Class	Adm No

Candidate Name: ____________________

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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There are **thirty** questions on this paper. Answer **ALL** questions. For each question there are four possible answers **A**, **B**, **C** and **D**.

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

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TOTAL (30 marks)	

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

1 2.0 g of helium gas
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A 1 only **B** 3 only
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2 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?

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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
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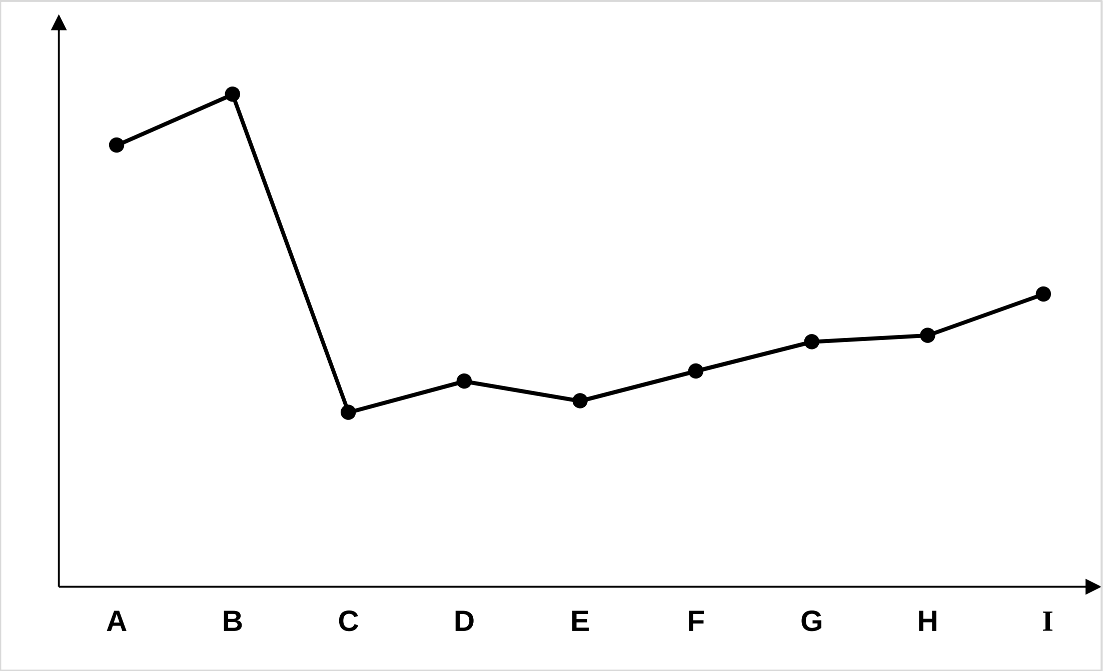
Third ionisation energy



elements

Which of the following statements is correct?

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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**?

A	4	**B**	8
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1 Only covalent bonds are present in the structures for both graphite and diamond.
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7 In which set of species do all three compounds have the same shape?

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

The rate equation of the reaction above can be written as rate = $k[\mathbf{X}][\mathbf{Y}]$.

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

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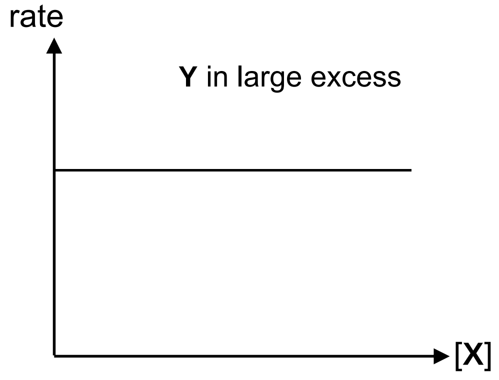

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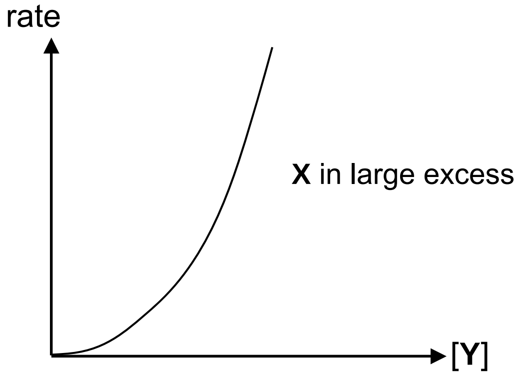

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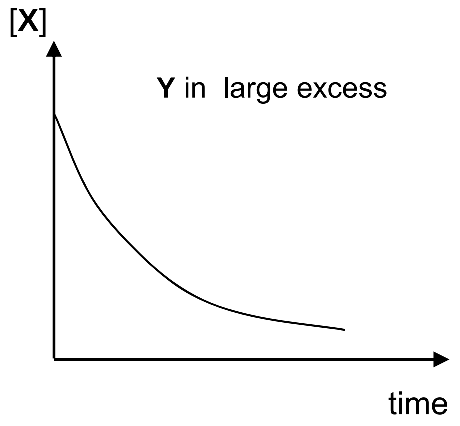

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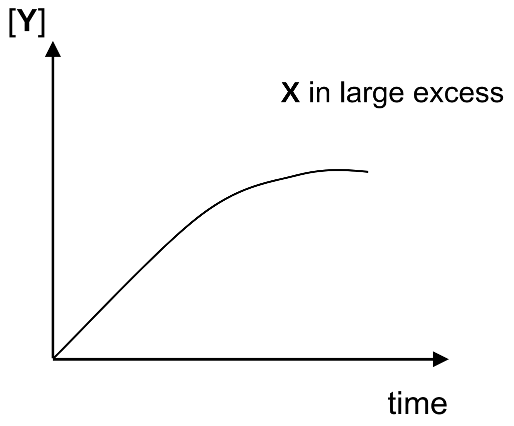

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$$Ag_2SO_4(s) \rightleftharpoons 2Ag^+(aq) + SO_4^{2-}(aq)$$

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?

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C $\left(\frac{\boldsymbol{S}}{2}\right)^{\frac{1}{3}}$ **D** $(2\boldsymbol{S})^{\frac{1}{3}}$

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Which factor best explains this trend?

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

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What will be observed when a few drops of acidified aqueous hydrogen peroxide are added to an excess of aqueous potassium iodide?

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A -1.18V **B** -1.48V

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21 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?

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

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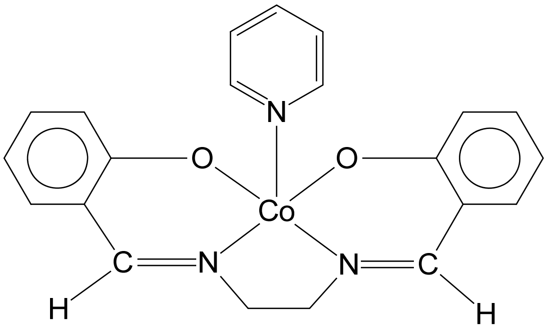
23 The following cobalt complex is known to be the functional model for biological oxygen carrier.



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]$3d^7 4s^2$

24 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
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25 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

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

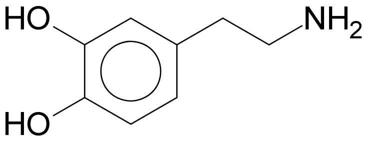
A $CH_2BrCH_2\bullet + Br_2 \longrightarrow CH_2BrCH_2Br + Br\bullet$

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

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

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

27 Dopamine is a neurotransmitter that is involved in addiction.



Dopamine

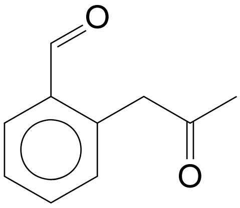
Which of the following statements is true about dopamine?

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

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

A



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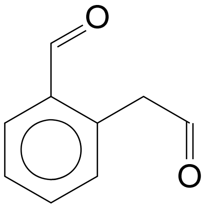

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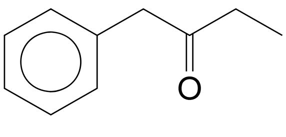

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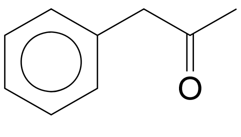

29 Phenol is weakly acidic and has a pK_a of 9.95. Which of the following substances, in the presence of water, has a higher pK_a than phenol?

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

30 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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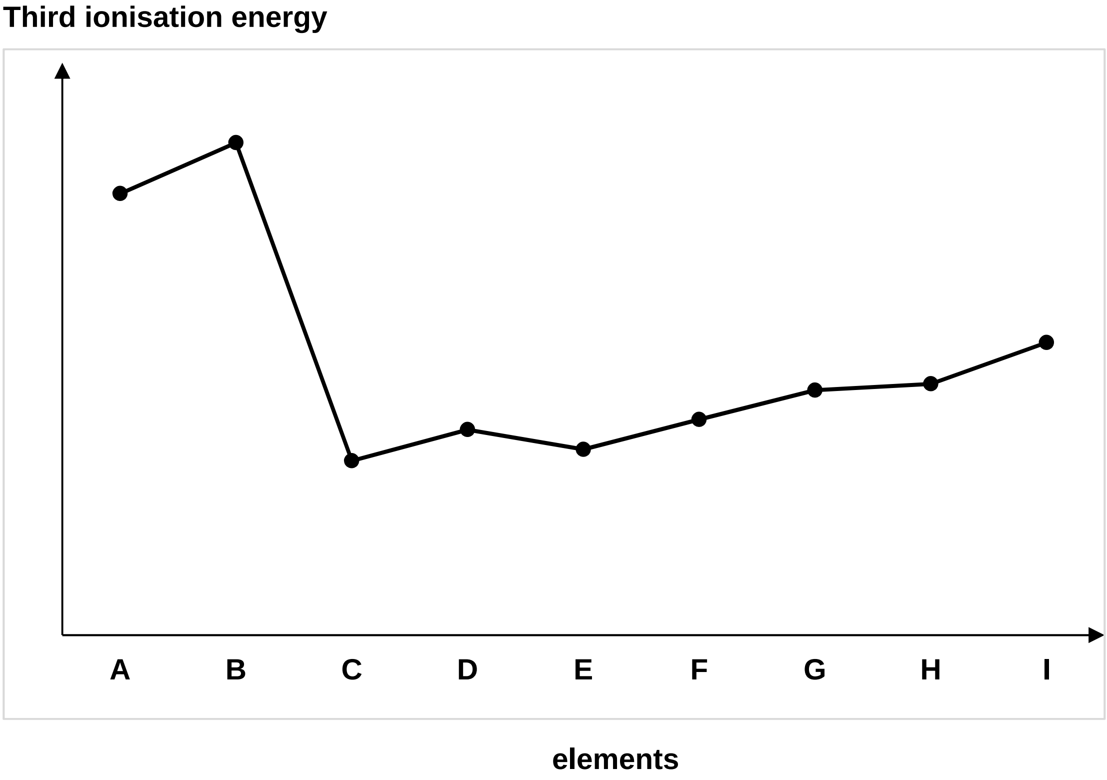

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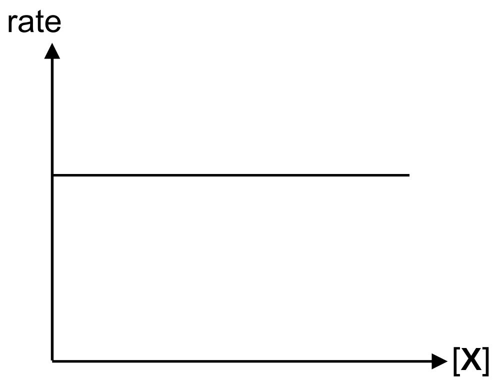

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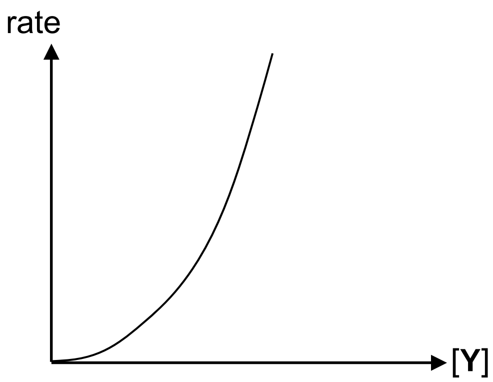

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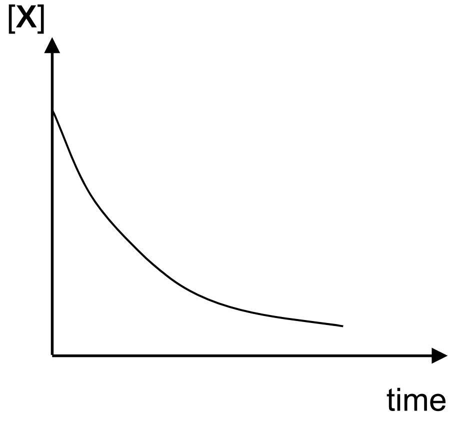

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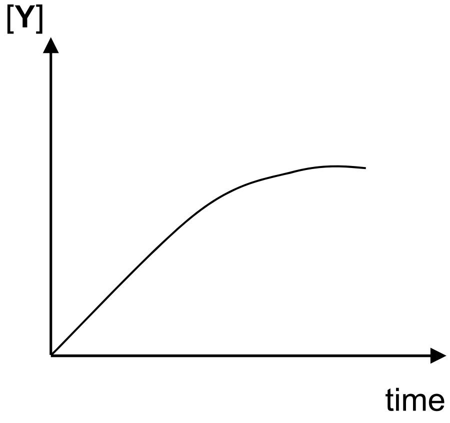

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$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g) \qquad \Delta H = -92\ kJ\ mol^{-1}$$

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2 It conducts electricity in the solid state.
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A **3** only **B** **1** and **2** only

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

18 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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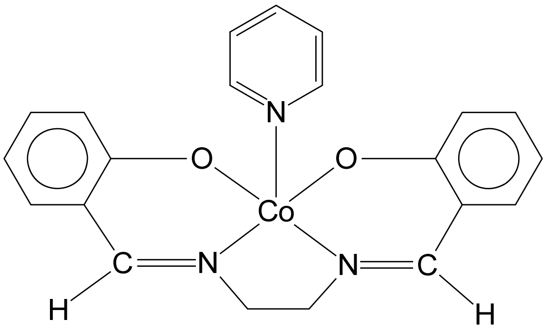

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A 1 only **B** 3 only

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

25 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

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

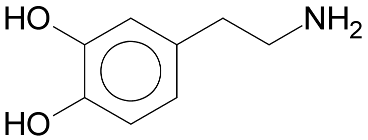
A $CH_2BrCH_2\bullet + Br_2 \longrightarrow CH_2BrCH_2Br + Br\bullet$

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

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

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

27 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

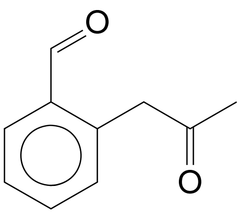
B 3 only

C 1 and 2 only

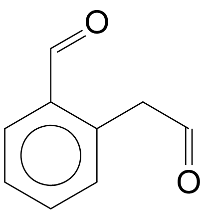
D 2 and 3 only

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

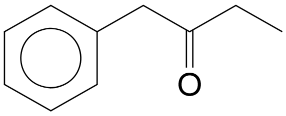
A



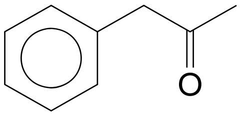
B



C



D



29 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

30 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: ____________________

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**

This question paper consists of **20** printed pages and **2** blank pages.

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.

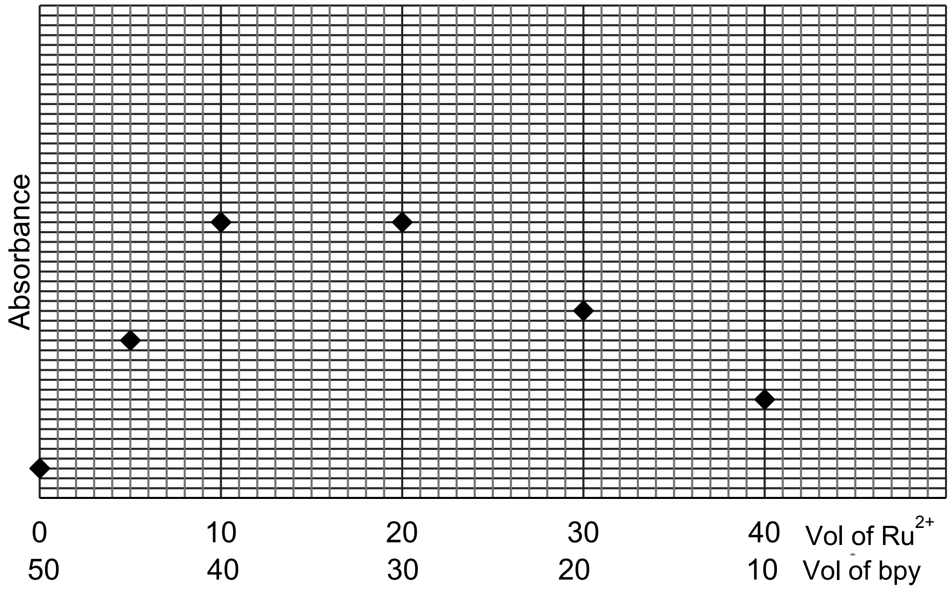


Fig 1.1

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

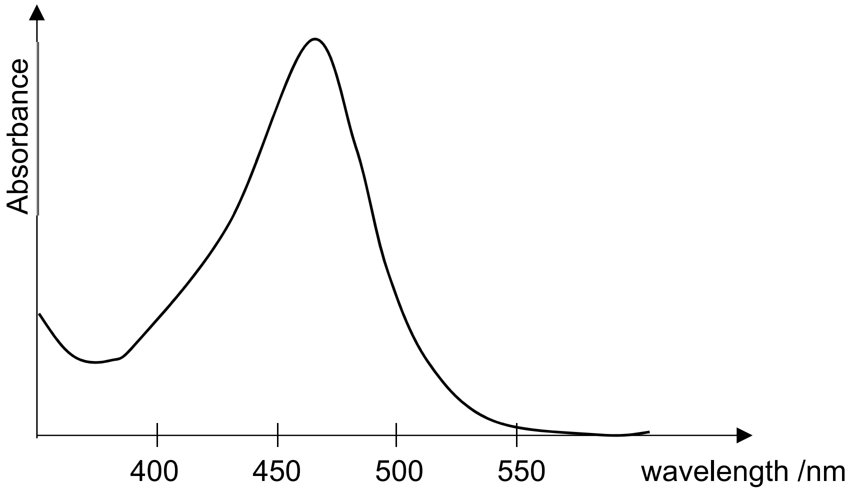
Formula of complex ion: …………………………..
Structure of complex ion:

[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.

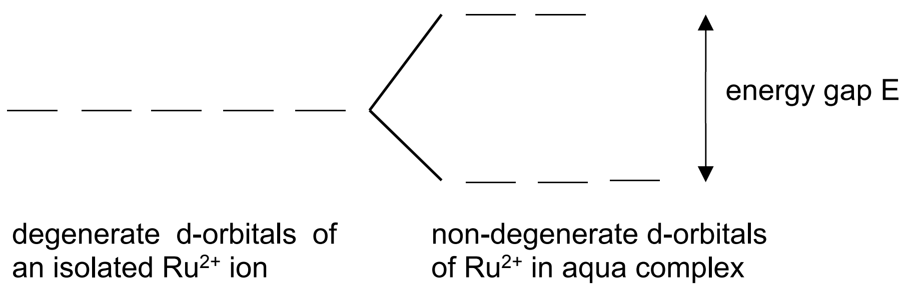


Fig 1.2

(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.

……………………………………………………………………………………………

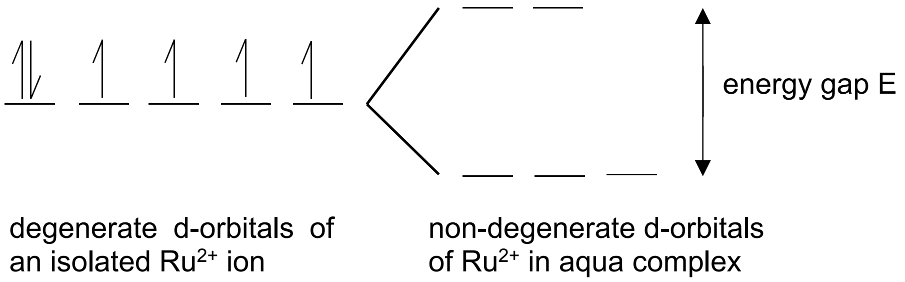
……………………………………………………………………………………………[1]

(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.

……………………………………………………………………………………………

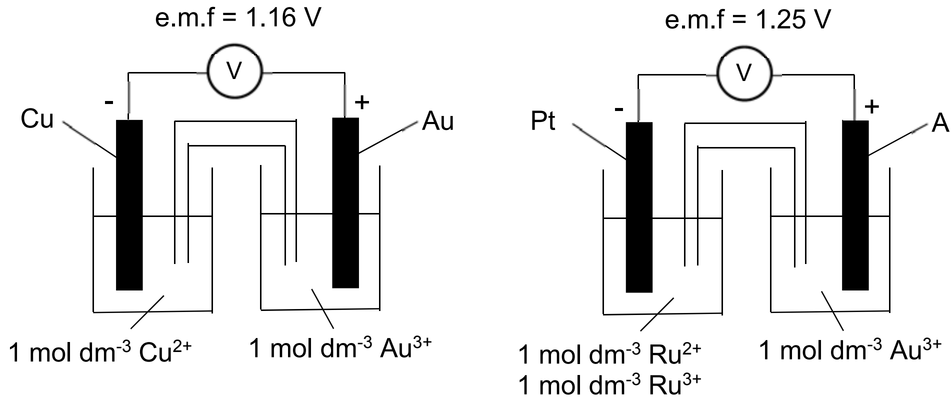
…………………………………………………………………………………………… [1]

(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^-.

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

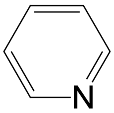
……………………………………………………………………………………

……………………………………………………………………………………

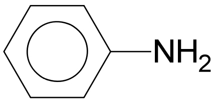
……………………………………………………………………………………

…………………………………………………………………………………… [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]

For Examiners' Use

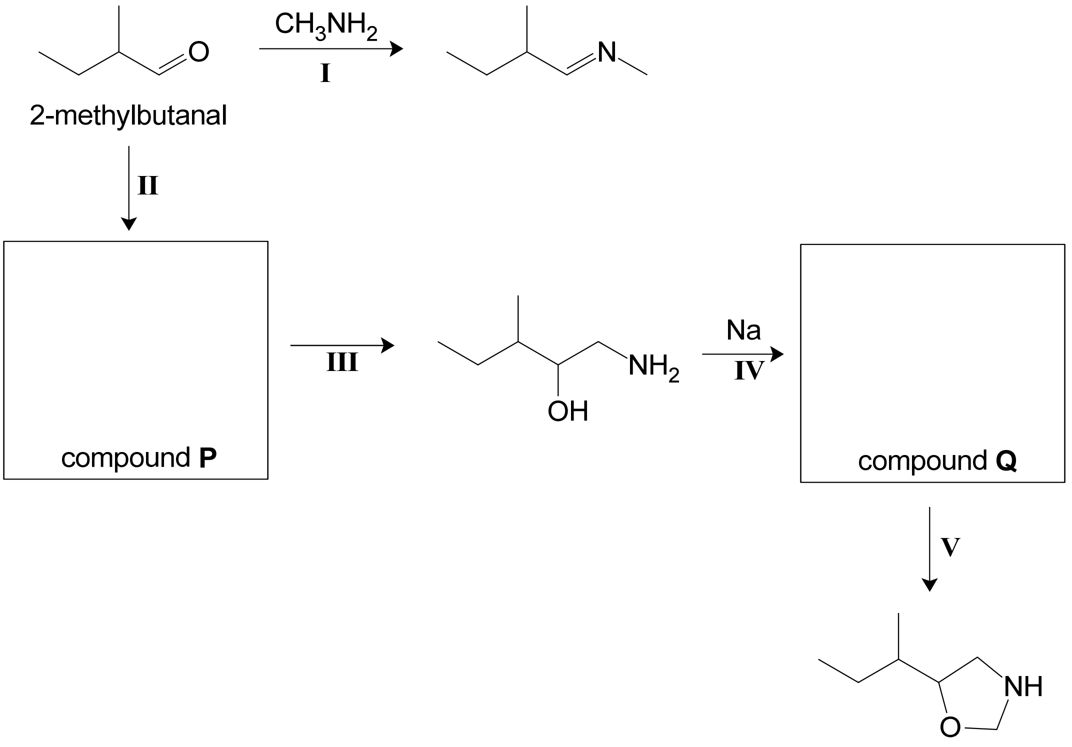
(v) Suggest why barium propanoate undergoes thermal decomposition more readily than barium carbonate.

……………………………………………………………………………………………

……………………………………………………………………………………………..

……………………………………………………………………………………………[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]

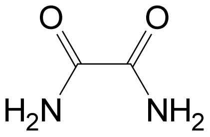
(c) Explain, in terms of bonding, why cyanogen dissolves readily in water.

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

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

……………………………………………………………………………………………….[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**.

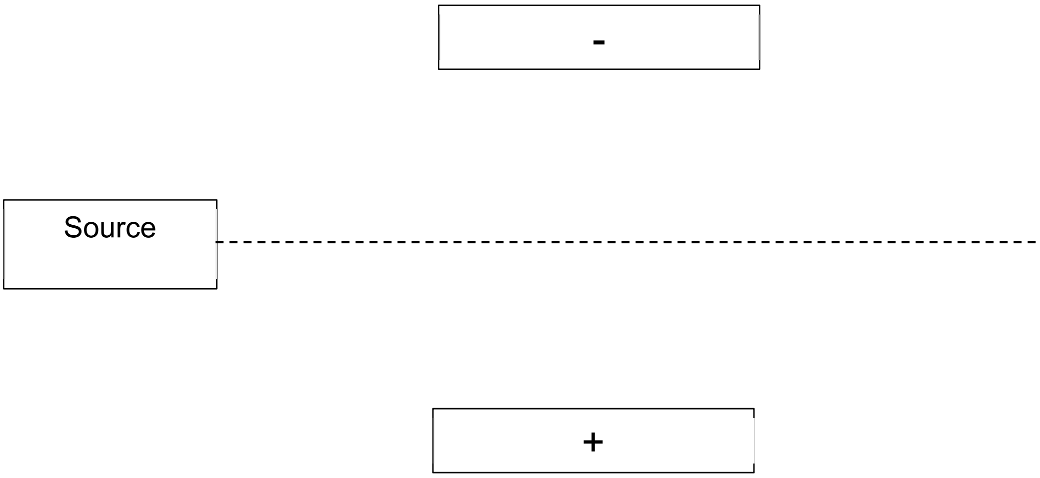
[3]

(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.



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

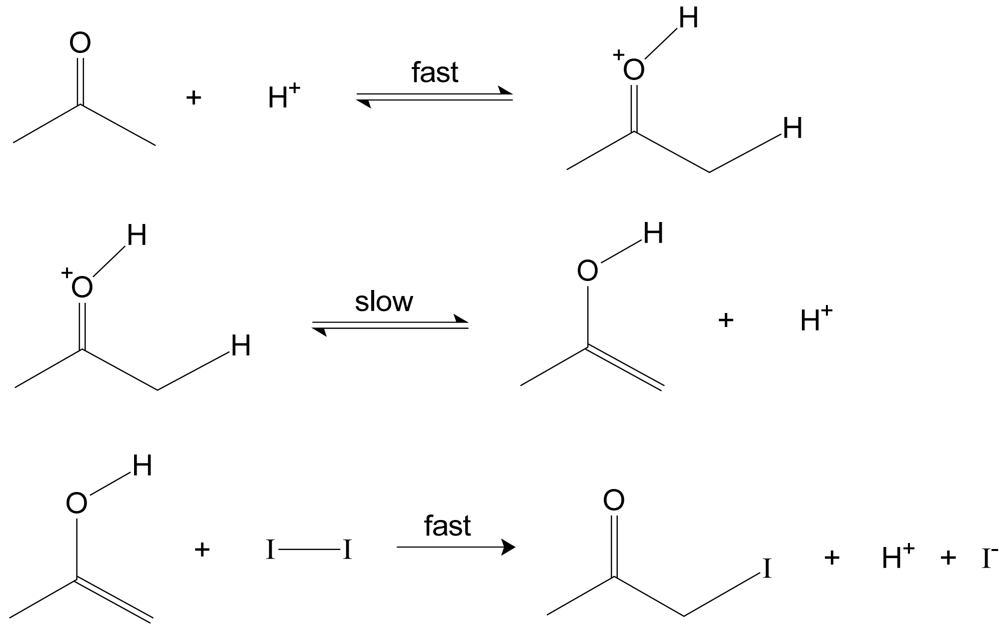
……………………………………………………………………………………………… [5]

[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.

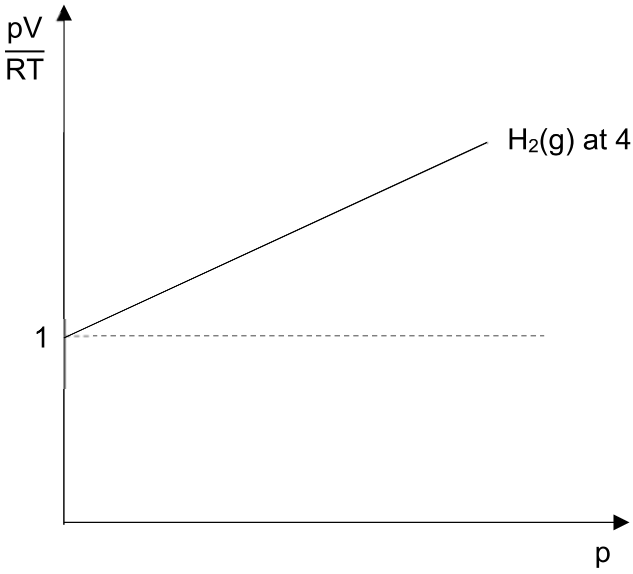


Fig 5.1

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

…………………………………………………………………………………………………

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

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

…………………………………………………………………………………………………

…………………………………………………………………………………………………

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

[Total: 16]

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H

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.

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Answer **all** questions.

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

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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]

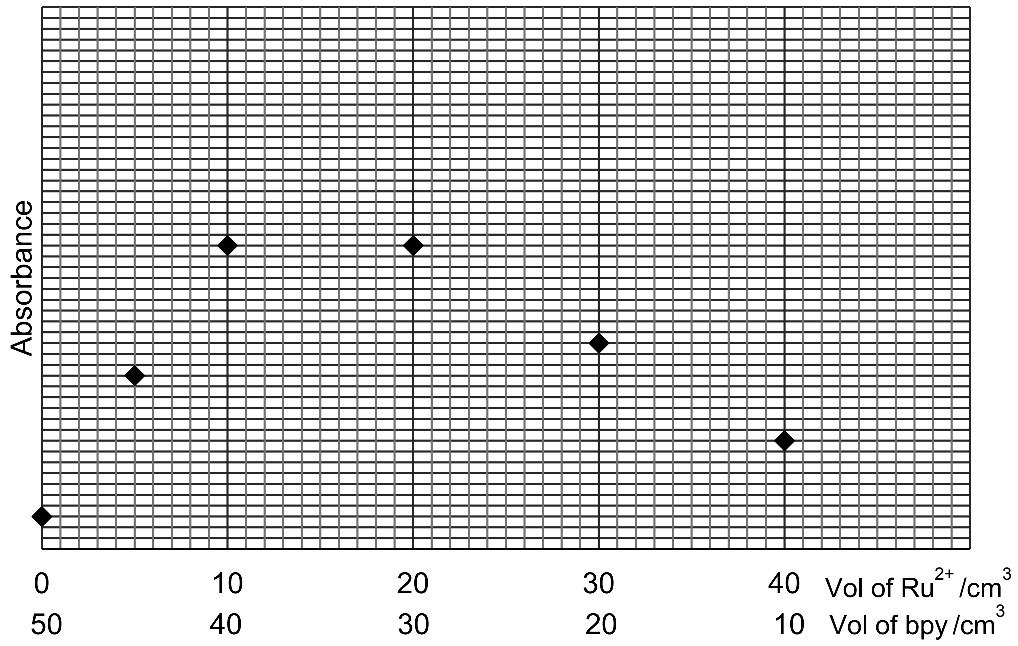
Ligand is a <u>neutral molecule or anion</u> which contain at least one atom bearing a <u>lone pair of electrons</u> which can form a <u>dative bond</u> to a central atom/ion, resulting in the formation of a complex.

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.

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

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.

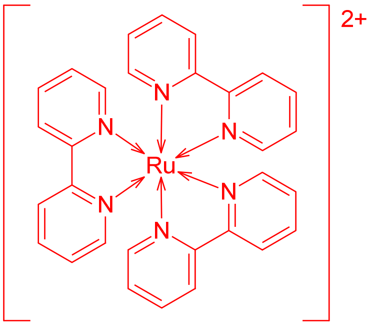
Formula of complex: …………………………..

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

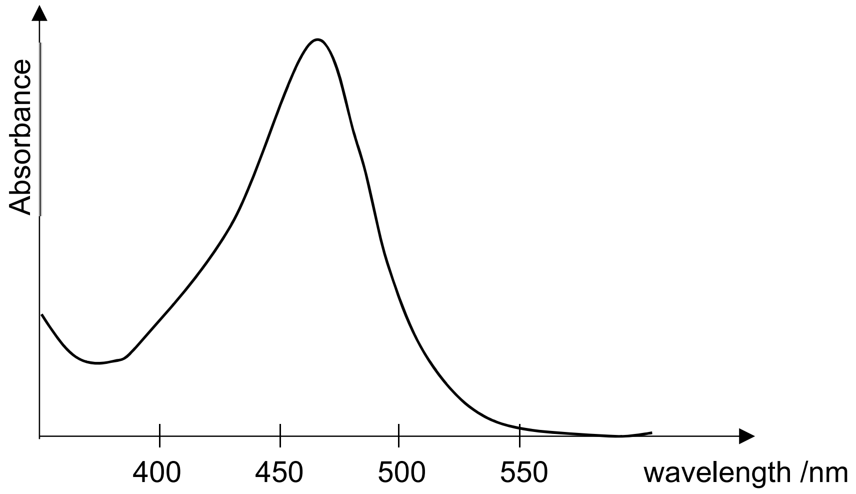


(c) The table below shows the colour of the radiation of the electromagnetic spectrum and the corresponding wavelength range.

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.

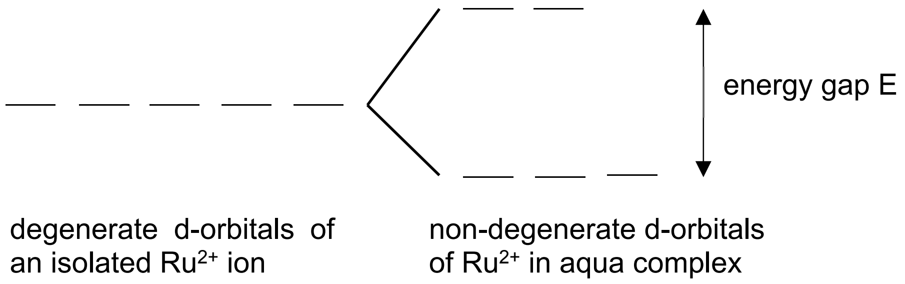
.... [1]

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.

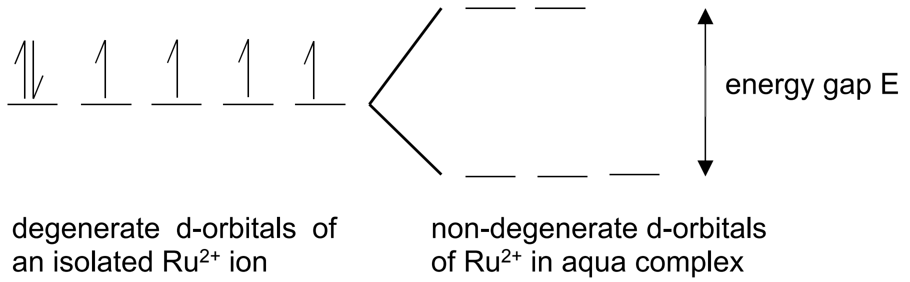
(iii) With reference to the relative sizes of 3d and 4d orbitals, suggest a reason why 4d electrons prefer to pair up in the lower energy d-orbital before filling the higher energy d-orbitals.

…………………………………………………………………………………………

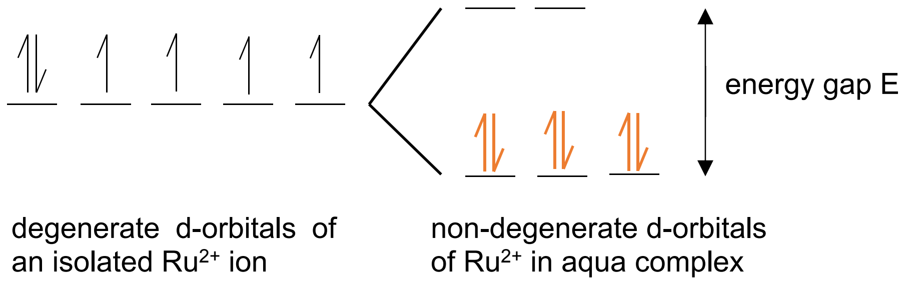
………………………………………………………………………………………… [1]

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.

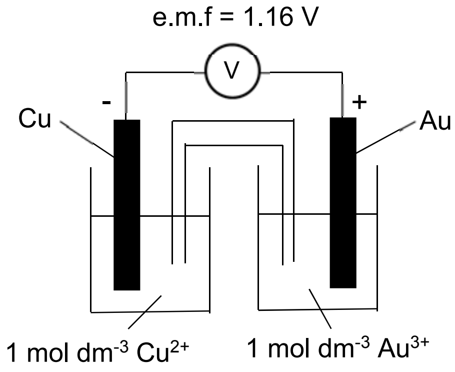
(iv) In the diagram below, show the electronic distribution of a Ru^{2+} ion in the ‘low spin’ state, given that the electronic configuration of Ru^{2+} is [Kr] $4d^6$.



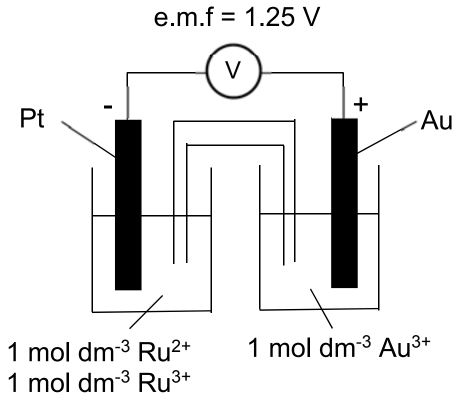
[1]



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



cell A



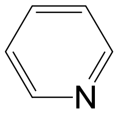
cell B

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

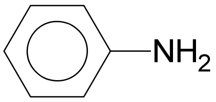
…………………………………………………………………………………………

…………………………………………………………………………………………[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 $MgCO_3$.

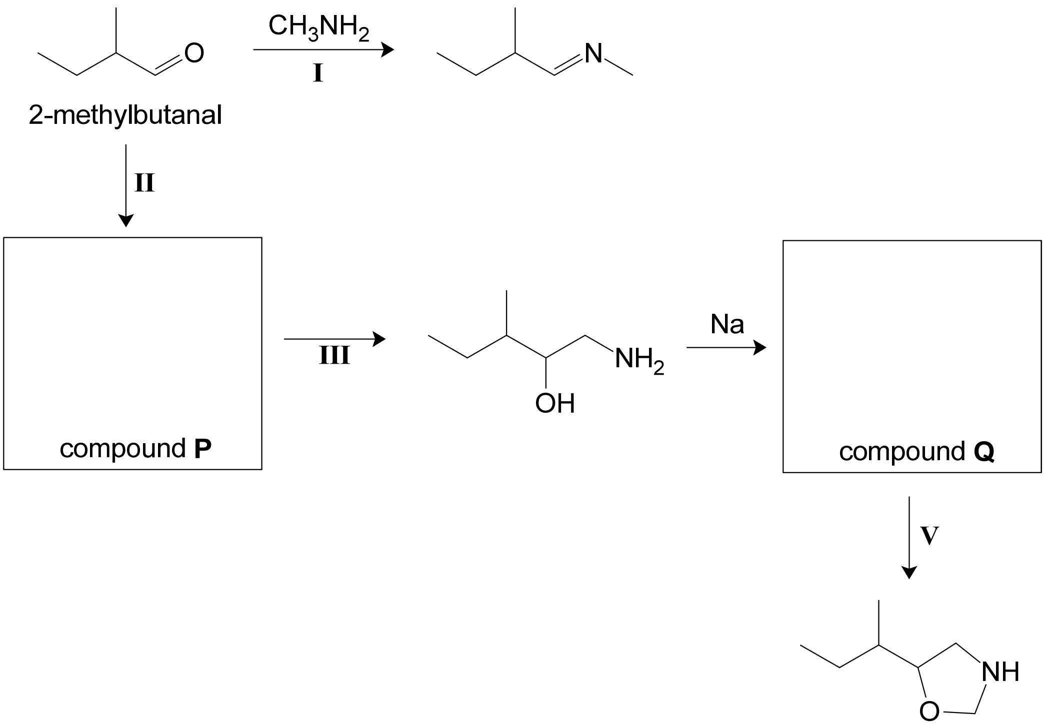
…………………………………………………………………………………[1]

$MgCO_3 \rightarrow MgO + CO_2$

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.

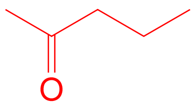
		(ii)	Explain why $MgCO_3$ undergoes thermal decomposition more readily than $BaCO_3$. ………………………………………………………………………………………... ………………………………………………………………………………………... ……………………………………………………………………………………… [2]	
			Mg^{2+} has a smaller ionic radius hence a higher charge density, its higher polarising power allows 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.		

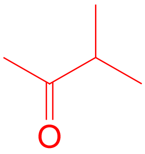


(i) **R** is a constitutional isomer of 2-methylbutanal. **R** gives yellow precipitate when warmed with aqueous iodine in an alkaline medium. **R** does not decolourise aqueous bromine.

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

[2]





;;

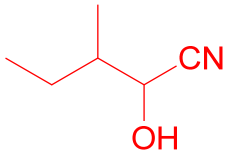
(ii) Draw the structure of compounds **P** and **Q** in the boxes provided in the reaction scheme and state the reagents and conditions for steps **II**, **III** and **V**.

Step	**Reagents and Conditions**
II	
III	

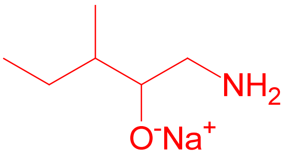
V	

[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

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

n= 0.01986 mol

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

$M_r = 51.87$ (;)

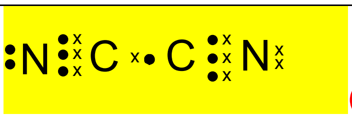
$MF = (CN)_y$

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

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.

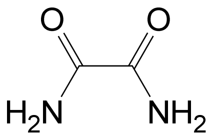
……………………………………………………………………………………………......

……………………………………………………………………………………………….

……………………………………………………………………………………………[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.

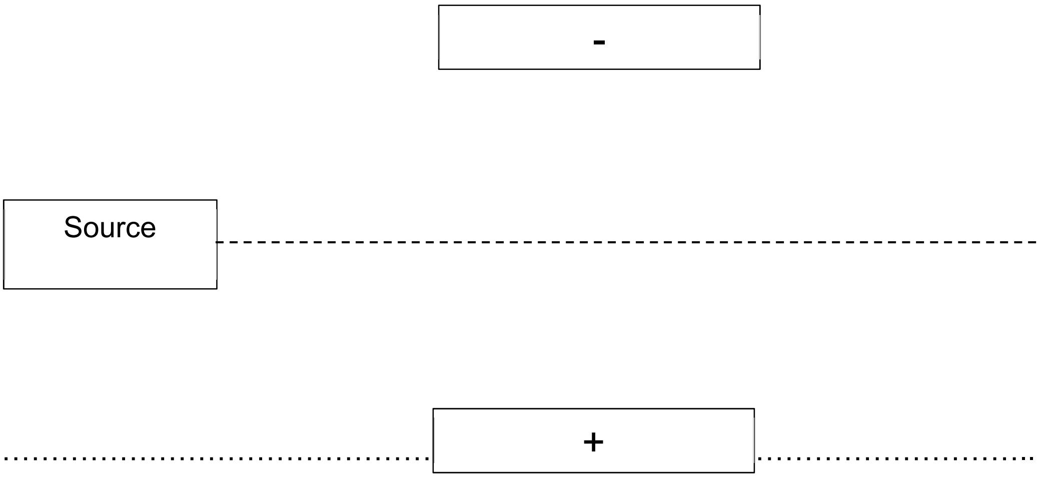
[3]

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 (;)

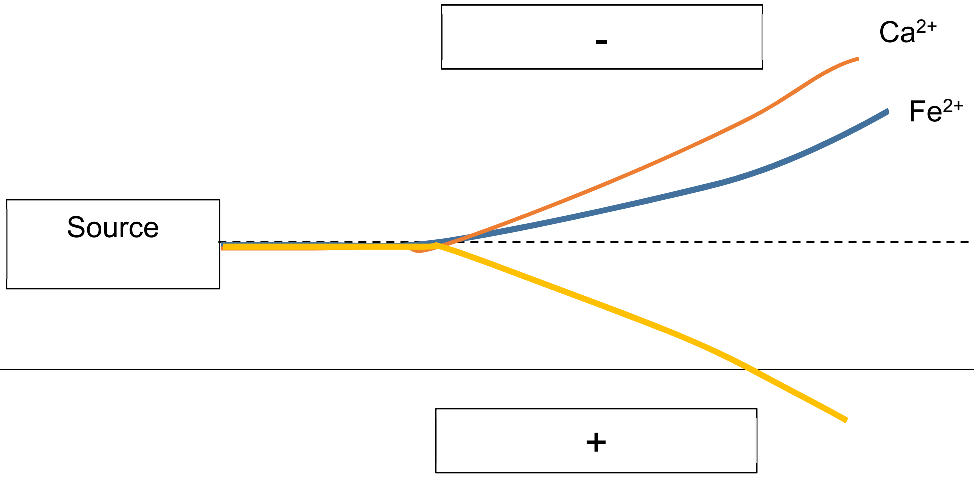
It is not within the % daily recommended allowance. (;)

(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]



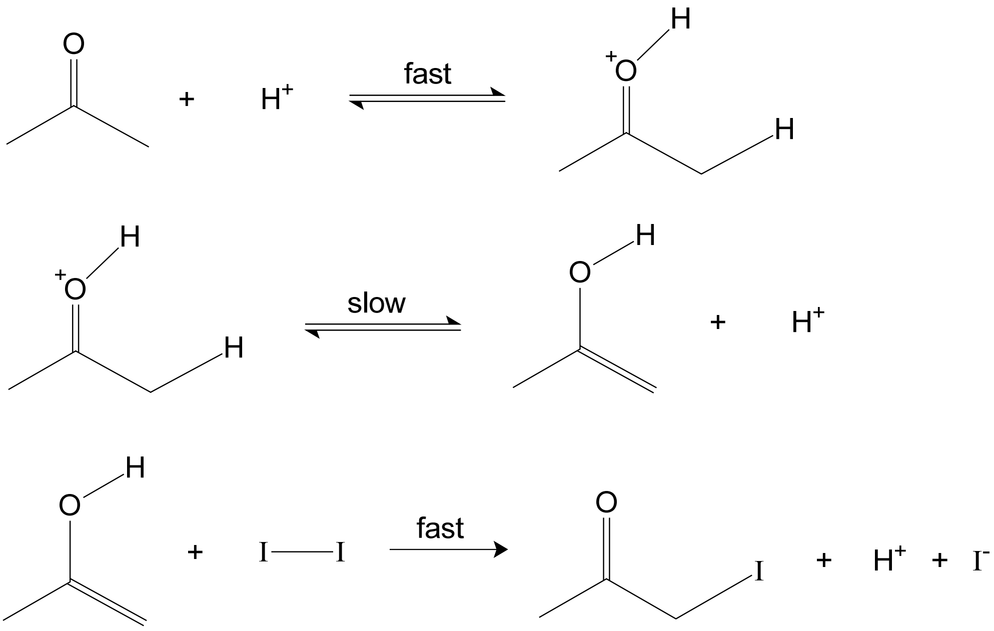
I^-

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.(;)

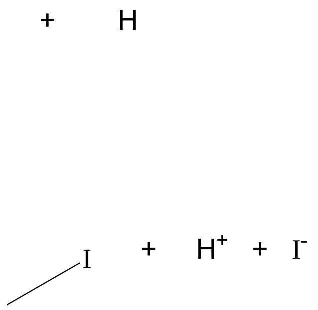
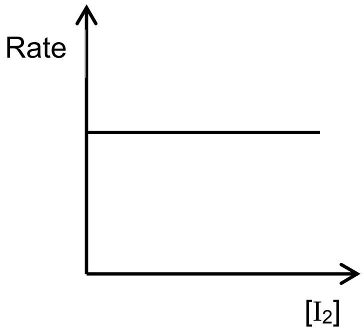
5 **(a)** Propanone reacts with iodine in the presence of an acid catalyst.

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

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(;)

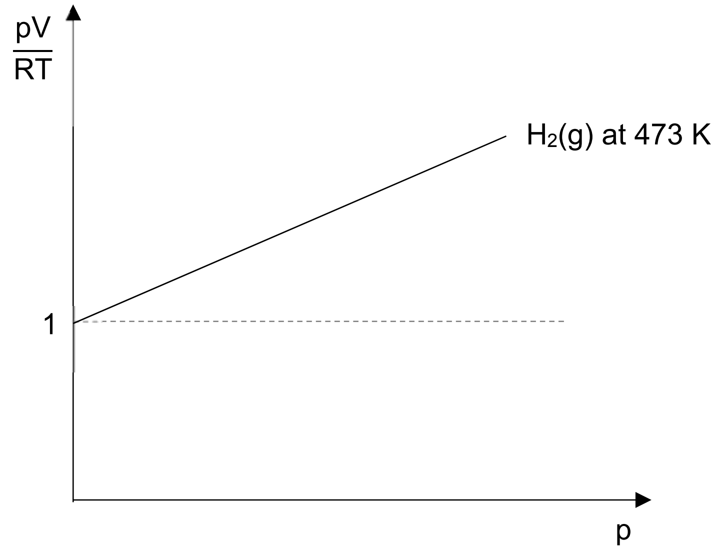
Amount of I_2 in the 100 cm^3 solution= 0.001005 x 4 = 0.00402 mol

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

(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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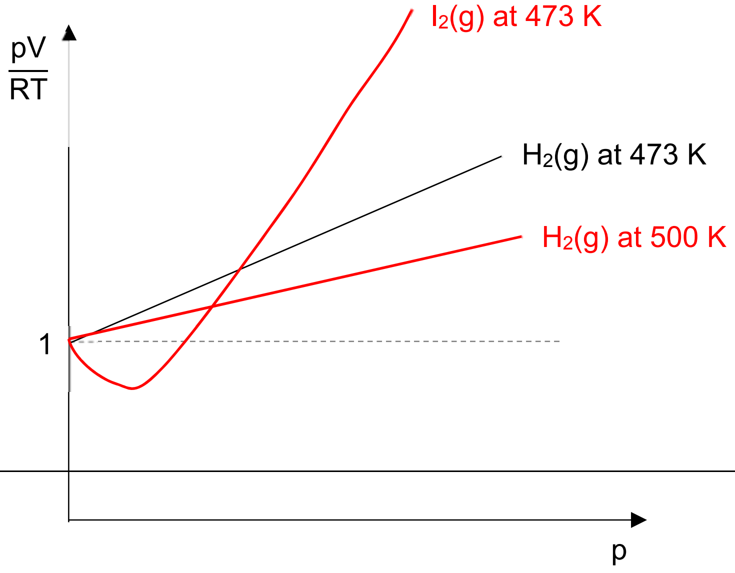
…………………………………………………………………………………………………

………………………………………………………………………………………… [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.

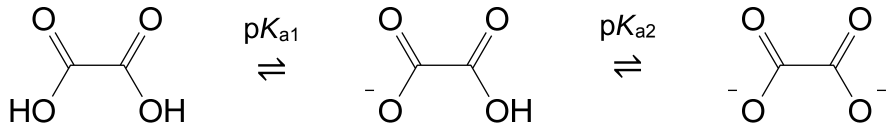
Question	**Section A**			**Section B**		Total
	1	**2**	**3**	**4**	**5**	
Marks	**23**	**20**	**17**	**20**	**20**	**80**

This question paper consists of **11** printed pages and **1** blank page.

Section A

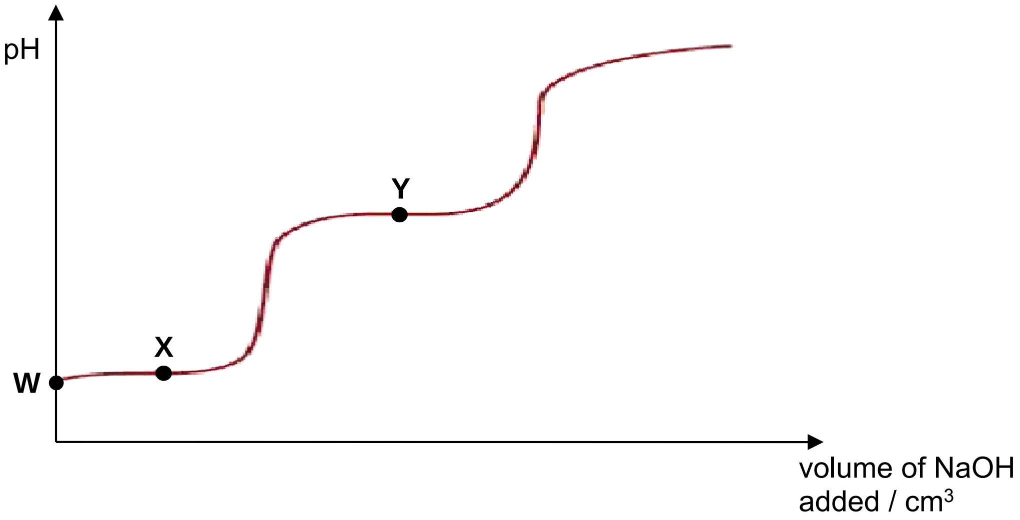
Answer **all** questions from this section.

1 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]

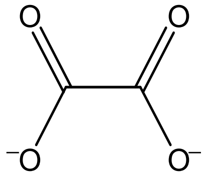
(c) **(i)** Define the term *buffer*. [1]

(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]

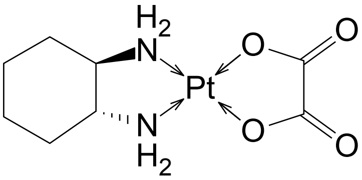
The oxalate ion, $C_2O_4^{2-}$, is known to form complexes with transition metal ions such as platinum(II). The structure of the oxalate ion is as follows.



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

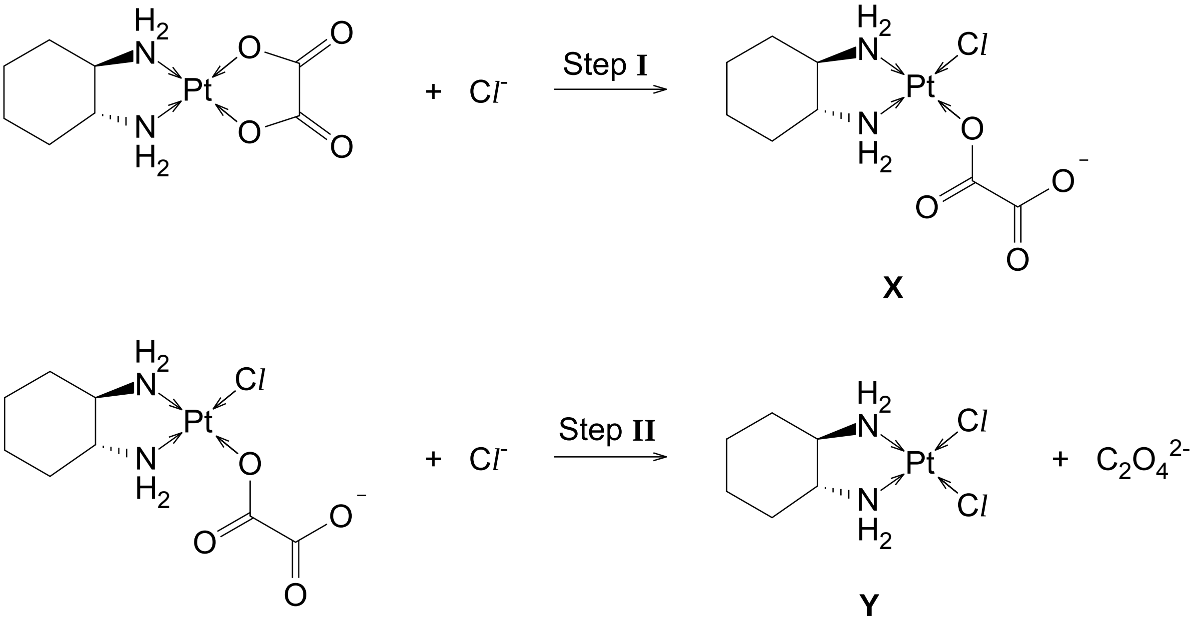
Given that platinum(II) is a transition metal ion known to form **square planar complexes**, explain the observation seen with the aid of a chemical equation. [3]

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]

2 **(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

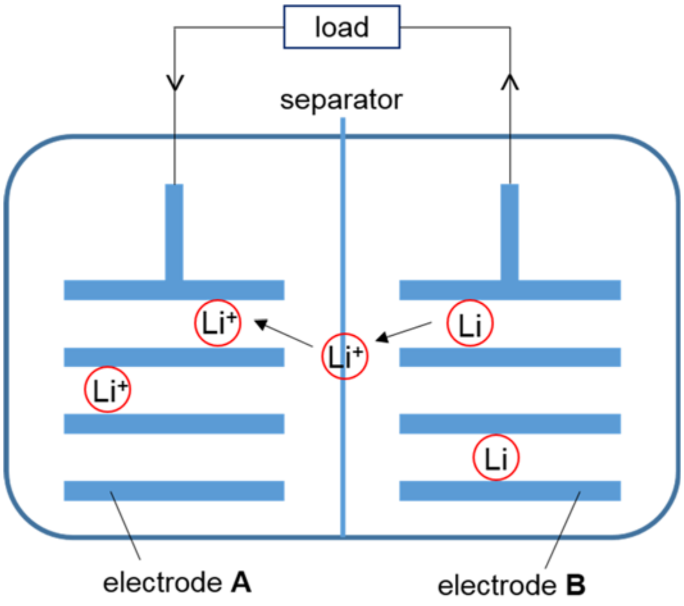
$$CoO_2 + Li^+ + e^- \rightarrow LiCoO_2,$$

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.

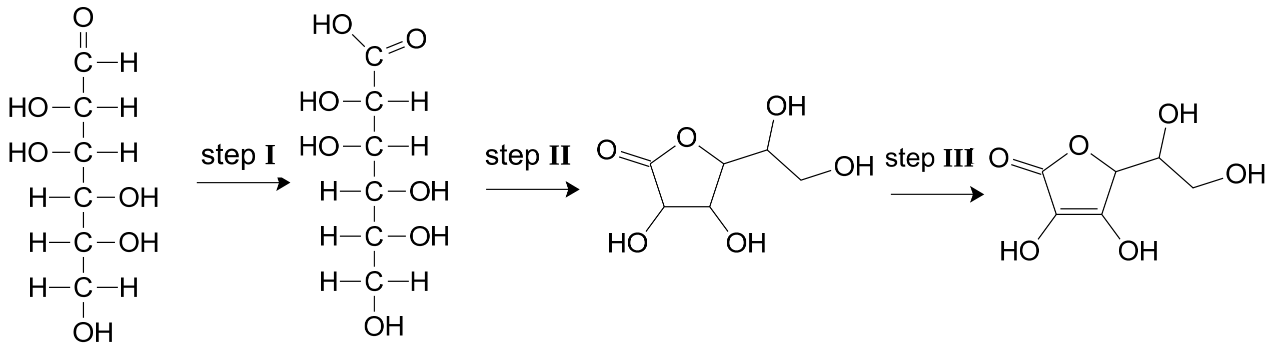
1st electron affinity of oxygen = -141.1 kJ mol^{-1}
2nd electron affinity of oxygen = +798 kJ mol^{-1}
enthalpy change of atomisation of lithium = +159.4 kJ mol^{-1}
enthalpy change of formation of lithium oxide = -597.9 kJ mol^{-1}

[4]

[Total: 20]

3 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]

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

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

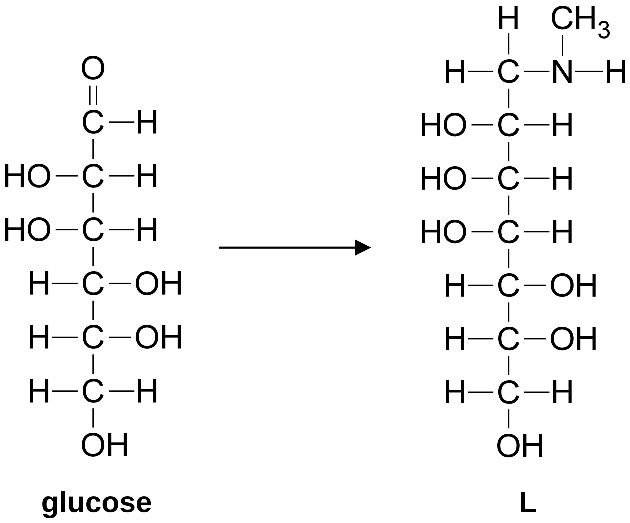
(d) Identify the type(s) of stereoisomerism shown by ascorbic acid. State the total number of possible stereoisomers. [2]

(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.

4 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]

(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]

5 **(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]

Class	Adm No

Candidate Name: ____________________

H

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.

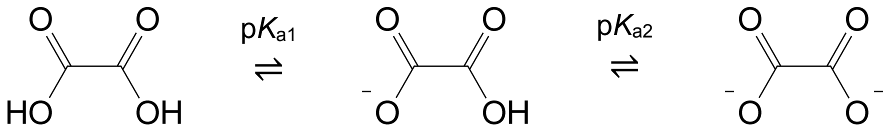
Question	**Section A**			**Section B**		Total
	1	**2**	**3**	**4**	**5**	
Marks	**23**	**20**	**17**	**20**	**20**	**80**

This question paper consists of **11** printed pages and **1** blank page.

Section A

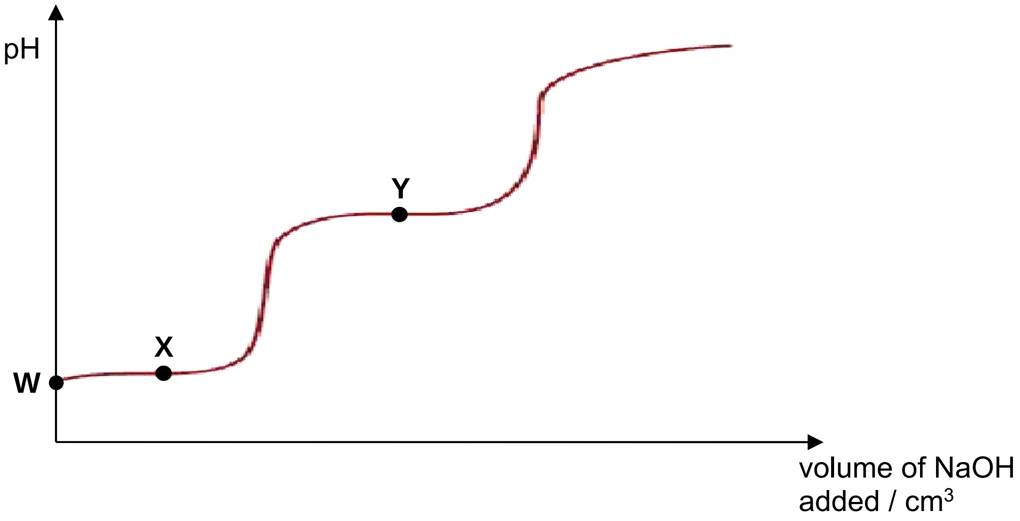
Answer **all** questions from this section.

1 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]

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

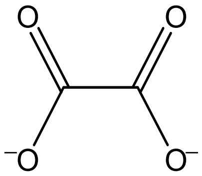
(d) **(i)** Describe how you would recognise the end point of the titration described. [1]

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.

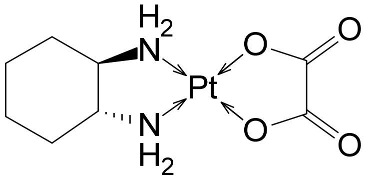
Given that platinum(II) is a transition metal ion known to form **square planar complexes**, explain the observation seen with the aid of a chemical equation. [3]

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

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

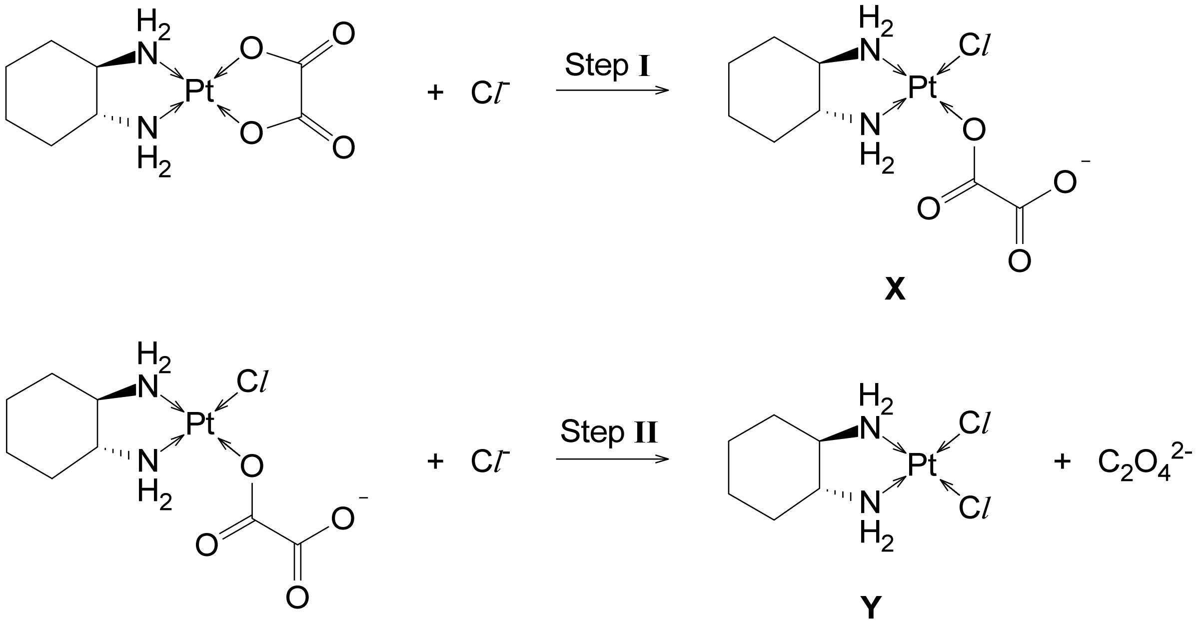
Transition metal ions such as Pt have a high charge density and can polarise the H_2O ligands to release H^+, making the solution acidic.

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]

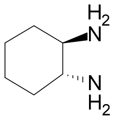
Not feasible, as entropy change of the ligand exchange reaction is negative / reaction is entropically disfavoured due to a decrease in the number of particles.

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

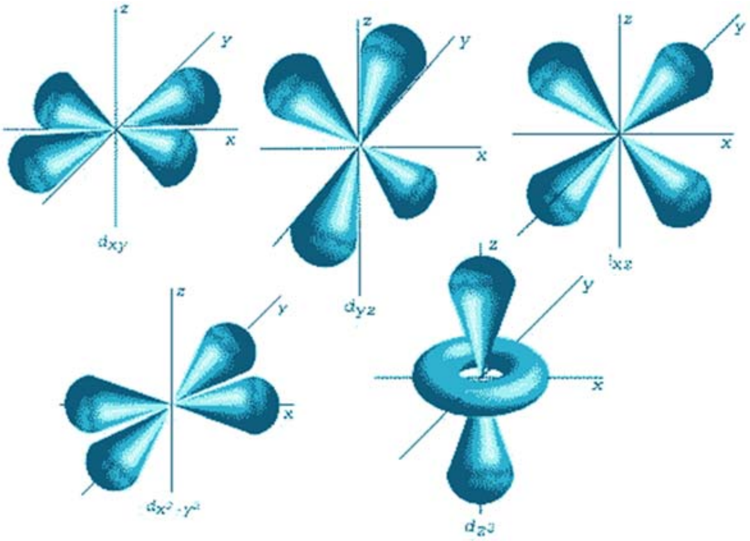
(ii) State the full electronic configuration of $^{52}Cr^{3+}$. [1]

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

[Turn over

(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]



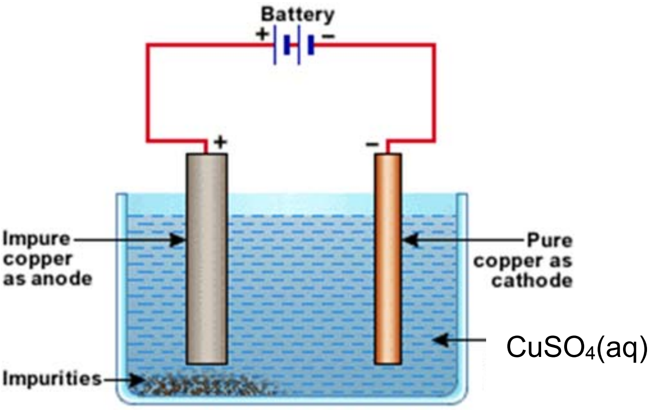
[Total: 23]

2 **(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

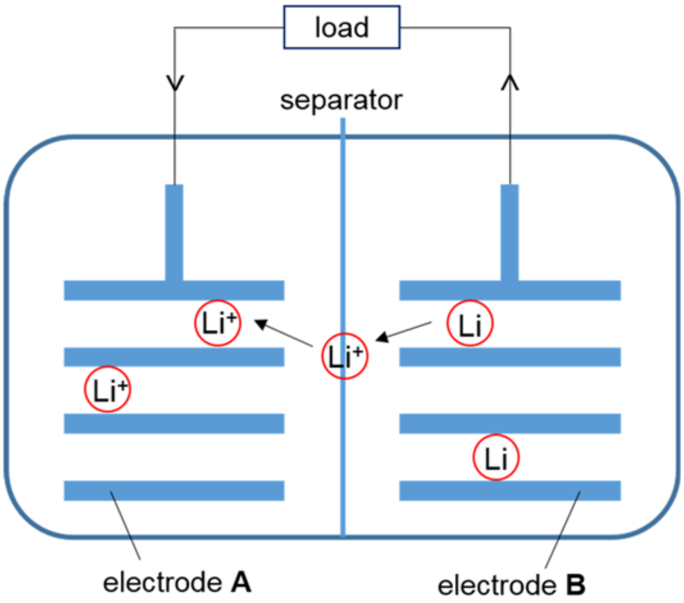
$$CoO_2 + Li^+ + e^- \rightarrow LiCoO_2,$$

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]

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

(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.

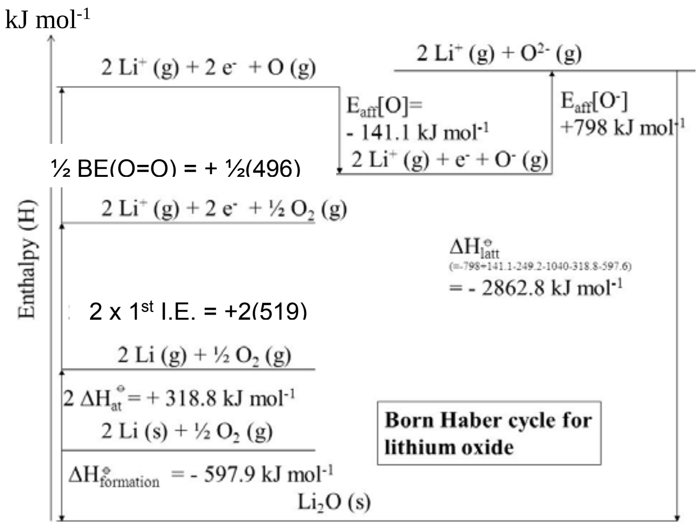
(i) Write an equation, with state symbols, to represent the lattice energy of lithium oxide. [1]

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

(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]



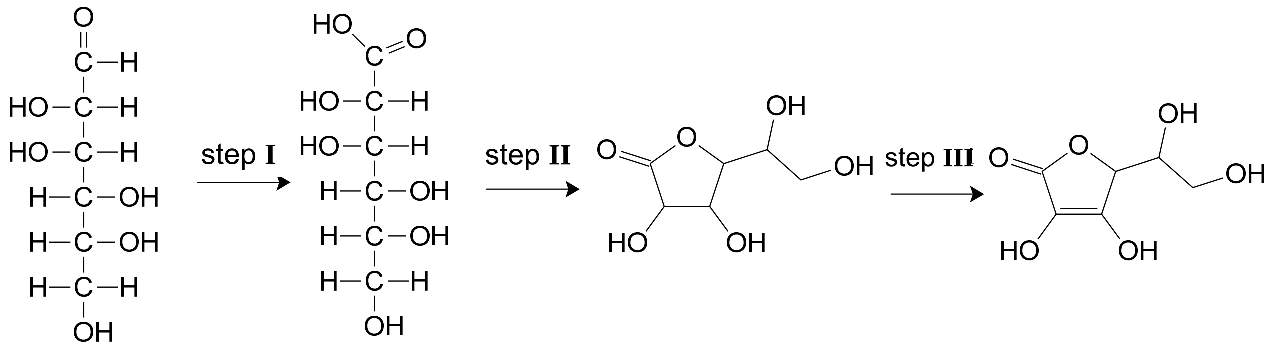
L.E. = -798 – (-141.1) – ½(496) – 2(519) – 2(159.4) + (-597.9)
= -2859.6 kJ mol^{-1}
= -2860 kJ mol^{-1} (3 sf)

[Total: 20]

[Turn over

3 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 = $2^2 = 4$

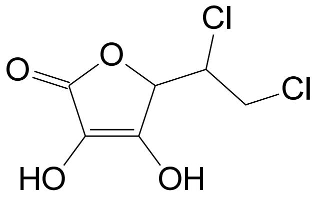
(e) Explain why ascorbic acid is water soluble. [2]

Energy released from the hydrogen bonding between ascorbic acid and water

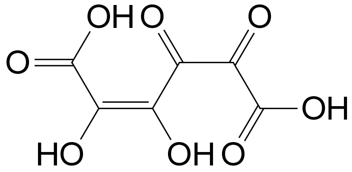
is sufficient to overcome the hydrogen bonding between ascorbic acid molecules and hydrogen bonding between water molecules. Hence, ascorbic acid is water soluble.

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

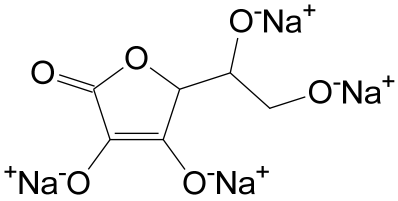
(i) PCl_5



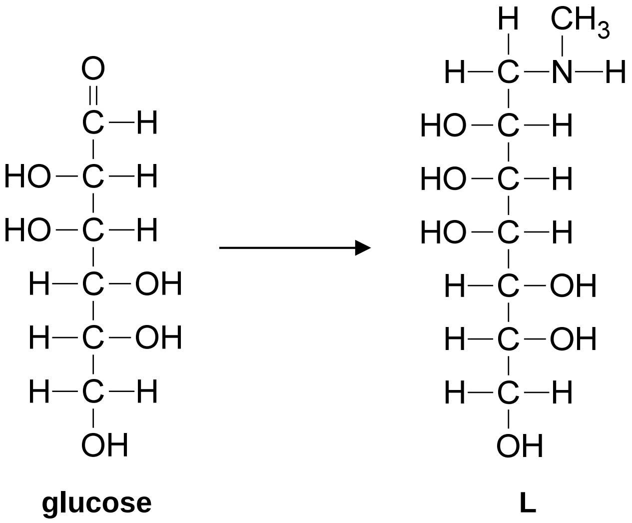
(ii) excess hot acidified $K_2Cr_2O_7$



(iii) Na(s)



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



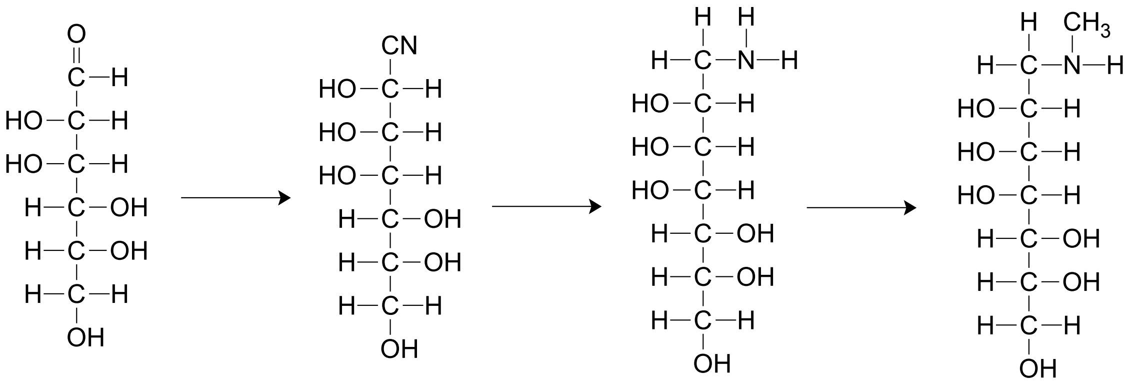
Suggest a synthetic route, involving *not more than three steps*, from **glucose** to **L**.

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: $LiAlH_4$ in dry ether

Step 3: Limited CH_3Cl, heat



[Total: 17]

Section B

Answer **one** question from this section.

4 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]

$Cl_2 + H_2 \rightarrow 2HCl$

(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 NaC*l* = 0.1479 x (23.0 + 35.5) = 8.654 g

% purity of NaC*l* = 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]

5 **(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]