H

millennia institute

2018 Preliminary Exams
Pre-University 3

H2 CHEMISTRY **9729/02**

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

2 hours

Candidates answer on the Question paper.

Additional materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

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

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

Write in dark blue or black pen.

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

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

Answer **all** questions.

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

A Data Booklet is provided.

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

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

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

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

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

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

……

……

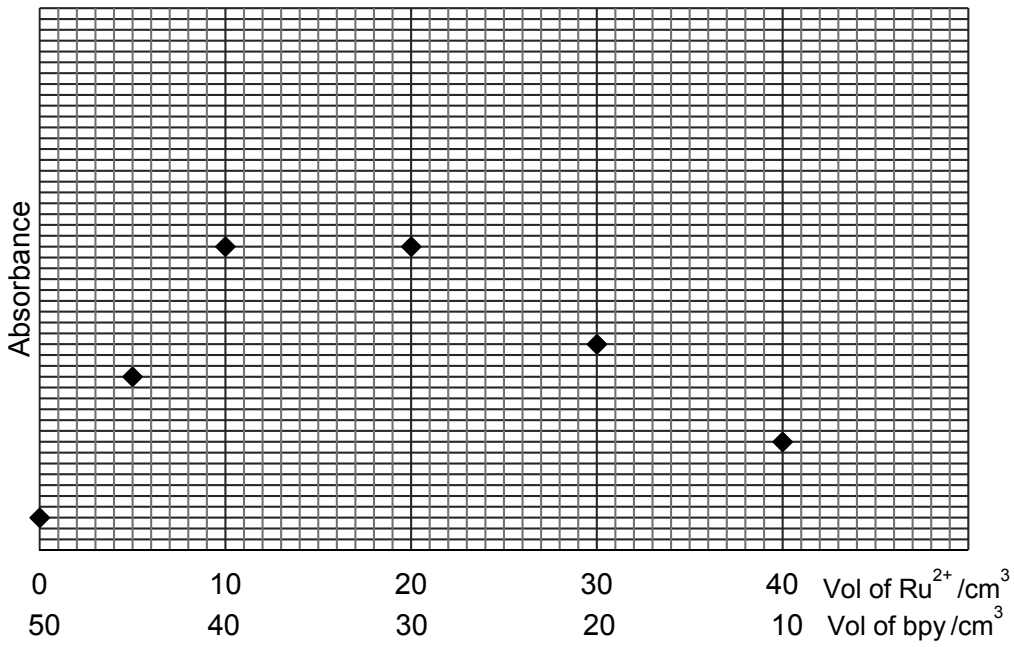
……[2]

Ligand is a neutral molecule or anion which contain at least one atom bearing a lone pair of electrons which can form a dative bond to a central atom/ion, resulting in the formation of a complex.
Bpy has 2 nitrogen atoms with a lone pair of electrons each, so it can form two dative bonds with the central atom/ion.

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

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

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



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

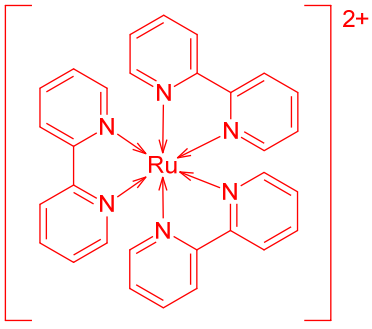
Formula of complex: ……..

Structure of complex ion:

[3]

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

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

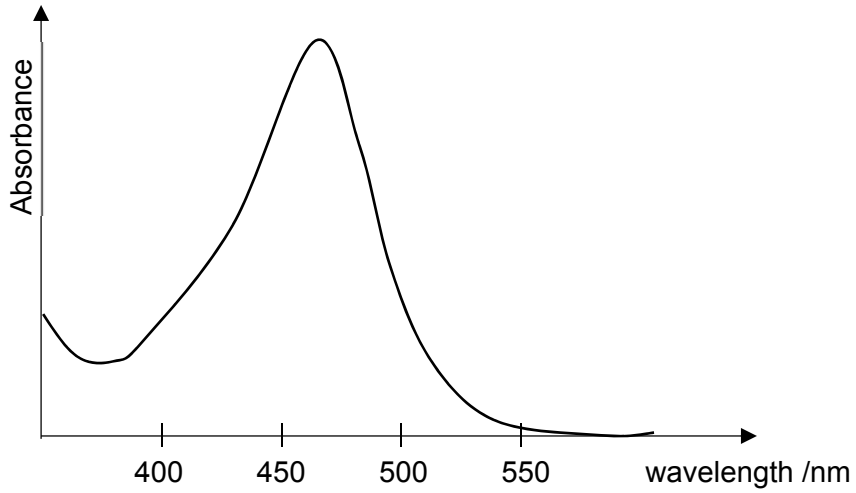


(c) The table below shows the colour of the radiation of the electromagnetic spectrum and the corresponding wavelength range.

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

650 – 700	red	green

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



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

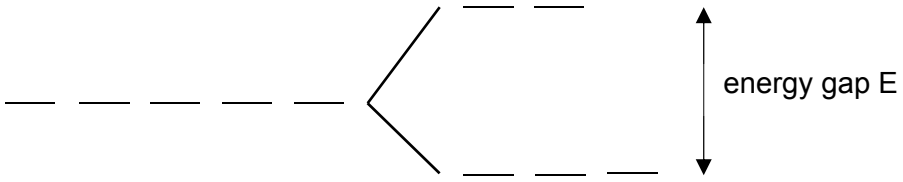
…… [1]

Blue is absorbed hence the complex is orange ;

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

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

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



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

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

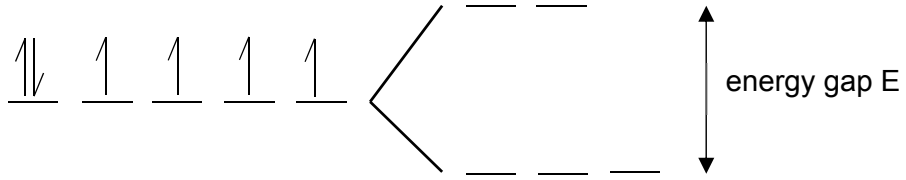
(i) With reference to this diagram, outline why $[Ru(H_2O)_6]^{2+}$ is coloured.

……

……

…… [2]

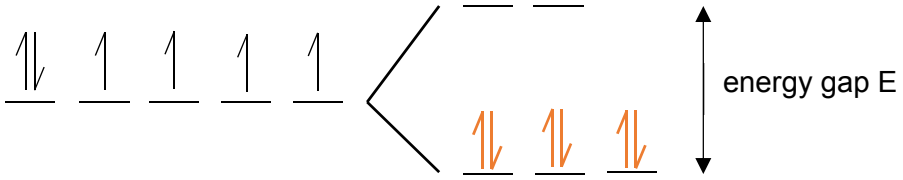
			The electrons in the lower energy d-orbital absorbs radiation from the visible region of the electromagnetic spectrum and get promoted to the higher energy d-orbital. The complementary colour of the light absorbed is shown as the colour of $[Ru(H_2O)_6]^{2+}$.	
		The electrons of transition metal ions 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] $4d^6$.	



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

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

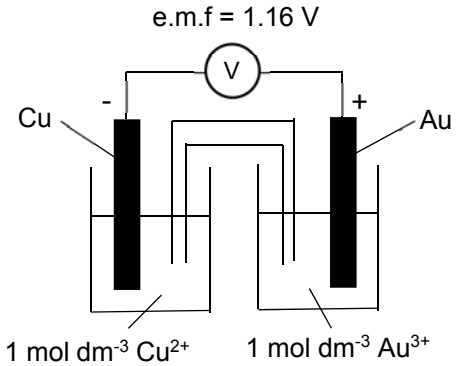
[1]



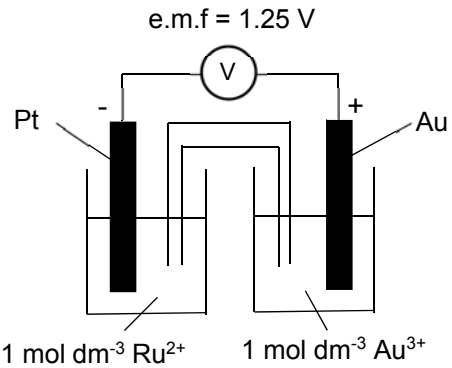
degenerate d-orbitals of an isolated Ru^{2+} ion

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

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



cell A



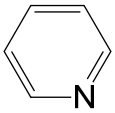
cell B

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

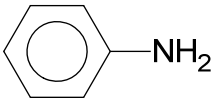
……

……[1]

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



pyridine
$pK_b = 8.75$



phenylamine
$pK_b = 9.33$

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

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

……

……

……

…….. [2]

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

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

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

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

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

Upon further heating, $MgCO_3$ undergoes further decomposition.

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

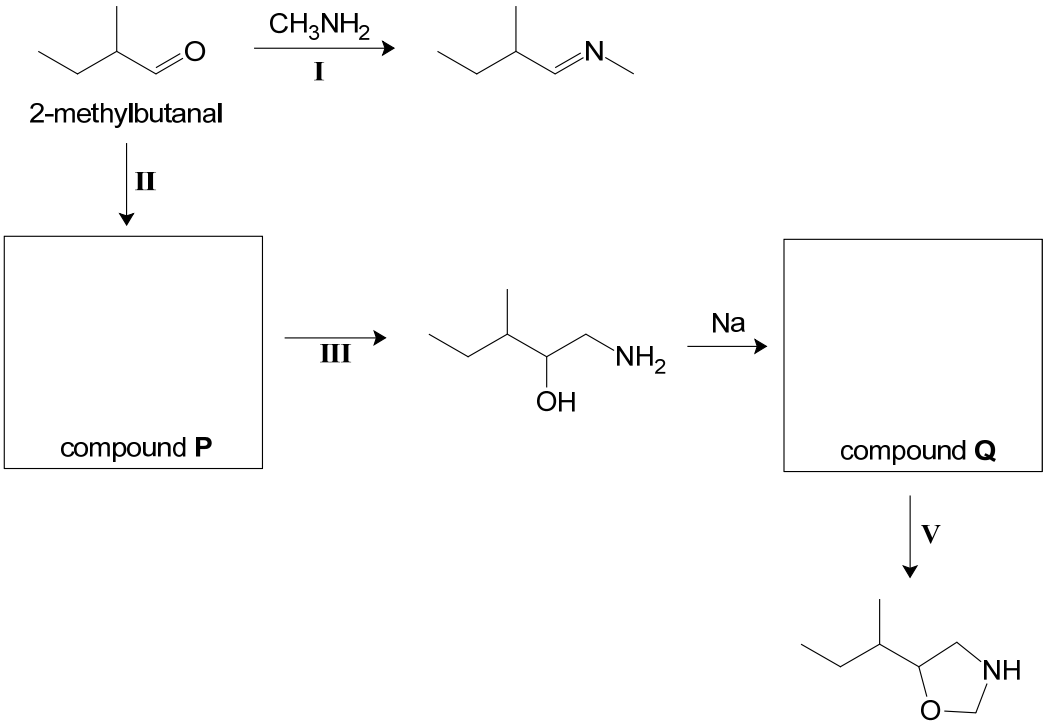
……...[1]

$MgCO_3 \rightarrow MgO + CO_2$

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

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

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



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

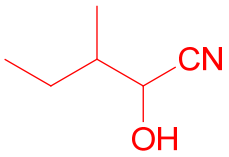
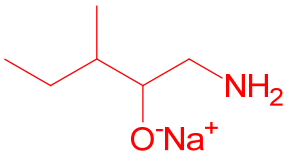
Draw the skeletal formulae of **two** possible structures of **R**.

[2]

;;

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

Step	Reagents and Conditions
II	
III	

			V	
			[5]	
			Step / **Reagents and Conditions** **II** — cold HCN, trace NaCN or NaOH **III** — $LiAlH_4$ in dry ether **V** — CH_2Cl_2  **P**  **Q**	
		(iii)	Suggest the type of reaction undergone by 2-methylbutanal in step **I**. ……[1]	
			condensation	

3	**(a)**	Cyanogen is a colourless yet extremely poisonous gas that is used in fumigation. Cyanogen is made up of carbon and nitrogen only, of which 46.2% is composed of carbon by mass. At 30°C and 1 bar, 1.03 g of cyanogen occupies 0.500 dm^3. It dissolves readily in water. Calculate the molecular formula of cyanogen.	

[3]

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

EF: CN (;)

pV=nRT

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

n= 0.01986 mol

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

M_r = 51.87 (;)

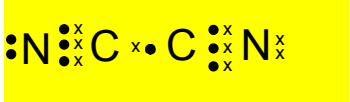
MF = $(CN)_y$

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

MF: $(CN)_2$ (;)

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

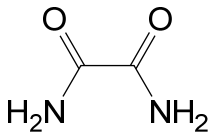
Shape: …… [2]



(;)

Shape: linear(;)

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

		…….....		
		……..		
		……..[2]		
		Energy given out from the formation of hydrogen bonding between cyanogen and water (;) is sufficient to overcome the instantaneous dipole-induced dipole between cyanogen molecules(;) and hydrogen bonding between water molecules.		
	(d)	Oxamide is manufactured from cyanogen by hydrolysis that only involves water.  Oxamide		
		(i)	Write the balanced equation for the reaction of manufacturing oxamide from cyanogen and water. You may use the molecular formula of oxamide in your equation. ……..[1]	
			$(CN)_2 + 2\ H_2O \rightarrow H_2NC(O)C(O)NH_2$	
		(ii)	With the use of Data Booklet, calculate the enthalpy change of the reaction in **(d)(i)**. [2]	
			ΔH_{rxn} = 890x2+ 350 + 4(460) – [4(390) + 2(305) +2(740) +350](;) = -30.0 kJ mol^{-1}(;)	
		(iii)	The entropy change for the reaction in **(d)(i)** is +64.1 J mol^{-1} K^{-1}. Use your answer in **(d)(ii)** to calculate ΔG at 298 K. Hence predict if the reaction is spontaneous at 298 K.	

			[2]	
			ΔG_{rxn} = -30 – 298(+64.1x10^{-3}) = -49.1 kJ mol^{-1} (;) ΔG_{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).

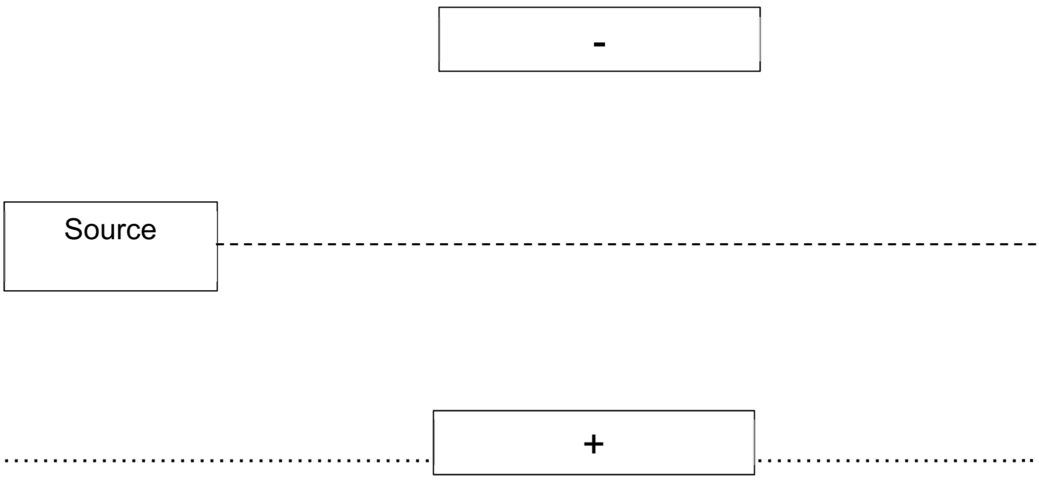
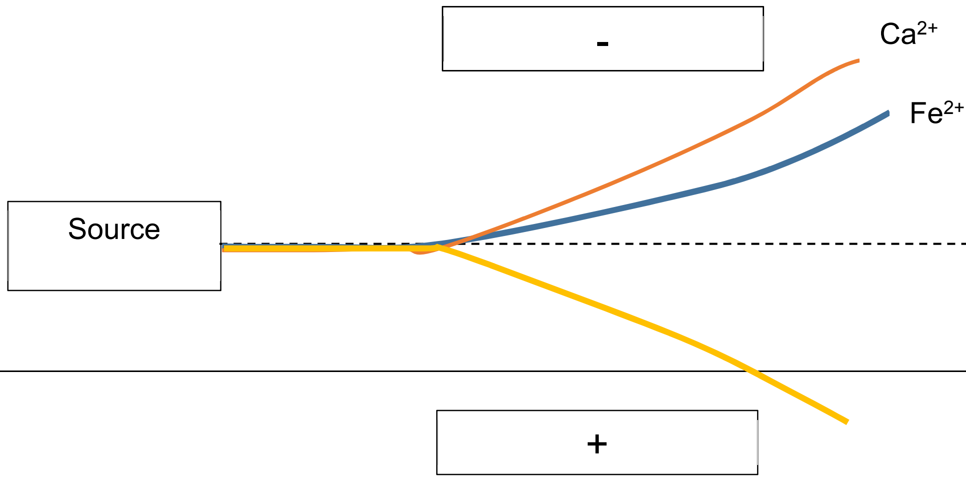
(i) Use the *Data Booklet* to construct an ionic equation for the reaction between Fe^{2+} in solution **A** and dichromate(VI) ions.

……..[1]

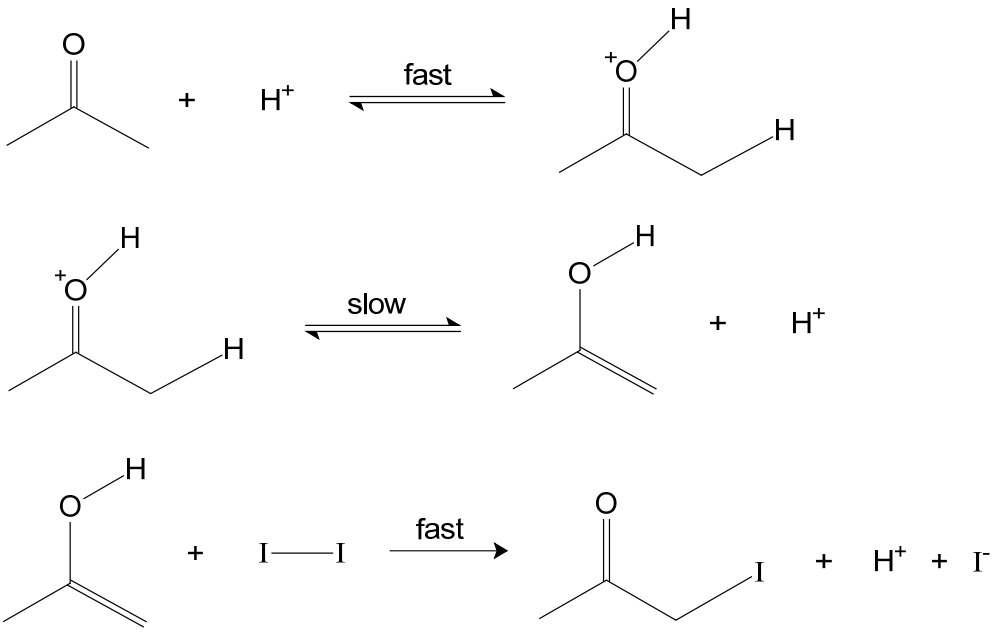
$6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \rightarrow 2Cr^{3+} + 7H_2O + 6Fe^{3+}$

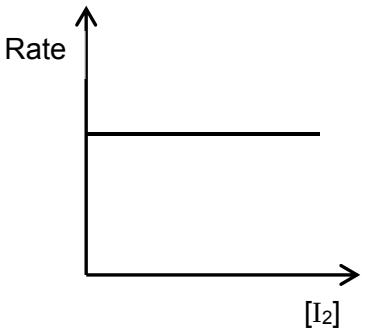
(ii) Calculate the volume of potassium dichromate(VI) solution that would be required to react with Fe^{2+} in 25.0 cm^3 of solution **A**.

			[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]	

			+ H I + H^+ + I^- [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(;)

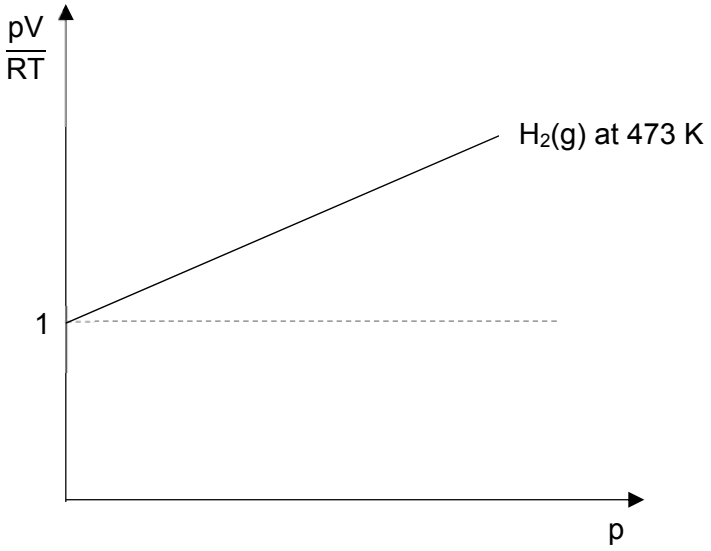
Amount of I_2 in the 100 cm^3 solution= 0.001005 x 4 = 0.00402 mol

$[I_2] = \frac{0.00402}{\frac{5}{1000}}$ = 0.804 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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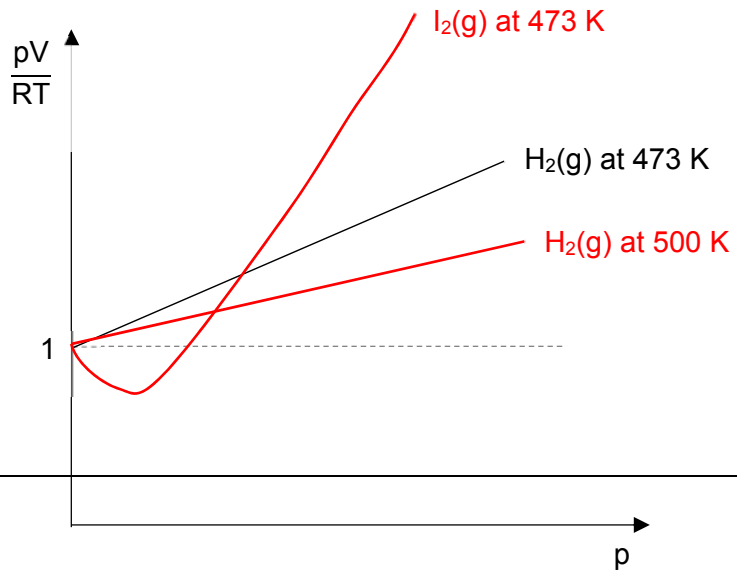
..... [4]



		$H_2(g)$ 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.(;)	