	Class	Adm No
Candidate Name: ____________________		

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.

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…………………………………………………………………………………………………[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.

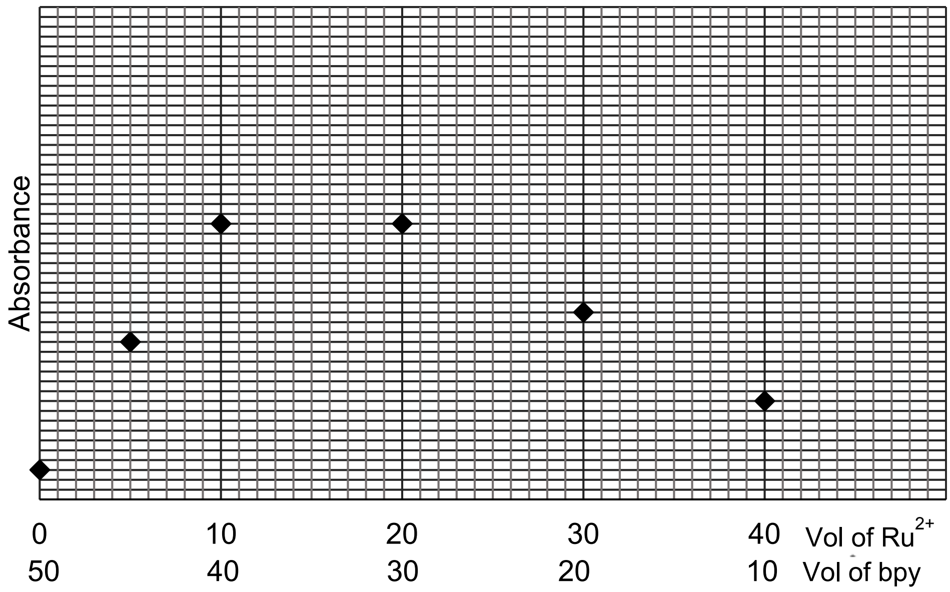


Fig 1.1

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.

Formula of complex ion: …………………………..

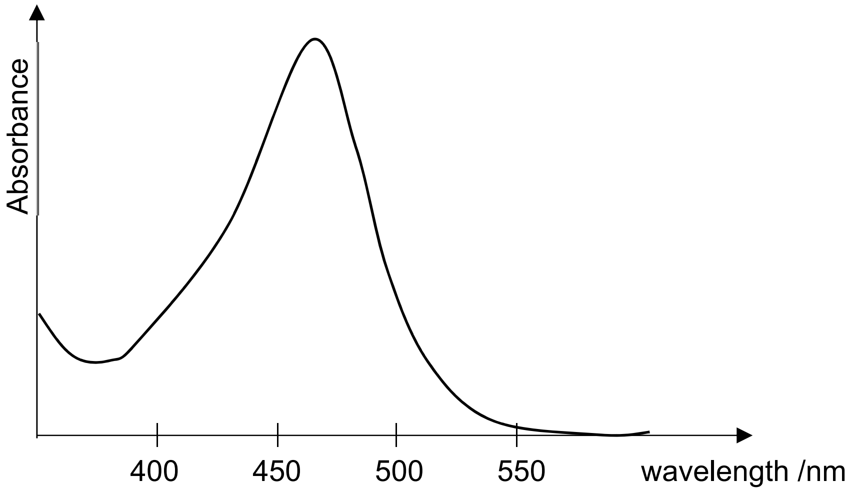
Structure of complex ion:

[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

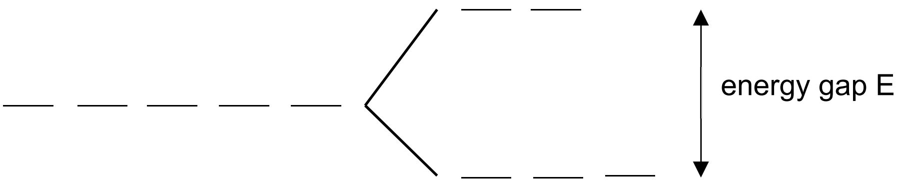
The diagram below shows the UV-Visible spectrum of the complex formed between Ru^{2+} and bpy.



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.



degenerate d-orbitals of an isolated Ru^{2+} ion

non-degenerate d-orbitals of Ru^{2+} in aqua complex

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.

……………………………………………………………………………………………

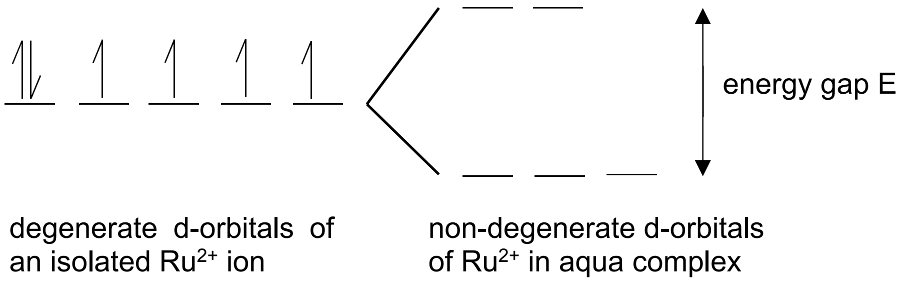
……………………………………………………………………………………………[1]

(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+}.

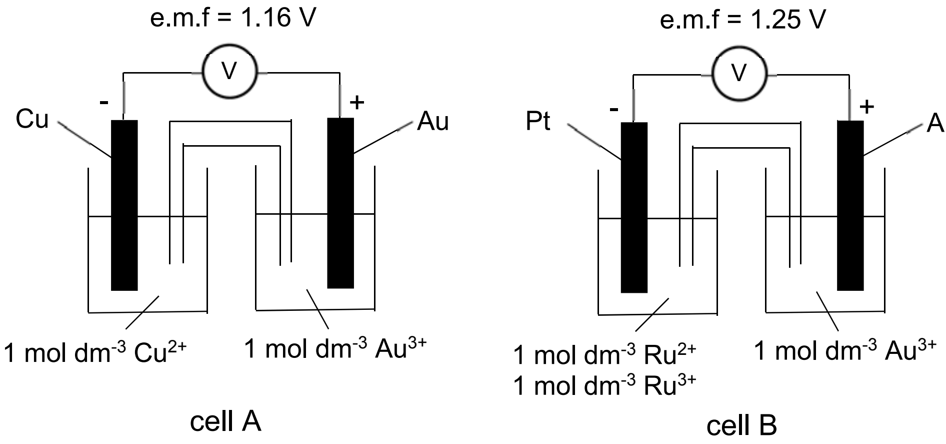


Fig 1.3

(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^-.

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

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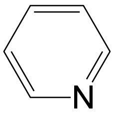
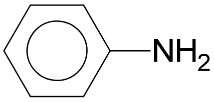
…………………………………………………………………………………………… [3]

(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.

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

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

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…………………………………………………………………………………………………… [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 $BaCO_3$.

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…………………………………………………………………………………...

…………………………………………………………………………………...

………………………………………………………………………………….. [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.

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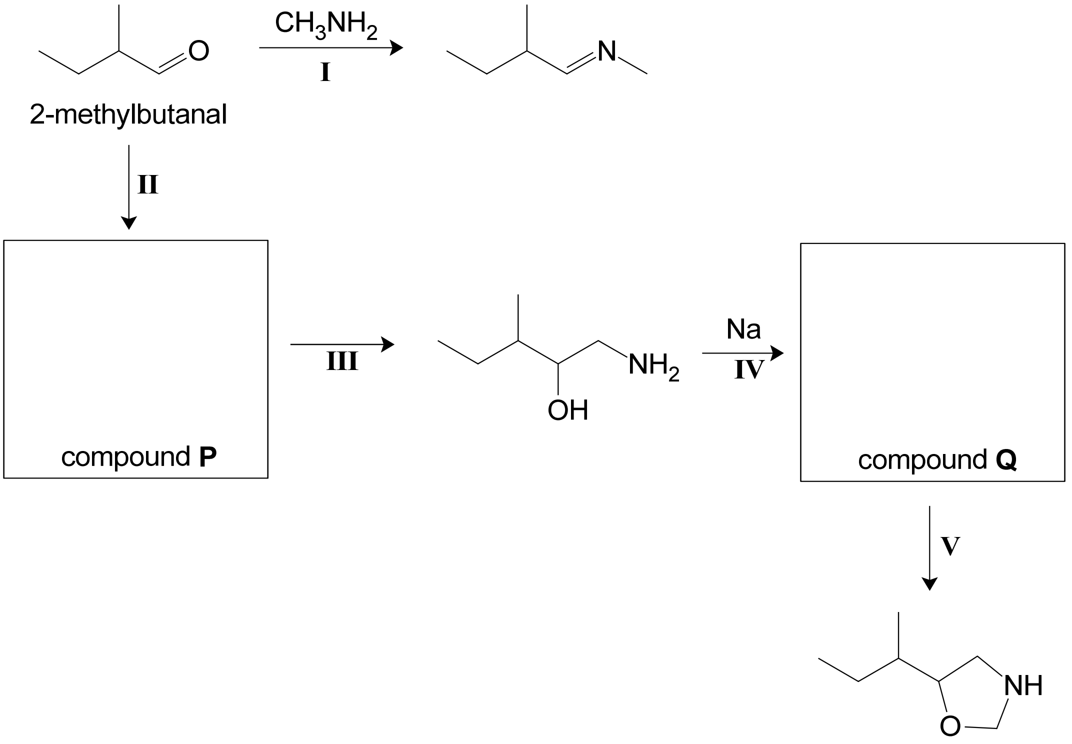
……………………………………………………………………………………………[2]

(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]

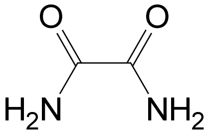
(c) Explain, in terms of bonding, why cyanogen dissolves readily in water.

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

…………………………………………………………………………………………….

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

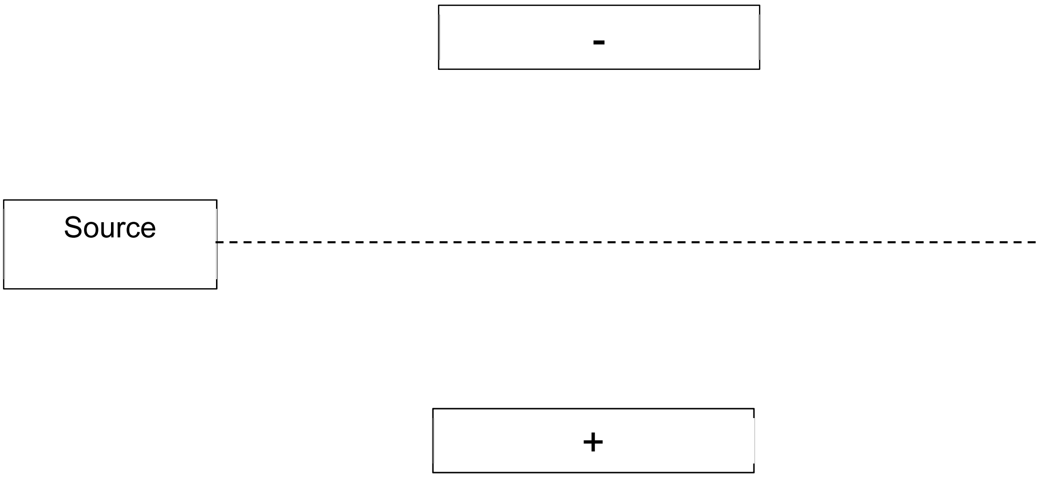
[3]

(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.



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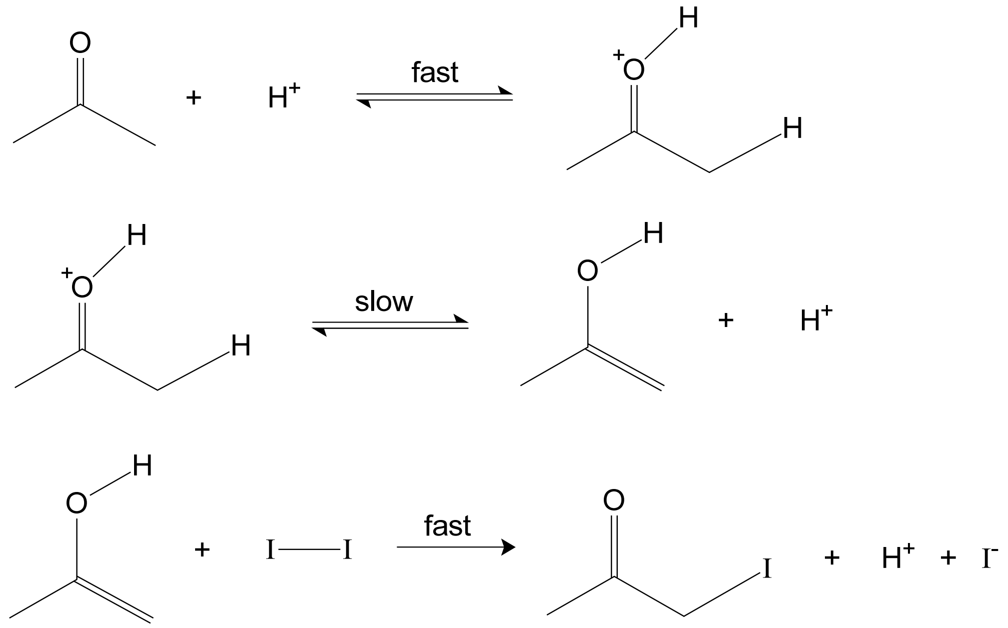
……………………………………………………………………………………………. [5]

[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.

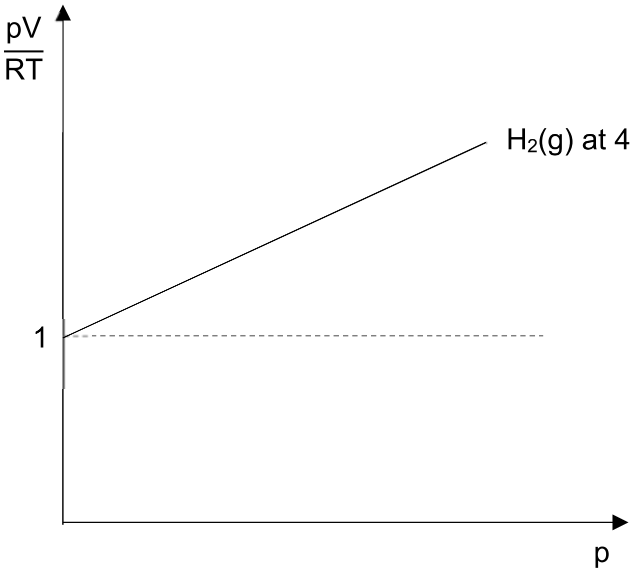


Fig 5.1

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

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

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

[Total: 16]

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