount of copper deposited = 0.299 / 63.5 = 0.004709 mol
$Cu^{2+} + 2e^- \rightarrow Cu$
Amount of e^- = 0.004709 x 2 = 0.00942 mol
Q = nF
F = 900 / 0.00942 = 95568.5

F= Le
L = 95568.5 / 1.602×10^{-19} = 5.97×10^{23} (3 sf)

(c) Rechargeable lithium ion batteries have been developed in Japan.

The standard electromotive force of a rechargeable lithium ion battery is 3.70 V. During discharge, Li^+ ions flow from the anode to the cathode through the electrolyte.

During the **discharging** process, the ion-electron equation at the cathode is

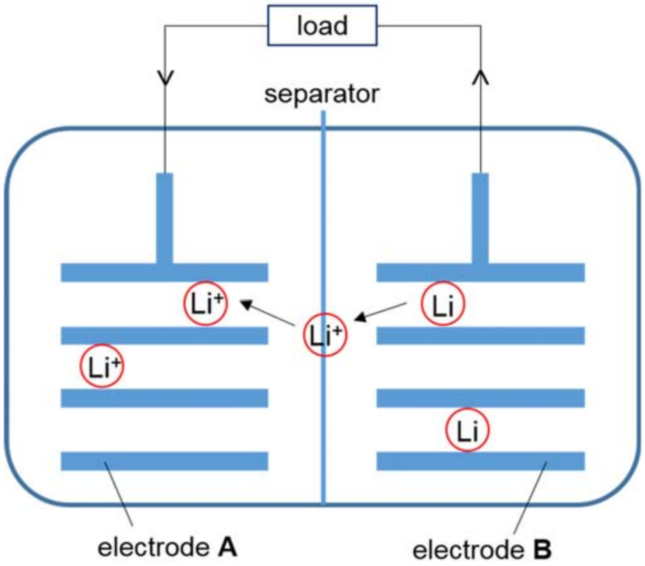
$$CoO_2 + Li^+ + e^- \rightarrow LiCoO_2,$$

and the ion-electron equation at the anode is

$$LiC_6 \rightarrow C_6 + Li^+ + e^-$$

where CoO_2 and graphite, C_6, are *layered* solid electrodes which can have Li^+ ions and Li atoms **embedded between their layers** respectively.

A schematic of the rechargeable lithium ion battery **during discharge** is shown below.



(i) By considering the overall equation of the battery during discharge, calculate a value for the standard Gibbs free energy of the reaction in kJ mol^{-1}. [1]

$CoO_2 + Li \rightarrow LiCoO_2$ *or* $CoO_2 + LiC_6 \rightarrow LiCoO_2 + C_6$ [no marks awarded]

$\Delta G = -nFE = -1 \times 96500\ C\ mol^{-1} \times 3.70V = -357\ kJ\ mol^{-1}$

(ii) A fully charged battery cell starts with 10.0 g of CoO_2 and 10.0 g of LiC_6.

Calculate the mass of electrode **A** when this cell is fully **discharged**. [3]

Electrode **A** is CoO_2 / $LiCoO_2$.

Amount of CoO_2 (charged) = 10.0 / [58.9 + 2(16.0)]
= 0.1100 mol

Amount of LiC_6 (charged) = 10.0 / [6.9 + 6(12.0)]
= 0.1267 mol
= Amount of Li^+ available

CoO_2 is the limiting reagent / Li^+ is in excess.

Amount of $LiCoO_2$ (discharged) = 0.1100 mol
Mass of $LiCoO_2$ (discharged) = 0.1100 x [6.9 + 58.9 + 2(16.0)] = 10.8 g (3 sf)

(iii) The fully discharged cell is plugged into a power source to recharge it. During the charging process, the direction of electron-flow is reversed.

Determine the mass of electrode **B** when the cell is fully **charged**. [1]

Electrode **B** is C_6 / LiC_6.
Mass of LiC_6 = 10.0 g ;

(iv) Suggest **two** reasons why water cannot be used as the electrolyte solvent in rechargeable lithium ion batteries. [2]

1. Water will undergo electrolysis to produce H_2 and O_2
2. Lithium reacts violently with water

(v) Rechargeable lithium ion batteries tend to perform poorly when used in cold countries. Suggest a reason for this. [1]

Rate of reaction / discharge / flow of ions is lowered when temperature decreases.

(d) Lithium oxide is a white solid that is used to lower the melting point of ceramic glazes.

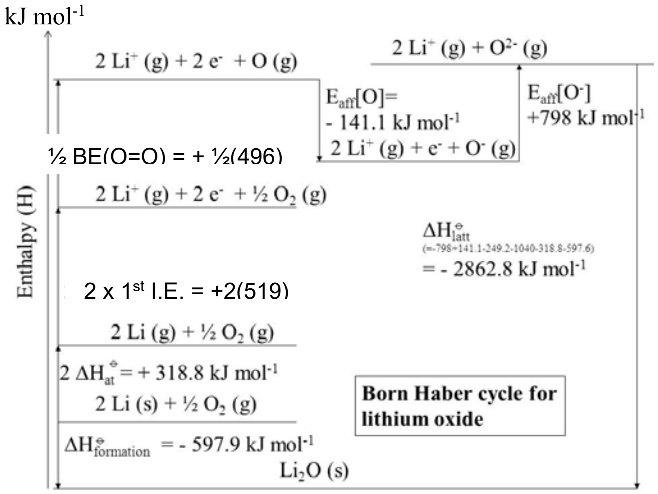
(i) Write an equation, with state symbols, to represent the lattice energy of lithium oxide. [1]

$2Li^+(g) + O^{2-}(g) \rightarrow Li_2O(s)$

(ii) Use the following data, together with appropriate data from the *Data Booklet*, to calculate a value for the lattice energy of lithium oxide.

1st electron affinity of oxygen = -141.1 kJ mol^{-1}
2nd electron affinity of oxygen = +798 kJ mol^{-1}
enthalpy change of atomisation of lithium = +159.4 kJ mol^{-1}
enthalpy change of formation of lithium oxide = -597.9 kJ mol^{-1}

[4]

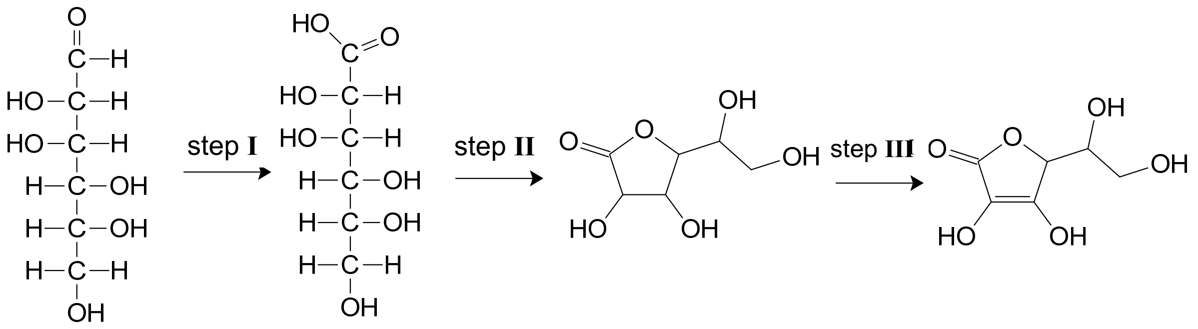


L.E. = -798 – (-141.1) – ½(496) – 2(519) – 2(159.4) + (-597.9)
= -2859.6 kJ mol^{-1}
= -2860 kJ mol^{-1} (3 sf)

[Total: 20]

. Ascorbic acid, also known as Vitamin C is required for the synthesis of collagen in humans. A vitamin C deficient diet leads to a disease called scurvy. Ascorbic acid is known to be water soluble and is commonly used as a food additive.

The building block for ascorbic acid is the glucose molecule. The following synthetic pathway for the formation of ascorbic acid was proposed.



Glucose **Intermediate A** **Intermediate B** **Ascorbic Acid**

(a) State the functional groups present in intermediate **B**. [2]

Ester, 2^0 alcohol, 1^0alcohol

(b) State the reagent and conditions required for step **II**. [1]

Conc. H_2SO_4, heat

(c) State the type of reaction for steps **I** and **II**. [2]

Step I: oxidation

Step II: condensation / nucleophilic (acyl) substitution

(d) Identify the type(s) of stereoisomerism shown by ascorbic acid. State the total number of possible stereoisomers. [2]

Enantiomerism.

total number of possible stereoisomers = $2^2 = 4$

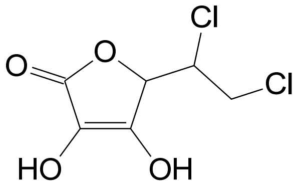
(e) Explain why ascorbic acid is water soluble. [2]

Energy released from the hydrogen bonding between ascorbic acid and water

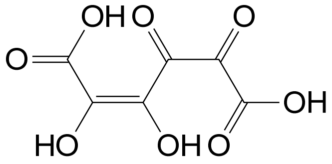
is sufficient to overcome the hydrogen bonding between ascorbic acid molecules and hydrogen bonding between water molecules. Hence, ascorbic acid is water soluble.

(f) Draw the structural formulae of all the organic products formed when ascorbic acid is treated with the following reagents. [3]

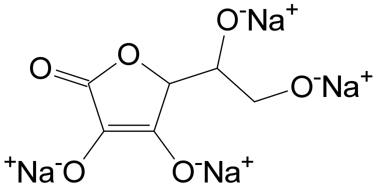
(i) PCl_5



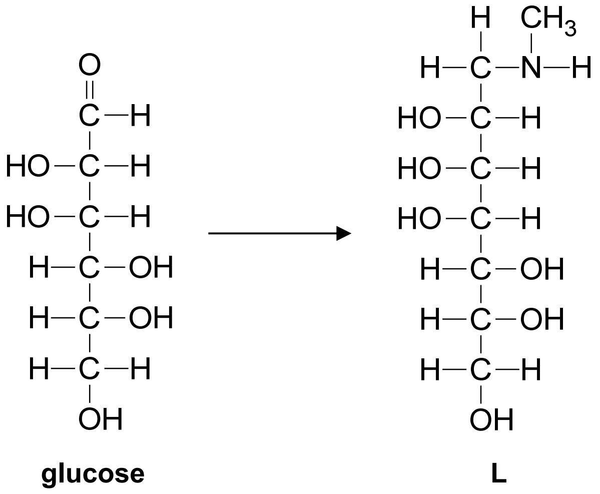
(ii) excess hot acidified $K_2Cr_2O_7$



(iii) Na(s)



(g) Compound **L** can be formed from glucose.



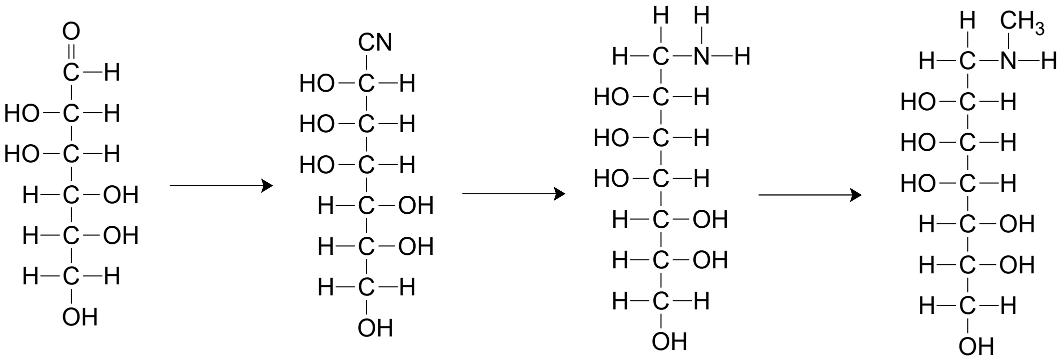
Suggest a synthetic route, involving *not more than three steps*, from **glucose** to **L**.

In your answer, suggest the reagents and conditions involved in each step and draw the structural formulae of the intermediate organic products. You may use R to represent the side chain of the compound that is not involved in the reaction. [5]

Step1: HCN, trace amount of NaOH, cold

Step 2: LiA*l*H_4 in dry ether

Step 3: Limited CH_3Cl, heat



[Total: 17]

Section B

Answer **one** question from this section.

. In the chlor-alkali industry, 19.8 g impure sample of NaCl(s) was dissolved in 150 cm^3 water to form sodium chloride solution. 50 cm^3 of the solution was electrolysed to produce chlorine, sodium hydroxide, and hydrogen.

$$2NaCl + 2H_2O \rightarrow Cl_2 + 2NaOH + H_2$$

The pure chlorine gas reacts with hydrogen gas to produce 1.8 g of hydrogen chloride gas in the presence of ultraviolet light.

(a) **(i)** Write an equation to show the production of hydrogen chloride gas. [1]

$Cl_2 + H_2 \rightarrow 2HCl$

(ii) Explain why ultraviolet light is required in the production of hydrogen chloride. [1]

Ultraviolet light provides sufficient energy to break the C*l*-C*l* bond to form the chlorine radicals for the reaction to start.

(iii) State the type of mechanism for the reaction between chlorine gas and hydrogen gas.[1]

Free radical substitution

(iv) Calculate the number of hydrogen chloride molecules produced at room temperature and pressure. [1]

Amount of hydrogen chloride = 1.8/36.5 = 0.0493 mol

Number of hydrogen chloride = 0.0493 x 6.02 x 10^{23} = 2.97 x 10^{22}

(v) Calculate the percentage of sodium chloride present in the impure solid, assuming that all of the chlorine gas and hydrogen gas had reacted. [3]

$HCl : Cl_2 : H_2 : NaCl$

2 : 1 : 1 : 2

Amount of sodium chloride in 50 cm^3 = 0.04931 mol

Amount of sodium chloride in 150 cm^3 = 0.04931 x 3 = 0.1479 mol

Mass of NaCl = 0.1479 x (23.0 + 35.5) = 8.654 g

% purity of NaCl = 8.654/19.8 x 100% = 43.7% (3 sf)

(b) Hydrogen chloride gas can also be produced by the reaction between concentrated sulfuric acid and dilute hydrochloric acid.

State the role of concentrated sulfuric acid. [1]

Dehydrating agent.

(c) Explain why hydrogen chloride has a lower boiling point than hydrogen bromide. [2]

Both HC*l* and HBr have simple molecular structures. HBr has a larger and more polarisable electron cloud / larger number of electrons compared to HC*l*,

thus more energy is needed to overcome the stronger instantaneous dipole-induced dipole forces of attraction between HBr molecules. Hence, HC*l* has a lower boiling point than HBr.

(d) When an equimolar mixture of gaseous ammonia and gaseous hydrogen chloride at an initial total pressure of 2.5 atm was injected into a chamber maintained at 400 °C, white crystals of ammonium chloride were formed as shown in the following dynamic equilibrium:

$$NH_3(g) + HCl(g) \rightleftharpoons NH_4Cl(s) \qquad \Delta H > 0$$

It was found that 84% of the gases had dissociated at equilibrium.

(i) Define the term *dynamic equilibrium*. [1]

Dynamic equilibrium refers to a reversible reaction in which the rates of the forward and backward reactions have become equal and there is no net change in the concentrations of the products and reactants.

(ii) Write an expression for the equilibrium constant, K_p, for this reaction. [1]

$$K_p = \frac{1}{P_{NH3}P_{HCl}}$$

(iii) Calculate the value of K_p at 400 °C, giving its units. [2]

100-84 = 16% of each gas remained at equilibrium.

Since V and T are constant, $P \propto n$.

Equilibrium pressure of HC*l* = NH_3 = $\frac{0.16 \times 2.5}{2}$ = 0.2 atm

$$K_p = \frac{1}{P_{NH3}P_{HCl}}$$

$$= \frac{1}{(0.2)^2}$$

$$= 25 \text{ atm}^{-2}$$

(iv) State and explain how the partial pressure of the gases and the value of K_p would change if the following changes were made separately:

I. the temperature of the chamber was halved to 200 °C
II. the volume of the chamber was increased (at constant temperature)
III. 2 atm of neon gas is inserted into the chamber [6]

I. By Le Chatelier's Principle, when temperature decreases, the system increases the temperature of the system by favouring the exothermic backward reaction. Position of equilibrium shifts to the left,
partial pressure of the gaseous reactants increases and the value of K_p decreases.

or

When temperature decreases at constant volume, total pressure decreases and partial pressure of the gases decrease. Hence K_p increases.

II. When the volume of the chamber increases, the pressure of the chamber decreases. By Le Chatelier's Principle, the system increases the pressure of the system by favouring the backward reaction to produce more gaseous particles. Position of equilibrium shifts to the left,
partial pressure of the gaseous reactants increases. Value of K_p does not change as temperature is constant.

or

When volume increases at constant temperature, total pressure decreases and partial pressure of the gases decrease. K_p does not change as temperature is constant.

III. When 2 atm of neon gas is inserted, the partial pressure of the gases and K_p remains unchanged
since neon is an inert noble gas and does not react with the other gases in the chamber.

[Total: 20]

. **(a)** The reaction between propanone, CH_3COCH_3, and bromine, Br_2, in the presence of acid, H^+, is found to have an overall order of reaction of 2.

(i) Given that rate is independent of the bromine concentration, write **three** possible rate expressions for this reaction. [3]

(1) Rate = k $[CH_3COCH_3][H^+]$
(2) Rate = k $[CH_3COCH_3]^2$
(3) Rate = k $[H^+]^2$

(ii) Three separate experiments were carried out. In each experiment, the concentration of one of the three different reactants was doubled respectively.

Predict the effect of doubling the concentration of each reactant on the rate of reaction for the **first** rate expression you have written in **(a)(i)**. [2]

Ecf from rate equation

(1) $[CH_3COCH_3]$ doubles, rate doubles **and** $[H^+]$ doubles, rate doubles
$[Br_2]$ doubles, no effect on rate

(2) $[CH_3COCH_3]$ doubles, rate quadruples
$[Br_2]$ or $[H^+]$ doubles, no effect on rate

(3) $[H^+]$ doubles, rate quadruples
$[CH_3COCH_3]$ or $[Br_2]$ doubles, no effect on rate

(iii) The table below shows how the concentration of propanone changes with time in a reaction.

Time / min	[propanone] / mol dm^{-3}
5.0	1.6
7.0	1.4
9.0	1.2
12.0	1.0
15.0	0.8
18.5	0.6
21.5	0.5
25.0	0.4
28.0	0.3
35.0	0.2

Without plotting a graph, use the data given in the table to confirm that the reaction is first order with respect to propanone. Show your working clearly. [2]

Constant half life

At least two sets of data to justify statement
e.g. [ ] from 1.6 to 0.8 mol dm^{-3} 10 min, 0.8 to 0.4 10min , 0.4 to 0.2 10min

(iv) The overall reaction described in **(a)** is:

$$CH_3COCH_3(aq) + Br_2(aq) \xrightarrow{H^+} CH_3COCH_2Br(aq) + HBr(aq)$$

State **one** dependent variable that you can readily measure in order to follow the progress of the reaction. [1]

Colour intensity / absorbance of aq bromine

(v) State and explain the role of acid in this overall reaction. [2]

Catalyst.

Increases rate of reaction by lowering activation energy.

(b) Similar to bromine, halogens like fluorine and chlorine are not naturally found in their elemental form due to their high reactivity.

(i) State and explain the trend in atomic radius down the halogen group. [2]

Atomic radius increases down Group 17.

Down the group, the number of principal quantum shells increases and the distance between the valence electron and the nucleus increases / effective nuclear charge decreases as the increase in screening effect outweighs the effect of increasing nuclear charge.

(ii) By citing relevant values from the *Data Booklet*, deduce and explain the relative reactivity of the halogens as oxidising agents. [2]

	E^o / V
$F_2 + 2e^- \rightarrow 2F^-$	+2.87
$Cl_2 + 2e^- \rightarrow 2Cl^-$	+1.36
$Br_2 + 2e^- \rightarrow 2Br^-$	+1.07

at least 3 values cited

Reactivity (oxidising power) increases in the order $Br_2 < Cl_2 < F_2$

The larger the E^o value, the more likely the halogen is reduced, and the stronger its oxidising power.

(iii) Describe **one** chemical test to illustrate the relative reactivity of any two halogens as oxidising agents. Clearly state any observations seen. [1]

Displacement reaction. Add aqueous chlorine to a solution of bromide ions. The colourless bromide solution turns orange as chlorine has oxidised bromide to bromine.

$Cl_2(aq) + 2Br^-(aq) \rightarrow Br_2(aq) + 2Cl^-(aq)$ $E^\theta_{cell} = +0.29V$ [equation not required]

(iv) Chlorine reacts explosively with hydrogen to form the hydride of chlorine, hydrogen chloride.

$$H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$$

Using your answer in **(b)(ii)** or otherwise, suggest a reason for the general reactivity of the halogens. [1]

In comparison to other substances, the halogens have relatively large positive E^o values. This makes them more reactive as oxidising agents.

(v) Describe and explain the trend in thermal stability of the halogen hydrides. [2]

Order of Thermal Stability: HF(g) > HCl(g) > HBr(g)
at least 3 stated, or trend down the group

Down Group 17, bond energy of the H–X bond decreases. The weaker the H–X bond, the lower the amount of energy required to break it, and the less thermally stable the HX.

(c) Chlorine is able to form an acidic oxide with the formula ClO_2. Another Period 3 element, magnesium, forms a basic oxide with the formula MgO.

(i) Write an equation to show how the oxide ion, O^{2-}, acts as a base in the reaction with water. [1]

$O^{2-} + H_2O \rightarrow 2OH^-$

(ii) Suggest why ClO_2 is not a basic oxide, unlike MgO. [1]

It is a simple covalent oxide and does not dissociate in water to give the oxide ion.

or

It is a non-metal oxide.

[Total: 20]

Class	Adm No

Candidate Name: ____________________

Shift
Laboratory

2018 Preliminary Exams
Pre-University 3

H2 CHEMISTRY **9729/04**

Paper 4 Practical **10th Sept 2018**

2 hour 30 mins

Candidates answer on the Question paper.

READ THESE INSTRUCTIONS FIRST

Do not turn over this question paper until you are told to do so

Write your name, class and admission number on all the work you hand in.

Write in dark blue or black pen.

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

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

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

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

You may lose marks if you do not show your working or if you do not use appropriate units.

Qualitative Analysis Notes are printed at the back of the Question Paper.

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.

Question	1	2	3	4	Total
Marks	26	13	6	10	55

. Investigation of acid-base titrations involving sodium hydrogen carbonate

According to the Arrhenius theory of acids and bases, an acid produces $H^+(aq)$ ions and a base produces $OH^-(aq)$ ions. The reaction of these two ions to form water molecules is known as acid-base neutralisation.

The equation for this neutralisation reaction is given below, and strong acid–strong base reactions are known to have an enthalpy change of neutralisation (ΔH_{neu}) of approximately –57.1 kJ mol^{-1}.

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l) \qquad \Delta H_{neu} = -57.1 \text{ kJ mol}^{-1}$$

However, the ΔH_{neu} for weak acid–strong base reactions are known to differ. Sodium hydrogen carbonate, $NaHCO_3$, is an example of a weak acid.

FA 1 is 1.8 mol dm^{-3} sodium hydrogen carbonate, $NaHCO_3$.
FA 2 is sodium hydroxide, NaOH, of concentration between 0.9 – 1.2 mol dm^{-3}.

$$NaHCO_3 + NaOH \rightarrow Na_2CO_3 + H_2O \qquad \Delta H_{neu}'$$

As the precise concentration of **FA 2** is unknown, determination of $\Delta H_{neu}'$ can be done using a thermometric titration to simultaneously determine both the concentration of **FA 2** as well as $\Delta H_{neu}'$. Thermometric titration is a technique whereby equivalence points of a reaction can be located by observing temperature changes, hence eliminating the need for an indicator.

In **1(a)**, you will perform a weak acid–strong base thermometric titration. The data from this titration will be used to determine:

- the titration value at equivalence point, V_{eq},
- the precise concentration of **FA 2**, [NaOH],
- the maximum temperature change, ΔT_{max},
- the enthalpy change of neutralisation, $\Delta H_{neu}'$.

(a) Determination of V_{eq} and ΔH_{neu}' using thermometric titration

For this experiment, you will need to measure the **maximum temperature** of the reaction mixture when specified volumes of **FA 1** have been added.

In an appropriate format in the space provided on the **next page**, prepare a table to record your results. Record all values of temperature, *T*, to 0.1°C, and each total volume of **FA 1** added.

Note: You should aim to perform each subsequent addition of **FA 1** quickly.

1. Fill a burette with **FA 1**.
2. Using a pipette, transfer 25.0 cm^3 of **FA 2** into a Styrofoam cup. Place this cup inside a second Styrofoam cup, which is placed in a 250 cm^3 glass beaker.
3. Stir and measure the temperature of this **FA 2**. Record this temperature.
4. Add 2.00 cm^3 of **FA 1** from the burette to the **FA 2** in the Styrofoam cup.
5. Using the thermometer, stir the mixture thoroughly and record the maximum temperature reached and the volume of **FA 1** added.
6. Repeat steps **4** and **5** until a total volume of 30.00 cm^3 of **FA 1** has been added.

Results

M1

M2

[2]

(i) Plot a graph of temperature, T, on the y-axis, against volume of **FA 1** added, on the x-axis on the grid in **Fig. 1.1**.

The temperature axis should allow you to include a point at least 1.5 °C greater than the maximum temperature recorded.

M3

M4

M5

Fig. 1.1

Draw **two** most appropriate best-fit lines in **Fig. 1.1**, taking into account all of your plotted points.

Extrapolate (extend) these two best-fit lines until they cross each other. [3]

(ii) From your graph in **Fig. 1.1**, determine:

- the titre at equivalence point, V_{eq},
- the maximum temperature reached, T_{max},
- the maximum temperature change, ΔT_{max}.

On your graph, show clearly how you obtained these values.

V_{eq} = ... cm^3

T_{max} = ... °C

ΔT_{max} = ... °C

[3]

M6

M7

M8

(iii) Determine the concentration of NaOH, [NaOH], in **FA 2**.

M9

[NaOH] in **FA 2** = ... [1]

(iv) Determine the enthalpy change of neutralisation, ΔH_{neu}'.

$$NaHCO_3 + NaOH \rightarrow Na_2CO_3 + H_2O \qquad \Delta H_{neu}'$$

Assume that the reaction mixture has a density of 1.00 g cm^{-3} and a specific heat capacity, *c*, of 4.18 J g^{-1} K^{-1}.

M10

M11

ΔH_{neu}' = ... [3]

M12

(v) Comment on your value of ΔH_{neu}' obtained compared to ΔH_{neu} = –57.1 kJ mol^{-1}.

....

....[1]

M13

(vi) From your graph in **Fig. 1.1**, explain the shape of your best-fit line **before** equivalence point.

....

....[1]

M14

(b) **Determination of titration value at equivalence point, V_{eq}', using 'regular' titration**

FA 3 is hydrochloric acid, HC*l*, of unknown concentration.

Sodium hydrogen carbonate, $NaHCO_3$, is also able to act as a weak base. In **1(a)**, $NaHCO_3$ acts as the acid while in **1(b)**, $NaHCO_3$ is acts as the base.

For this experiment, you will titrate **FA 3** against **FA 1** to determine the titration value at equivalence point, V_{eq}', using methyl orange as the indicator.

(i) The use of thermometric titration in **1(a)** eliminated the need for an indicator as the equivalence point was located by observing temperature changes. 'Regular' acid-base titrations however, require the use of an indicator.

Explain why an indicator is required for 'regular' acid-base titrations (such as in **1(b)**).

……………………………………………………………………………………………………

……………………………………………………………………………………………………[1] **M15**

Titration of FA 3 against FA 1

1. Fill the burette with **FA 1**.
2. Using a pipette, transfer 25.0 cm^3 of **FA 3** into a conical flask.
3. Add 2 – 3 drops of methyl orange indicator into the same conical flask.
4. Run **FA 1** from the burette into this flask until end-point is reached.
5. Record your titration results in the space provided. 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

M16

M17

M18

[3]

(ii) From your titrations, obtain a suitable volume of **FA 1** to be used in your calculations (titre at equivalence point, V_{eq}'). Show clearly how you obtained this value.

V_{eq}' = ……………………… cm^3 [1] **M19**

(iii) Determine the concentration of HC*l*, [HC*l*], in **FA 3**.

M20

[HC*l*] in **FA 3** = ..………………………. [1]

(iv) Suggest if the use of more drops of methyl orange indicator is appropriate for this titration.

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

M21

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

(c) Planning

The same 'regular' titration in **1(b)** can also be performed using an alternative method involving a pH meter, which is an instrument that can measure the pH of water-based solutions at any one instance of time.

Usage of a pH meter is simple as a digital pH reading will be displayed upon placing it into the solution of interest. However, it is known that most pH meters have to be calibrated (correlate to a standard) before each experiment to ensure the accuracy of measurements. For this titration, the standard chosen for calibration is usually a buffer solution of pH ≈ 4.0.

Plotting pH against titration volume, V, will give a pH curve that enables the determination of titration value at equivalence point, V_{eq}''.

Plan an experiment to determine the titration value at equivalence point, V_{eq}'', for the titration of **FA 3** against **FA 1** using a pH meter.

You may assume that you are provided with

- a pH meter,
- **FA 1** and **FA 3**,
- 1.0 mol dm^{-3} of ethanoic acid, CH_3COOH ($K_a = 1.8 \times 10^{-5}$),
- 1.0 mol dm^{-3} of sodium ethanoate solution, $CH_3COO^-Na^+$,
- the glassware and equipment normally found in a school or college laboratory.

In your plan you should include brief details of

- the preparation of a suitable standard solution for calibration of the pH meter,
- the procedure that you would follow,
- the measurements you would take,
- an outline of how you would use your results to determine V_{eq}''.

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

……………………………………………………………………………………………………

For Examiners' Use

M22

M23

M24

M25

M26

[5]

[Total: 26]

. **Determination of the major component in a solid mixture**

Sodium hydrogen carbonate, $NaHCO_3$, also commonly known as *baking soda*, is a white crystalline solid primarily used in baking as a raising agent.

To increase the strength of *baking soda* as a raising agent, cream of tartar (a dry acid) is mixed with sodium hydrogen carbonate. This mixture is known as *baking powder*.

FA 4 is a sample of *baking powder*.

In this experiment, you will determine if sodium hydrogen carbonate is the major component, by mass, of the mixture **FA 4**.

(a) Thermal decomposition of *baking powder*

You may assume that the cream of tartar in **FA 4** is inert and does not decompose when heated.

1. Weigh and record the mass of an empty boiling-tube.
2. Transfer approximately 2 g of **FA 4** into the weighed boiling-tube. Reweigh and record the mass of the boiling-tube and **FA 4**.
3. Gently heat the **FA 4** in the boiling-tube for 2 minutes, then heat strongly for a further 2 minutes. **Take care not to lose any solid from the tube during heating.**
4. Warm the upper parts of the boiling-tube to evaporate any water that may have condensed while heating the solid.
5. Place the hot tube on the test-tube rack and leave to cool. **You are advised to continue with part 2(c) or to start another question while the tube cools.**
6. When cool, reweigh the boiling-tube and the residual solid.
7. Reheat, cool and reweigh the tube until decomposition is complete.

In an appropriate form in the space below, record all your balance readings, the mass of **FA 4** heated, the mass of residual solid, and the mass lost on heating.

Results

M27

M28

M29

M30

M31

[5]

The thermal decomposition of $NaHCO_3$ produces Na_2CO_3 and two gases at the temperature of decomposition, CO_2 and H_2O.

$$2NaHCO_3(s) \rightarrow Na_2CO_3(s) + CO_2(g) + H_2O(g)$$

(i) By finding the average M_r of the two gases produced, use your results in **(a)** calculate the **total** amount of gases lost upon complete decomposition of **FA 4**.

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

total amount of gases lost = …………………… mol [1]

M32

(ii) Taking into account the mole ratio of gases in the decomposition equation given, calculate the amount of CO_2(g) lost upon complete decomposition of **FA 4**.

M33

amount of CO_2(g) lost = …………………… mol [1]

(iii) Hence, calculate the mass of $NaHCO_3$ in the sample of **FA 4** heated.

M34

mass of $NaHCO_3$ = ……………………… g [1]

(iv) By means of calculation or otherwise, justify if $NaHCO_3$ is the major component, by mass, of **FA 4**.

…………………………………………………………………………………………………

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

M35

(b) **Do not carry out your suggestions.**

Suggest two ways in which you could show that cream of tartar does not decompose on heating.

(i) ....

....

(ii) ....

.... [2]

M36

M37

(c) A student is asked to weigh, with maximum precision, a solid.

Three balances are available.

- Balance A, reading to 1 decimal place,
- Balance B, reading to 2 decimal places,
- Balance C, reading to 3 decimal places.

> Balance readings can be treated similarly to burette readings.
>
> For example, the smallest division on a burette is 0.1 cm^3.
> The maximum error in a single burette reading is ±0.05 cm^3.

Complete the following table.

balance	maximum error for a single balance reading /g	maximum % error when weighing:
A	±	8.0 g of solid =
B	±	4.00 g of solid =
C	±	0.400 g of solid =

[2]

M38

M39

[Total: 13]

. **Qualitative Analysis of an unknown double salt**

Double salts are salts that contain more than one cation or anion, and are synthesised by crystallising a solution containing the different ions.

FA 5 is a double salt which contains **two cations** and **one anion**.

Empty out the **FA 5** provided into a 50 cm^3 beaker. To this beaker, add 10 cm^3 of water and stir to dissolve as much of the solid as possible.

This solution will be referred to as '**FA 5** solution'.

(a) Perform the tests described in **Table 3.1**, and record your observations in the table. Test and identify any gases evolved.

Table 3.1

tests		observations
1.	Add about 1 cm depth of **FA 5** solution to a boiling-tube, followed by NaOH(aq) dropwise, until excess (a further 2 cm depth). Warm the solution gently.	
2.	Add about 2 cm depth of **FA 5** solution to a test-tube. To this test-tube, add about half a spatula of zinc powder. Observe the mixture until no further changes are seen.	
3.	Add about 1 cm depth of **FA 5** solution into a test-tube. To this test-tube, add barium nitrate dropwise.	

[4]

M40

M41

M42

M43

(b) Based on your observations in **3(a)**, deduce the identities of the ions present in **FA 5**.

M44

cation 1: ………… cation 2: ………… anion: ………… [1]

(c) Hence, suggest a possible chemical formula of the double salt **FA 5**.

M45

chemical formula of **FA 5**: …………………… [1]

[Total: 6]

4 Planning

The condenser is an apparatus frequently used in organic synthesis. It comprises of concentric glass tubes, an inner one through which hot gases can pass through, and an outer one through which a cool fluid can pass through.

Use of the condenser is required for the organic synthesis of aldehydes and carboxylic acids from alcohols. The product of the reaction between potassium dichromate, $K_2Cr_2O_7$, and primary alcohols can either be an aldehyde or a carboxylic acid depending on how the condenser is orientated.

(a) Some organic synthesis procedures require *heating under reflux*.

Explain the role of the condenser in such procedures.

………………………………………………………………………………………………… **M46**

……………………………………………………………………………………………….. [2] **M47**

(b) Plan an experiment to synthesise **propanal** (boiling point: 20 °C) from **propan-1-ol** (boiling point: 97 °C).

You may assume that you are provided with

- propan-1-ol, $CH_3CH_2CH_2OH$,
- potassium dichromate, $K_2Cr_2O_7$,
- commonly used organic chemicals
- the glassware and equipment normally found in a school or college laboratory.

In your plan you should include

- the reactants and conditions that you would use,
- a well-labelled diagram of the set-up that you would use,
- the procedure that you would follow and the safety precautions taken,
- how you would check the purity of your product.

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For Examiners' Use

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.... **M48**

.... **M49**

.... **M50**

.... **M51**

....[4]

(c) Suggest appropriate modifications to your plan to synthesise **propanoic acid** (boiling point: 141 °C) from propan-1-ol instead of propanal.

You may wish to use diagrams to complement your answer.

....

.... **M52**

.... **M53**

....[2]

(d) Give an explanation for any **two** modifications you have made in **(c)**.

....

.... **M54**

.... **M55**

....[2]

[Total: 10]

End of Paper 4

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. insoluble in excess	green ppt. 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. insoluble in excess	off-white ppt. insoluble in excess
zinc, Zn^{2+}(aq)	white ppt. soluble in excess	white ppt. soluble in excess

(b) Reactions of anions

ions	*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) Test for gases

ions	*reaction*
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

Class	Adm No

Candidate Name: ____________________

H

Shift
Laboratory

2018 Preliminary Exams
Pre-University 3

H2 CHEMISTRY **9729/04**

Paper 4 Practical **10th Sept 2018**

2 hour 30 mins

Candidates answer on the Question paper.

READ THESE INSTRUCTIONS FIRST

Do not turn over this question paper until you are told to do so

Write your name, class and admission number on all the work you hand in.

Write in dark blue or black pen.

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

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

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

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

You may lose marks if you do not show your working or if you do not use appropriate units.

Qualitative Analysis Notes are printed at the back of the Question Paper.

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.

Question	1	2	3	4	Total
Marks	26	13	6	10	55

. Investigation of acid-base titrations involving sodium hydrogen carbonate

According to the Arrhenius theory of acids and bases, an acid produces $H^+(aq)$ ions and a base produces $OH^-(aq)$ ions. The reaction of these two ions to form water molecules is known as acid-base neutralisation.

The equation for this neutralisation reaction is given below, and strong acid–strong base reactions are known to have an enthalpy change of neutralisation (ΔH_{neu}) of approximately –57.1 kJ mol^{-1}.

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l) \qquad \Delta H_{neu} = -57.1 \text{ kJ mol}^{-1}$$

However, the ΔH_{neu} for weak acid–strong base reactions are known to differ. Sodium hydrogen carbonate, $NaHCO_3$, is an example of a weak acid.

FA 1 is 1.8 mol dm^{-3} sodium hydrogen carbonate, $NaHCO_3$.
FA 2 is sodium hydroxide, NaOH, of concentration between 0.9 – 1.2 mol dm^{-3}.

$$NaHCO_3 + NaOH \rightarrow Na_2CO_3 + H_2O \qquad \Delta H_{neu}'$$

As the precise concentration of **FA 2** is unknown, determination of $\Delta H_{neu}'$ can be done using a thermometric titration to simultaneously determine both the concentration of **FA 2** as well as $\Delta H_{neu}'$. Thermometric titration is a technique whereby equivalence points of a reaction can be located by observing temperature changes, hence eliminating the need for an indicator.

In **1(a)**, you will perform a weak acid–strong base thermometric titration. The data from this titration will be used to determine:

- the titration value at equivalence point, V_{eq},
- the precise concentration of **FA 2**, [NaOH],
- the maximum temperature change, ΔT_{max},
- the enthalpy change of neutralisation, $\Delta H_{neu}'$.

(a) **Determination of V_{eq} and ΔH_{neu}' using thermometric titration**

For this experiment, you will need to measure the **maximum temperature** of the reaction mixture when specified volumes of **FA 1** have been added.

In an appropriate format in the space provided on the **next page**, prepare a table to record your results. Record all values of temperature, *T*, to 0.1°C, and each total volume of **FA 1** added.

Note: You should aim to perform each subsequent addition of **FA 1** quickly.

1. Fill a burette with **FA 1**.
2. Using a pipette, transfer 25.0 cm^3 of **FA 2** into a Styrofoam cup. Place this cup inside a second Styrofoam cup, which is placed in a 250 cm^3 glass beaker.
3. Stir and measure the temperature of this **FA 2**. Record this temperature.
4. Add 2.00 cm^3 of **FA 1** from the burette to the **FA 2** in the Styrofoam cup.
5. Using the thermometer, stir the mixture thoroughly and record the maximum temperature reached and the volume of **FA 1** added.
6. Repeat steps **4** and **5** until a total volume of 30.00 cm^3 of **FA 1** has been added.

Results

Vol of FA 1 added / cm^3	T / °C
0.00	29.4
2.00	30.4
4.00	31.5
6.00	32.2
8.00	32.9
10.00	33.4
12.00	34.0
14.00	33.9
16.00	33.6
18.00	33.3
20.00	33.0
22.00	32.8
24.00	32.6
26.00	32.4
28.00	32.3
30.00	32.2

M1
all 16 readings of vol and T tabulated with correct headers and units

M2
T to ±0.1 °C

[2]

(i) Plot a graph of temperature, *T*, on the *y*-axis, against volume of **FA 1** added, on the *x*-axis on the grid in **Fig. 1.1**.

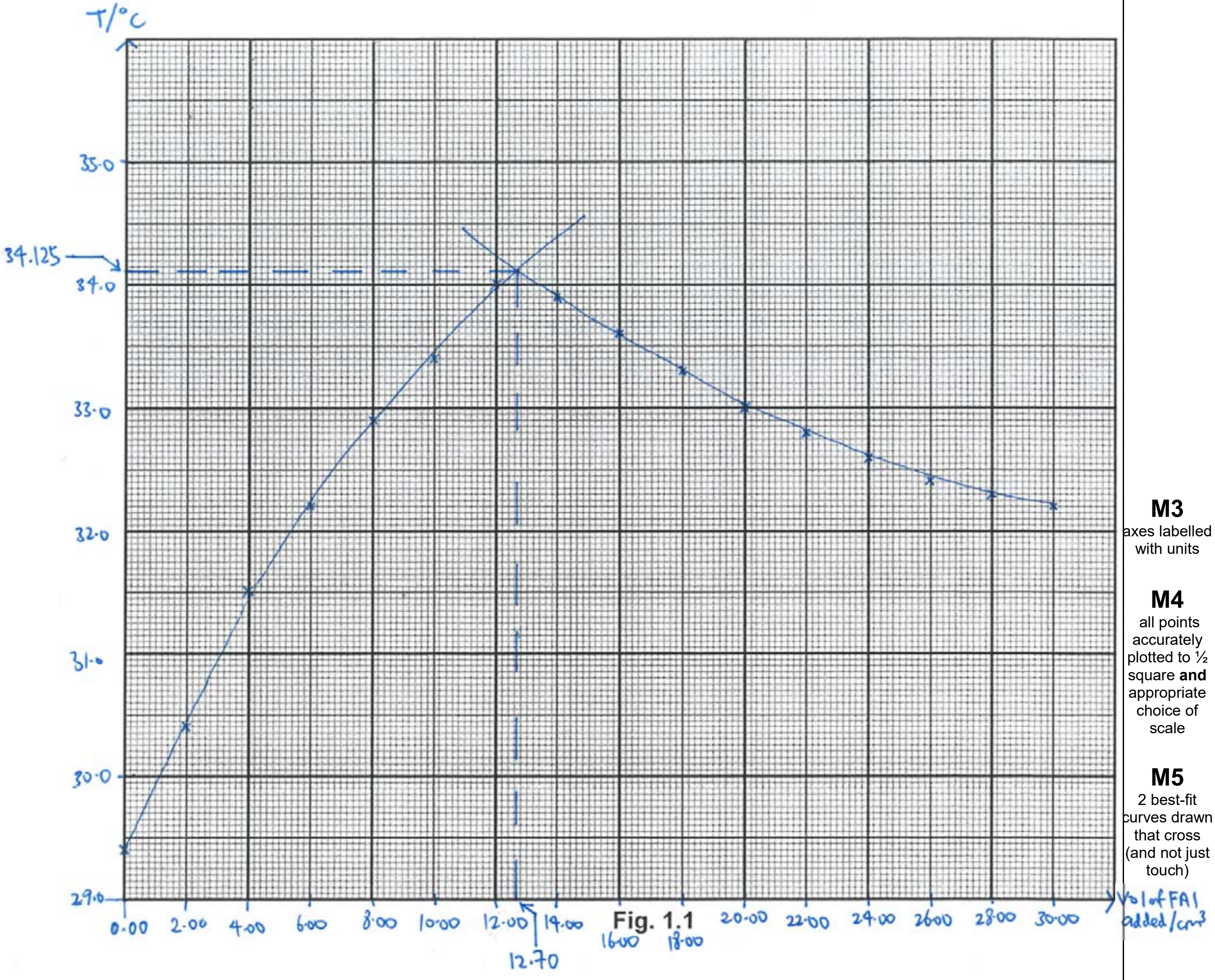


Fig. 1.1

M3
axes labelled with units

M4
all points accurately plotted to ½ square **and** appropriate choice of scale

M5
2 best-fit curves drawn that cross (and not just touch)

Draw **two** most appropriate best-fit lines in **Fig. 1.1**, taking into account all of your plotted points.

Extrapolate (extend) these two best-fit lines until they cross each other. [3]

For Examiners' Use

(ii) From your graph in **Fig. 1.1**, determine:

- the titre at equivalence point, V_{eq},
- the maximum temperature reached, T_{max},
- the maximum temperature change, ΔT_{max}.

On your graph, show clearly how you obtained these values.

M6 both construction lines shown on graph

ΔT_{max} = 34.125 – 29.4 = 4.7 °C

M7 both readings correct to ½ square

V_{eq} = 12.70 cm^3

T_{max} = 34.1 °C

M8 accuracy of ΔT_{max}, student value ≤0.6 from supervisor's value

ΔT_{max} = 4.7 °C

[3]

(iii) Determine the concentration of NaOH, [NaOH], in **FA 2**.

Amount of $NaHCO_3$ reacted = 1.8 x 12.70 x 10^{-3} = 0.02286 mol

$$[NaOH] = \frac{0.2286}{25.0\times10^{-3}} = 0.914 \text{ mol dm}^{-3}$$

M9

[NaOH] in **FA 2** = 0.914 mol dm^{-3} [1]

(iv) Determine the enthalpy change of neutralisation, ΔH_{neu}'.

$$NaHCO_3 + NaOH \rightarrow Na_2CO_3 + H_2O \qquad \Delta H_{neu}'$$

Assume that the reaction mixture has a density of 1.00 g cm^{-3} and a specific heat capacity, c, of 4.18 J g^{-1} K^{-1}.

M10 correct mass used

m = 25.0 + 12.70 = 37.7 g

M11 correct calculations, do not mark for sign

q = mcΔT = (37.7)(4.18)(4.7) = 740.6 J

$$\Delta H = -\frac{q}{n_{LR}} = -\frac{740.6}{0.02286} = -32.4 \text{ kJ mol}^{-1} \text{ (3 sf)}$$

M12 all calc in (a) to 3 or 4 sf and have correct units and correct sign for ΔH

ΔH_{neu}' = –32.4 kJ mol^{-1} [3]

(v) Comment on your value of ΔH_{neu}' obtained compared to ΔH_{neu} = –57.1 kJ mol^{-1}.

M13 comparison unambiguous (do not accept "value is more/less")

The value of ΔH_{neu}' obtained is less exothermic, as some of the heat energy released was used to completely dissociate the weak acid $NaHCO_3$. [1]

(vi) From your graph in **Fig. 1.1**, explain the shape of your best-fit line **before** equivalence point.

The curve is increasing with a decreasing gradient as the exothermic reaction releases the same amount of heat energy for each addition of FA 1, which causes a smaller temperature rise as the mass of the mixture increases. [1]

M14

(b) Determination of titration value at equivalence point, V_{eq}', using 'regular' titration

For Examiners' Use

FA 3 is hydrochloric acid, HC*l*, of unknown concentration.

Sodium hydrogen carbonate, $NaHCO_3$, is also able to act as a weak base. In **1(a)**, $NaHCO_3$ acts as the acid while in **1(b)**, $NaHCO_3$ is acts as the base.

For this experiment, you will titrate **FA 3** against **FA 1** to determine the titration value at equivalence point, V_{eq}', using methyl orange as the indicator.

(i) The use of thermometric titration in **1(a)** eliminated the need for an indicator as the equivalence point was located by observing temperature changes. 'Regular' acid-base titrations however, require the use of an indicator.

Explain why an indicator is required for 'regular' acid-base titrations (such as in **1(b)**).

M15

To give a visible observation that corresponds to completion of reaction. [1]

Titration of FA 3 against FA 1

1. Fill the burette with **FA 1**.
2. Using a pipette, transfer 25.0 cm^3 of **FA 3** into a conical flask.
3. Add 2 – 3 drops of methyl orange indicator into the same conical flask.
4. Run **FA 1** from the burette into this flask until end-point is reached.
5. Record your titration results in the space provided. 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

	1	2	3
Initial burette reading / cm^3	0.00	6.70	
Final burette reading / cm^3	21.60	28.20	
Volume of **FA 1** added / cm^3	21.60	21.50	
	✓	✓	

[3]

M16 correct headers and units

M17 volumes to ±0.05 cm^3 and correct subtraction

M18 accuracy, student value ≤0.6 from supervisor's value

(ii) From your titrations, obtain a suitable volume of **FA 1** to be used in your calculations (titre at equivalence point, V_{eq}'). Show clearly how you obtained this value.

$$V_{eq}' = \frac{21.60+21.50}{2} = 21.55 \text{ cm}^3$$

V_{eq}' = 21.55 cm^3 [1]

M19

(iii) Determine the concentration of HC*l*, [HC*l*], in **FA 3**.

$NaHCO_3 + HCl \rightarrow NaCl + CO_2 + H_2O$

Amount of $NaHCO_3$ = 1.8 x 21.55 x 10^{-3} = 0.03879 mol
= Amount of HC*l*

[HC*l*] = $\frac{0.03879}{25.0\times10^{-3}}$ = 1.55 mol dm^{-3} (3 sf)

[HC*l*] in **FA 3** = <u>1.55 mol dm^{-3}</u> [1]

M20

(iv) Suggest if the use of more drops of methyl orange indicator is appropriate for this titration.

No, it is <u>not appropriate</u> as indicators are <u>weak acids or bases</u> and will <u>affect the pH of the solution</u>. [1]

M21

(c) Planning

The same ‘regular’ titration in **1(b)** can also be performed using an alternative method involving a pH meter, which is an instrument that can measure the pH of water-based solutions at any one instance of time.

Usage of a pH meter is simple as a digital pH reading will be displayed upon placing it into the solution of interest. However, it is known that most pH meters have to be calibrated (correlate to a standard) before each experiment to ensure the accuracy of measurements. For this titration, the standard chosen for calibration is usually a buffer solution of pH ≈ 4.0.

Plotting pH against titration volume, V, will give a pH curve that enables the determination of titration value at equivalence point, V_{eq}’’.

Plan an experiment to determine the titration value at equivalence point, V_{eq}’’, for the titration of **FA 3** against **FA 1** using a pH meter.

You may assume that you are provided with

- a pH meter,
- **FA 1** and **FA 3**,
- 1.0 mol dm^{-3} of ethanoic acid, CH_3COOH ($K_a = 1.8 \times 10^{-5}$),
- 1.0 mol dm^{-3} of sodium ethanoate solution, $CH_3COO^-Na^+$,
- the glassware and equipment normally found in a school or college laboratory.

In your plan you should include brief details of

- the preparation of a suitable standard solution for calibration of the pH meter,
- the procedure that you would follow,
- the measurements you would take,
- an outline of how you would use your results to determine V_{eq}’’.

$$\mathrm{pH} = \mathrm{p}K_a + \lg\frac{[\mathrm{CH_3COO^-}]}{[\mathrm{CH_3COOH}]}$$

$$4.0 = -\lg(1.8 \times 10^{-5}) + \lg\frac{n_{\mathrm{CH_3COO^-}}/V}{n_{\mathrm{CH_3COOH}}/V}$$

$$\frac{n_{\mathrm{CH_3COO^-}}}{n_{\mathrm{CH_3COOH}}} = 0.18$$

Since concentrations of ethanoic acid and sodium ethanoate are the same, $n \propto V$.
∴ for 18 cm^3 of ethanoic acid used, use 100 cm^3 of sodium ethanoate.

M22
correct choice of volumes to obtain pH between 3.9-4.1

Preparation of standard solution and calibration of pH meter

1. Using two separate burettes, add 18.00 cm^3 of 1.0 mol dm^{-3} ethanoic acid and 100.00 cm^3 of 1.0 mol dm^{-3} sodium ethanoate to a 250 cm^3 volumetric flask.
2. Top up the volumetric flask to the mark with distilled water, stopper, invert and shake until homogeneous.
3. Pour out some of the standard solution into a 50 cm^3 beaker and place the pH meter probe into it. Calibrate the pH meter to read 4.0.
4. Wash the pH meter probe with distilled water before usage in experiment.

M23
correct procedures for preparation of std sol

M24
calibration of pH meter, including washing of probe

Procedures for titration and measurements taken

5. Carry out the same ‘regular’ titration as in **1(b)**, replacing the methyl orange indicator with the pH meter probe.
6. Record the pH measurements at 1 cm^3 intervals until 25.00 cm^3 of **FA 3** has been added.

M25
correct modification and measurements taken

Determining V_{eq}''

7. Plot a graph of pH against volume of **FA 3** added. The vertical region corresponds to the equivalence point.
8. Draw a vertical construction line from this vertical region to the x-axis to determine the value of V_{eq}''.

M26
correct usage of plot / sketch of plot to determine V_{eq}''

[5]

[Total: 26]

. Determination of the major component in a solid mixture

Sodium hydrogen carbonate, $NaHCO_3$, also commonly known as *baking soda*, is a white crystalline solid primarily used in baking as a raising agent.

To increase the strength of *baking soda* as a raising agent, cream of tartar (a dry acid) is mixed with sodium hydrogen carbonate. This mixture is known as *baking powder*.

FA 4 is a sample of *baking powder*.

In this experiment, you will determine if sodium hydrogen carbonate is the major component, by mass, of the mixture **FA 4**.

(a) Thermal decomposition of *baking powder*

You may assume that the cream of tartar in **FA 4** is inert and does not decompose when heated.

1. Weigh and record the mass of an empty boiling-tube.
2. Transfer approximately 2 g of **FA 4** into the weighed boiling-tube. Reweigh and record the mass of the boiling-tube and **FA 4**.
3. Gently heat the **FA 4** in the boiling-tube for 2 minutes, then heat strongly for a further 2 minutes. **Take care not to lose any solid from the tube during heating.**
4. Warm the upper parts of the boiling-tube to evaporate any water that may have condensed while heating the solid.
5. Place the hot tube on the test-tube rack and leave to cool. **You are advised to continue with part 2(c) or to start another question while the tube cools.**
6. When cool, reweigh the boiling-tube and the residual solid.
7. Reheat, cool and reweigh the tube until decomposition is complete.

In an appropriate form in the space below, record all your balance readings, the mass of **FA 4** heated, the mass of residual solid, and the mass lost on heating.

Results

Mass of empty boiling-tube / g	30.03
Mass of boiling-tube + **FA 4** / g	32.14
Mass of **FA 4** heated / g	2.11
Mass of boiling-tube + residual solid (1) / g	31.55
Mass of boiling-tube + residual solid (2) / g	31.53
Mass of residual solid / g	1.50
Mass lost / g	0.61

[5]

-

M27 at least 4 balance readings and 1 calculation (accept tare)

M28 correct headers (at most 1 missing) and units and all mass readings to 2dp

M29 correct subtractions (all three)

M30 evidence of constant mass (within 0.05g)

M31 accuracy of ratio (mass heated / mass of residue) ≤0.2 from supervisor's value

The thermal decomposition of $NaHCO_3$ produces Na_2CO_3 and two gases at the temperature of decomposition, CO_2 and H_2O.

$$2NaHCO_3(s) \rightarrow Na_2CO_3(s) + CO_2(g) + H_2O(g)$$

(i) By finding the average M_r of the two gases produced, use your results in **(a)** calculate the **total** amount of gases lost upon complete decomposition of **FA 4**.

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

average $M_r = \frac{[12.0+2(16.0)]+[2(1.0)+16.0]}{2} = 31.0$

total amount of gases lost $= \frac{0.61}{31.0} = 0.0197$ mol (3 sf)

M32

total amount of gases lost = 0.0197 mol [1]

(ii) Taking into account the mole ratio of gases in the decomposition equation given, calculate the amount of $CO_2(g)$ lost upon complete decomposition of **FA 4**.

amount of CO_2 lost = 0.0197 / 2

= 0.00984 mol (3 sf)

M33

amount of $CO_2(g)$ lost = 0.00984 mol [1]

(iii) Hence, calculate the mass of $NaHCO_3$ in the sample of **FA 4** heated.

amount of $NaHCO_3$ decomposed = 2 x 0.009838

= 0.01967 mol

mass of $NaHCO_3$ = 0.01967 x [23.0 + 1.0 + 12.0 + 3(16.0)]

= 1.65 g (3 sf)

M34

mass of $NaHCO_3$ = 1.65 g [1]

(iv) By means of calculation or otherwise, justify if $NaHCO_3$ is the major component, by mass, of **FA 4**.

% by mass of $NaHCO_3$ = $\frac{1.652}{2.11} \times 100$

= 78.3 % (3 sf)

$NaHCO_3$ is the major component as it makes up more than 50% of the sample.

M35

[1]

(b) **Do not carry out your suggestions.**

For Examiners' Use

Suggest two ways in which you could show that cream of tartar does not decompose on heating.

(i) There is no change in mass when cream of tartar is heated. **M36**

(ii) There is no change in the volume of a gas syringe connected to the boiling-tube when cream of tartar is heated. [2]

M37
award 1m if both mass and volume stated but no mention of absence of change

(c) A student is asked to weigh, with maximum precision, a solid.

Three balances are available.

- Balance A, reading to 1 decimal place,
- Balance B, reading to 2 decimal places,
- Balance C, reading to 3 decimal places.

Balance readings can be treated similarly to burette readings.

For example, the smallest division on a burette is 0.1 cm^3.
The maximum error in a single burette reading is ±0.05 cm^3.

Complete the following table.

balance	maximum error for a single balance reading / g	maximum % error when weighing:
A	± 0.05	8.0 g of solid = $\frac{2\times0.05}{8.0}\times100$ = 1.25%
B	± 0.005	4.00 g of solid = $\frac{2\times0.005}{4.00}\times100$ = 0.250%
C	± 0.0005	0.400 g of solid = $\frac{2\times0.0005}{0.400}\times100$ = 0.250%

[2]

M38
correct max error

M39
ecf only if
(i) max error given is x2
(ii) max errors are incorrect by factor 10

[Total: 13]

For Examiners' Use

. Qualitative Analysis of an unknown double salt

Double salts are salts that contain more than one cation or anion, and are synthesised by crystallising a solution containing the different ions.

FA 5 is a double salt which contains **two cations** and **one anion**.

Empty out the **FA 5** provided into a 50 cm^3 beaker. To this beaker, add 10 cm^3 of water and stir to dissolve as much of the solid as possible.

This solution will be referred to as '**FA 5** solution'.

(a) Perform the tests described in **Table 3.1**, and record your observations in the table. Test and identify any gases evolved.

Table 3.1

	tests	observations	
1.	Add about 1 cm depth of **FA 5** solution to a boiling-tube, followed by NaOH(aq) dropwise, until excess (a further 2 cm depth). Warm the solution gently.	Red-brown ppt forms, insoluble in excess NaOH(aq). Gas produced turns red litmus paper blue.	M40 M41
2.	Add about 2 cm depth of **FA 5** solution to a test-tube. To this test-tube, add about half a spatula of zinc powder. Observe the mixture until no further changes are seen.	Yellow solution decolourises / turns pale green. *accept: gas produced extinguishes lighted splint with a 'pop' sound*	M42
3.	Add about 1 cm depth of **FA 5** solution into a test-tube. To this test-tube, add barium nitrate dropwise.	White ppt forms, insoluble in excess HNO_3(aq). *allow omission of solubility in strong acid, but do not award M44 if sulfite is proposed as anion*	M43

[4]

(b) Based on your observations in **3(a)**, deduce the identities of the ions present in **FA 5**.

cation 1: Fe^{3+} cation 2: NH_4^+ anion: SO_4^{2-} [1]

M44
do not accept H+ as it was not in original salt

(c) Hence, suggest a possible chemical formula of the double salt **FA 5**.

chemical formula of **FA 5**: $\underline{Fe(NH_4)(SO_4)_2}$ [1]

M45
ecf only if H^+ instead of NH_4^+ and others correct

[Total: 6]

4 Planning

The condenser is an apparatus frequently used in organic synthesis. It comprises of concentric glass tubes, an inner one through which hot gases can pass through, and an outer one through which a cool fluid can pass through.

Use of the condenser is required for the organic synthesis of aldehydes and carboxylic acids from alcohols. The product of the reaction between potassium dichromate, $K_2Cr_2O_7$, and primary alcohols can either be an aldehyde or a carboxylic acid depending on how the condenser is orientated.

(a) Some organic synthesis procedures require *heating under reflux*.

Explain the role of the condenser in such procedures. **M46**

To prevent the loss of volatile / low boiling point organic reagents **M47**
by condensing hot vapour back into the reaction flask. [2]

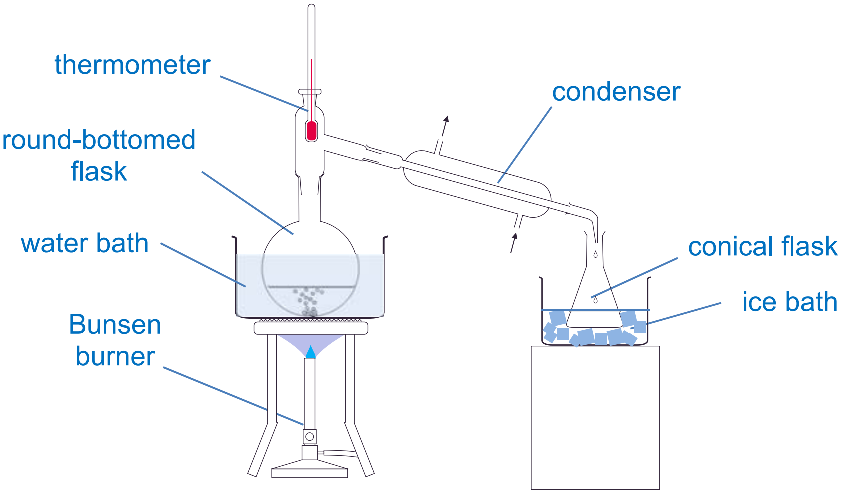
(b) Plan an experiment to synthesise **propanal** (boiling point: 20 °C) from **propan-1-ol** (boiling point: 97 °C).

You may assume that you are provided with

- propan-1-ol, $CH_3CH_2CH_2OH$,
- potassium dichromate, $K_2Cr_2O_7$,
- commonly used organic chemicals
- the glassware and equipment normally found in a school or college laboratory.

In your plan you should include

- the reactants and conditions that you would use,
- a well-labelled diagram of the set-up that you would use,
- the procedure that you would follow and the safety precautions taken,
- how you would check the purity of your product.



M48 correct distillation setup with labels (accept hot plate, do **not** mark for ice bath)

Reactants: $CH_3CH_2CH_2OH$, $K_2Cr_2O_7$, dilute H_2SO_4
Conditions: heat with distillation

M49 correct R&C (must have dilute acid added), do **not** mark for precalc of quantities

Procedure

1. To the 100 cm^3 round-bottomed flask, add $CH_3CH_2CH_2OH$, $K_2Cr_2O_7$, and dilute H_2SO_4.
2. Set up the apparatus as shown in the diagram above in the fume cupboard / while wearing gloves / safety goggles.
3. Start the flow of water through the condenser and turn on the Bunsen burner to start the reaction. Maintain the water bath at approximately 40 °C. The temperature reading should remain constant at approximately 20 °C until all the propanal synthesised has boiled off.
4. When the temperature starts to increase further / no further distillate is collected in the conical flask, turn off the Bunsen burner to stop the reaction.
5. Test the purity of the propanal distillate by means of thin layer chromatography. A pure sample would only contain one spot after chromatography.

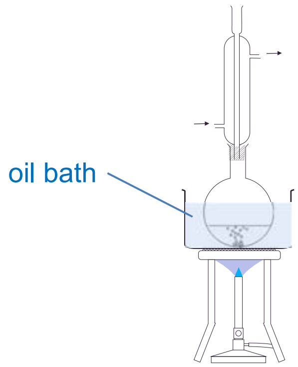
[4]

M50
any 1 safety procedure written

M51
use of TLC to test for purity of product

(c) Suggest appropriate modifications to your plan to synthesise **propanoic acid** (boiling point: 141 °C) from propan-1-ol instead of propanal.

You may wish to use diagrams to complement your answer.



Use a reflux setup instead of a distillation setup by orientating the condenser vertically.

Use a separatory funnel to extract out the propanoic acid product from the reaction mixture before testing its purity.

[2]

M52
diagram *or* mention of orientating condenser vertically. do not accept simply changing to $KMnO_4$

M53
mentions method to extract product from reaction mixture

(d) Give an explanation for any **two** modifications you have made in **(c)**.

Reflux: To ensure that the volatile propanal does not escape the reaction flask and can continue to further be oxidised by $K_2Cr_2O_7$ into propanoic acid.

Separatory funnel: Unlike distillation, the propanoic acid product is mixed with residual reagents (such as propan-1-ol, $K_2Cr_2O_7$ and water) and has to be purified.

M54

M55

$KMnO_4$: Stronger oxidising agent used to ensure that all the propan-1-ol is fully oxidised into propanoic acid.

Heat longer: To ensure that all the propan-1-ol is fully oxidised into propanoic acid.

Oil bath: To allow for heating at higher temperatures close to boiling point of propan-1-ol as water will boil.

[2]

[Total: 10]

End of Paper 4

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. insoluble in excess	green ppt. 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. insoluble in excess	off-white ppt. insoluble in excess
zinc, Zn^{2+}(aq)	white ppt. soluble in excess	white ppt. soluble in excess

(b) Reactions of anions

ions	*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) Test for gases

ions	*reaction*
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