RIVER VALLEY HIGH SCHOOL
YEAR 6 PRELIMINARY EXAMINATION II

CANDIDATE NAME											
CLASS	6										
CENTRE NUMBER	S					INDEX NUMBER					

H2 CHEMISTRY 9729/03

Paper 3 Free Response

19 September 2017

2 hours

Candidates answer on separate paper.

Additional Materials: Answer Paper
Cover Page
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, class, centre number and index number on all the work you hand in.
Write in dark blue or black pen on both sides of paper.
You may use a soft pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Section A
Answer **all** questions.

Section B
Answer **one** question.

Begin each question on a fresh sheet of paper.
The use of an approved scientific calculator is expected, where appropriate.
A Data Booklet is provided. Do not write anything on it.
You are reminded of the need for good English and clear presentation in your answers.

The number of marks is given in brackets [ ] at the end of each question or part question.
At the end of the examination, fasten all your work securely together, with the cover page on top.

This document consists of **14** printed pages and **2** blank pages.

Section A

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

1 **(a)** Under suitable conditions, SCl_2 reacts with water to produce a yellow solid and an acidic solution **A**. Solution **A** contains a mixture of SO_2(aq) and another compound.

(i) State the oxidation number of S in SCl_2 . **[1]**

(ii) Construct an equation for the reaction between SCl_2 and water. **[1]**

(iii) In the Contact Process, one important step is the conversion of SO_2 to SO_3 as shown below.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

A 2.00 L flask was filled with 0.0400 mol SO_2 and 0.0200 mol O_2. At equilibrium, the flask contained 0.0296 mol of SO_3. Determine the value of K_c, stating its unit. **[3]**

(b) During the electrolysis of dilute sulfuric acid using a current of 0.75 A for 90 min and platinum electrodes, the volume of oxygen gas collected was recorded and is shown in Table 1.1 below.

Table 1.1

Time / min	Volume of O_2 gas / cm^3
20	55
40	110
60	165
80	220

(i) Plot a graph of volume of O_2 gas over time.
Use x axis: 2 cm for 10 min ; y axis: 2 cm for 50 cm^3 **[2]**

(ii) Give equations for the reactions that occur at each electrode in the electrolysis of sulfuric acid. **[2]**

(iii) On the same graph, draw and label a line (H_2) to predict the volume of hydrogen that would be given off during the same experiment. **[1]**

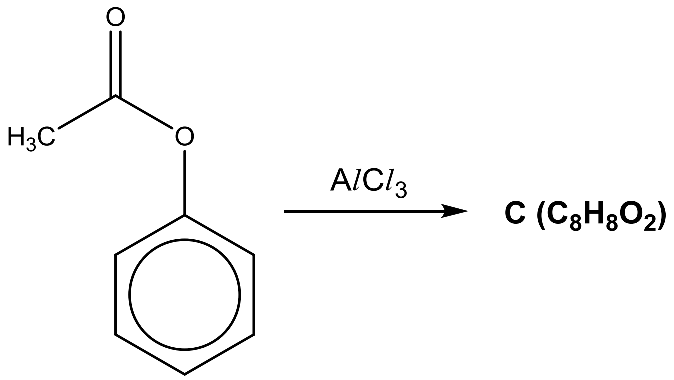
(iv) On the same graph, draw and label a line (O_2) to predict the volume of oxygen that would be given off if a current of 0.3 A was used instead in the original experiment. **[1]**

(v) In a second experiment, the platinum electrodes were replaced with graphite electrodes. The volume of gas collected at the anode was 150 cm^3 while the volume of hydrogen gas collected was 220 cm^3.

The difference in volume of gas collected at the anode between the two experiments was due to the production of CO gas at the anode.

Calculate the volume of CO gas produced at the anode. **[2]**

(c) About 100 years ago, in a reaction discovered by German chemist Karl Fries, compound **B** was converted into compound **C** when heated with $AlCl_3$.



B

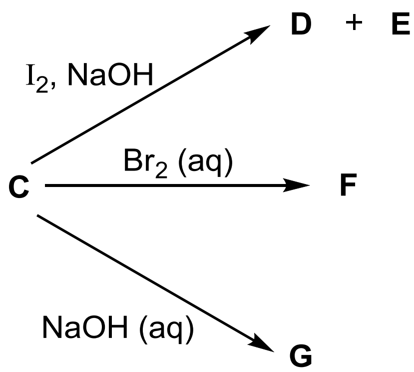
Compound **C** is a structural isomer of **B**.

It is insoluble in water but dissolves in aqueous sodium hydroxide.

It gives a yellow ppt with alkaline aqueous iodine and a white ppt with aqueous bromine.

(i) Suggest the structure for compound **C**. **[1]**

The various reactions of compound **C** can be represented as follows:

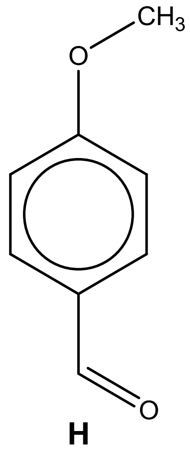


(ii) Suggest the structures for **D** to **G**. **[4]**

Compound **H**, as shown below, is another structural isomer of **B.**

It has a ether functional group whose general formula is R–O–R'.

Compound **H** can be formed via a reaction between a substituted phenoxide ion and an alkyl halide molecule.



H

(iii) Describe the mechanism when compound **H** is formed as described above. **[3]**

[Total: 21]

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2 In the late 1940s, Willard Libby developed the radiocarbon dating method for determining the age of an object containing organic material by using the properties of radiocarbon (^{14}C), a radioactive isotope of carbon. The principle of carbon dating is as such:

During its life, a plant or animal is exchanging carbon with its surroundings, so the carbon it contains will have the same proportion of ^{14}C as the atmosphere. Once it dies, it ceases to acquire ^{14}C, but the ^{14}C within its biological material at that time will continue to decay, and so the ratio of ^{14}C to ^{12}C in its remains will gradually decrease.

Because ^{14}C decays with first order kinetics, the proportion of radiocarbon can be used to determine how long it has been since a given sample stopped exchanging carbon – the older the sample, the less ^{14}C will be left.

(a) A sample of carbon dioxide gas (that contained both $^{12}CO_2$ and $^{14}CO_2$) was analysed to determine the proportion of $^{14}CO_2$ found within. Analysis results showed that there is one $^{14}CO_2$ molecule for every 10^{12} CO_2 molecules.

(i) Calculate the number of $^{14}CO_2$ molecules in a 10.0 dm^3 carbon dioxide gas sample, measured under s.t.p. **[2]**

(ii) Calculate the mass of $^{14}CO_2$ in the 10.0 dm^3 sample. **[1]**

(iii) Hence, explain why it would be difficult to determine the proportion of $^{14}CO_2$ by means of mass measurement. **[1]**

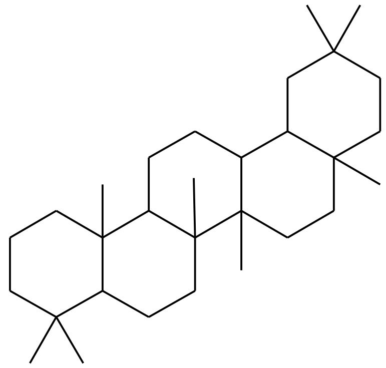
(b) To more accurately determine the proportion of ^{14}C in a sample of graphite, the graphite is vaporised and ionised to $C^+(g)$ ions. These ions were then passed through 2 electric plates.

Given that H^+ is deflected with an angle of 8.4°, what is the angle of deflection for $^{14}C^+$ ions under the same experimental set-up? **[1]**

(c) The half-life of ^{14}C is 5730 years. Determine the time that has elapsed for a piece of wood from a dead tree to contain 30.0% of its original ^{14}C. **[2]**

(d) The age of crude oil is far older than what could be determined from radiocarbon dating.

To measure the age of a crude oil sample, a method involving the measurement of the relative amount of oleanane is used instead.



Oleanane

(i) What is the number of chiral carbons in an oleanane molecule? **[1]**

(ii) Free radical substitution of oleanane with Cl_2 produces a mixture of various products.

Given that tertiary hydrogen atoms are the most reactive towards free radical substitution, suggest the structures of two possible mono-chlorinated oleanane which are formed in high proportions. **[2]**

(e) Benzene is obtained from the fractional distillation of crude oil. It can be converted to a series of different useful chemicals such as phenylamine. The formation of phenylamine involves the direct reaction of nitrobenzene and hydrogen gas in the presence of a heterogeneous catalyst.

A series of experiments were carried out at a specific temperature to investigate the kinetics of this reaction:

Experiment	[nitrobenzene] / mol dm^{-3}	[H_2] / mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}
1	0.010	0.010	4.50×10^{-5}
2	0.015	0.010	6.74×10^{-5}
3	0.020	0.020	1.80×10^{-4}
4	0.030	x	4.05×10^{-4}

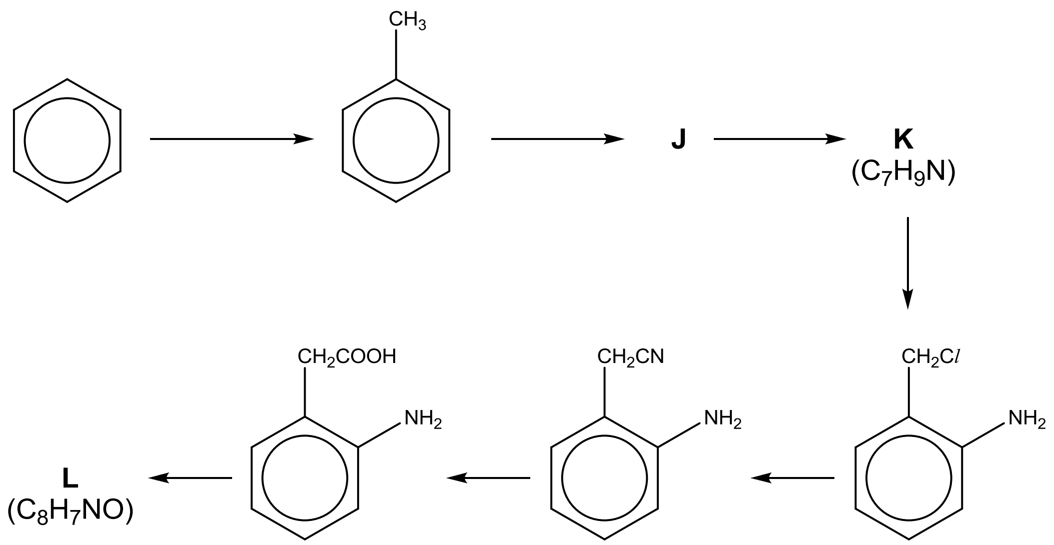
(i) Define the term *heterogeneous catalyst*. **[2]**

(ii) Determine the order of reaction with respect to nitrobenzene and H_2. **[2]**

(iii) Calculate the rate constant, stating its units. **[1]**

(iv) Hence, determine the value of x. **[1]**

(f) Benzene is made to undergo a series of reactions as shown:



(i) Suggest the structures of **J** and **K**. **[2]**

(ii) Given that compound **L** is neutral, suggest the reagent used in the final step and the structure of **L**. **[2]**

[Total: 20]

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3 Chromium is a transition metal commonly found in the earth's crust. It is usually mined as chromite.

Period 4 Element	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
Atomic radius / nm	0.132	0.122	0.117	0.117	0.116	0.116	0.115	0.117

(a) Explain why the atomic radius for transition elements remains relatively constant. **[2]**

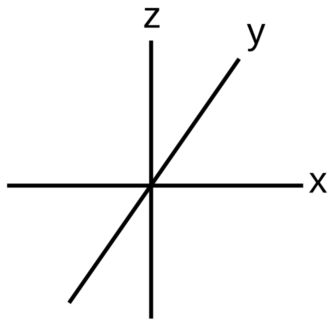
(b) **(i)** Write the electronic configuration for Cr^{3+} ion. **[1]**

(ii) Chromium forms octahedral complexes with the general formula $CrCl_3.6H_2O$. One of them dissolves in water to form a violet solution which turned green upon warming. An excess of aqueous silver nitrate was added separately to solutions containing 0.0100 mol of each complex. The violet complex gave 1.50 g of precipitate, while the green complex gave 4.40 g of precipitate.

Deduce the formulae of the two complex ions.

Write the equation for the conversion of the violet complex to the green complex. **[3]**

(iii) Using the Cartesian axes, like those shown below,



draw **fully-labelled** diagrams of the following :

- One of the d orbital at the lower energy level in an octahedral complex. Label this diagram "Lower energy level".
- One of the d orbital at the upper energy level in an octahedral complex. Label this diagram "Upper energy level". **[2]**

(c) When sodium carbonate is added to a dichromate(VI) solution, the solution turned yellow.

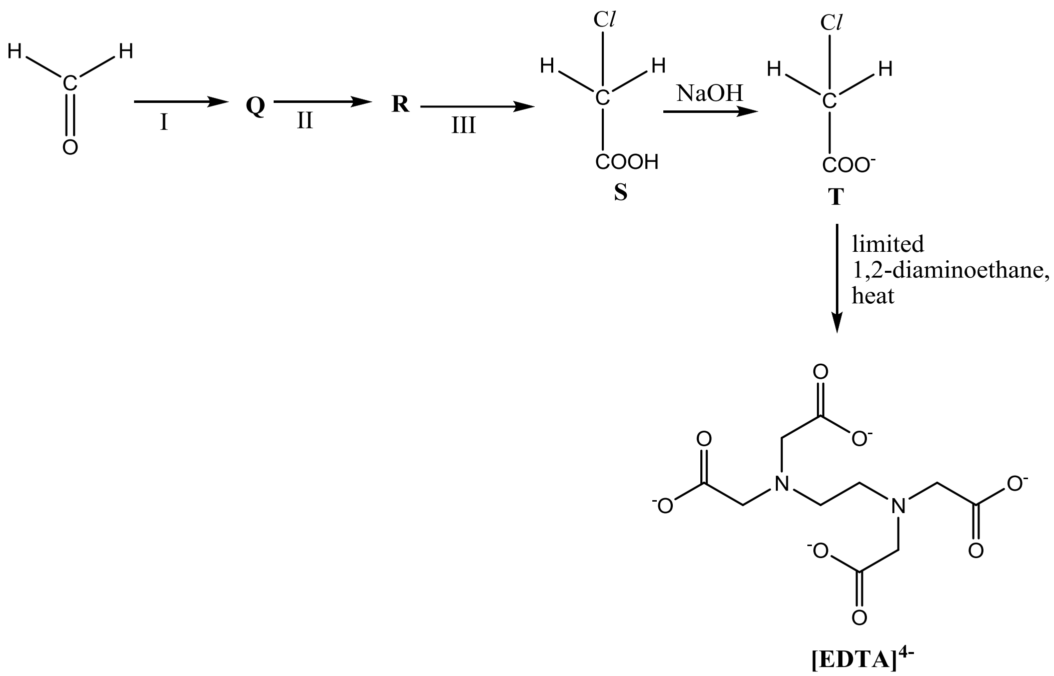
$$Cr_2O_7^{2-}(aq) + 2OH^-(aq) \rightleftharpoons 2CrO_4^{2-}(aq) + H_2O(l)$$

orange yellow

Using a relevant equation, explain the above observation. **[2]**

(d) Ethylenediamine tetraacetate, $[EDTA]^{4-}$, is a ligand that acts as a chelating agent. It is widely used to remove transition metal ions such as those of chromium from aqueous solutions.

A possible reaction scheme used to synthesise $[EDTA]^{4-}$ from methanal is given below.



(i) Suggest the reagents and conditions in steps I, II and III. **[3]**

(ii) Draw the displayed formulae of intermediates **Q** and **R**. **[2]**

(iii) State the type of reaction when **T** is converted to $[EDTA]^{4-}$.

Give a reason why a limited amount of 1,2-diaminoethane is used. **[2]**

(iv) Define the term *ligand*. State the number of coordinate bonds that a $[EDTA]^{4-}$ ligand can form with a central metal ion. **[2]**

[Total: 19]

Section B

Answer **one** question from this section.

4 This question concerns the chemistry of the oxides of some elements.

(a) The oxides of Period 3 show different reactions with water.

Describe the reactions, if any, of the oxides SiO_2 and SO_3 with water.

Include the approximate pH value of any resulting solutions, and write equations for any reactions that occur. **[3]**

(b) Carbon combusts in oxygen to form two common oxides, CO and CO_2. These oxides are also formed when solid magnesium oxalate, MgC_2O_4, is heated strongly.

(i) Write an equation, with state symbols, to represent the thermal decomposition of solid magnesium oxalate. **[1]**

(ii) Explain why magnesium oxalate decomposes at a lower temperature than barium oxalate, BaC_2O_4. **[2]**

Carbon also forms compounds with other Group 16 elements like sulfur and selenium. The properties of some of these compounds, along with CO_2, are given in Table 4.1.

Table 4.1

Compound	Structure	Dipole moment	Boiling point / °C
CO_2	O=C=O	0	sublimes
CS_2	S=C=S	0	46
COS	S=C=O	0.71	–50
COSe	Se=C=O	0.73	–22

(iii) Explain, in terms of structure and bonding, the difference in the boiling point of CS_2 and COS. **[2]**

(iv) Explain why

- CO_2 has no overall dipole moment.
- COSe has a greater dipole moment than COS. **[2]**

(c) Aside from the common oxides, carbon forms a series of reactive oxocarbons. One such compound is tricarbon monoxide, C_3O, a reactive molecule found in space.

(i) Suggest a structure of tricarbon monoxide. Indicate clearly any lone pairs present. **[1]**

Tricarbon monoxide is isoelectronic to cyanogen, $(CN)_2$. The molecule of cyanogen contains a C–C single bond.

(ii) Draw the dot-and-cross diagram of cyanogen. In your diagram, you should distinguish the electrons originating from each of the two carbon atoms and those from the two nitrogen atoms. **[1]**

(iii) Suggest the shapes of tricarbon monoxide and cyanogen. **[1]**

(d) Another oxycarbon is pentacarbon dioxide, C_5O_2. It can be obtained by heating compound **X**, $C_6H_6O_3$, at a high temperature. **X** exists in equilibrium with its isomer, **Y**.

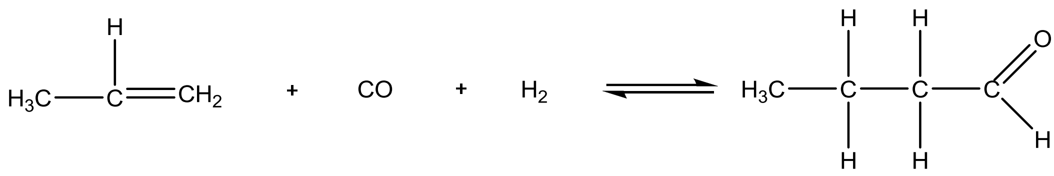
X does not react with aqueous bromine. **X** also gives an orange precipitate with 2,4-DNPH but does not give a silver mirror with Tollens' reagent. When reacted with limited bromine under ultraviolet light, **X** produced **only one** mono-brominated compound.

Y reacts with dilute nitric acid to form **only one** mono-nitrated compound, **Z**.

Suggest the structures of compounds **X**, **Y** and **Z**. Explain your reasoning. **[7]**

[Total: 20]

5 **(a)** Hydroformylation is an industrial process for the formation of aldehydes from alkenes.



propene butanal

(i) Determine the oxidation numbers of carbon-1, carbon-2 and carbon-4 in butanal. **[1]**

(ii) The hydroformylation of propene can result in the formation of two isomeric products. Given that the mechanism of hydroformylation resembles the electrophilic addition of alkenes, suggest the structure of the other isomer apart from butanal. **[1]**

(iii) Write the K_p expression for the reaction above, stating its units. **[1]**

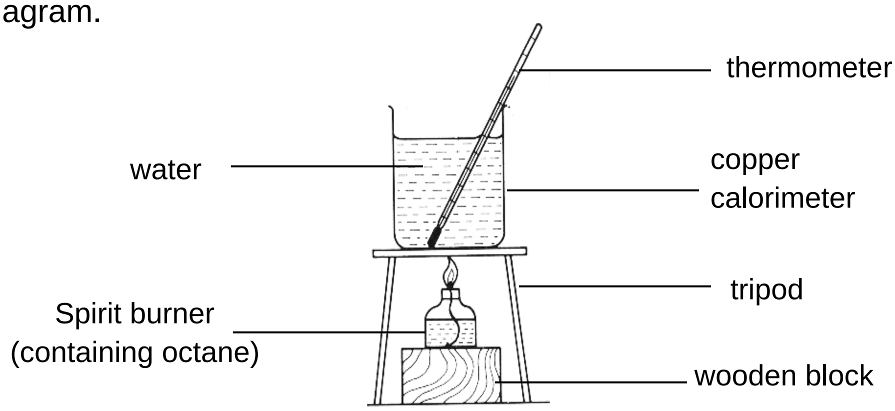
(iv) When an equimolar mixture of propene, CO and H_2 at an initial pressure of 120 Pa was allowed to reach equilibrium at 550 K, the partial pressure of butanal was found to be 38.5 Pa.

Calculate a value of K_p at 550 K. **[2]**

(v) Hence, predict the sign of ΔG for the reaction. Explain your reasoning taking into account the thermodynamic considerations of the reaction. **[2]**

(b) Other important use of hydrocarbons include fuels, plastics, paints and solvents. In some countries, where crude oil is either scarce or expensive, biofuels such as ethanol are also increasingly being used for fuels instead of hydrocarbons.

(i) James carried out an experiment to determine the enthalpy change of combustion of octane, C_8H_{18}, using the apparatus shown in the diagram.



These are the results that James obtained:

Volume of water = 1000 cm^3

Initial temperature of water = 29.6 °C

Highest temperature of water = 50.0 °C

Initial mass of burner and octane = 59.35 g

Final mass of burner and octane = 53.77 g

Heat capacity of calorimeter = 770 J K^{-1}

Use these results and data from the *Data Booklet* to determine the experimental enthalpy change of combustion of octane. **[3]**

(ii) The accurate experimental enthalpy change of combustion of three hydrocarbons are given in Table 5.1.

Table 5.1

Alkane	Formula	ΔH_c/ kJ mol^{-1}
Heptane	C_7H_{16}	–4817
Octane	C_8H_{18}	–5470
Nonane	C_9H_{20}	–6125

Suggest what the regular increase in the values of ΔH_c given in the table represents. **[1]**

(iii) Draw a pair of enantiomers of heptane. **[1]**

(iv) Alkanes are also used in dry cleaning of clothing and textiles. Dry cleaning involves soaking the clothes in a solvent other than water. Recently, the use of supercritical carbon dioxide as a dry cleaning solvent has also been gaining popularity. Supercritical carbon dioxide is a fluid state of carbon dioxide which is maintained at or above its critical temperature.

Suggest two possible reasons why supercritical carbon dioxide is a better solvent than organic solvents like hexane. **[2]**

(c) Many modern methods of chemical analysis rely on the use of sophisticated instruments. For many years, scientists relied on traditional laboratory apparatus for chemical analysis.

Many qualitative tests and some volumetric analysis used depended on an application of the principles of solubility product.

Data for use in this question are given in Table 5.2.

Table 5.2

	Colour	Solubility / mol dm^{-3}	K_{sp} (25 °C)
AgC*l*	White	1.42×10^{-5}	2.02×10^{-10}
AgI	Yellow	8.95×10^{-9}	8.01×10^{-17}
Ag_2CrO_4	Red	9.10×10^{-5}	3.01×10^{-12}

(i) Aqueous $AgNO_3$ is added to solutions containing 0.100 mol dm^{-3} Cl^-(aq) or 0.0100 mol dm^{-3} CrO_4^{2-}(aq). What concentration of Ag^+ must be present to cause the precipitation of

I: AgC*l*

II: Ag_2CrO_4? **[2]**

(ii) Standard solutions of silver nitrate can be used in volumetric analysis to determine the concentration of chloride ions in a sample of water. When the titration is carried out, $AgNO_3$(aq) of known concentration is added slowly to the solution that contains Cl^- ions. A small quantity of aqueous potassium chromate(VI), K_2CrO_4 (0.01 mol dm^{-3}) is also added as an indicator.

Using the data given in Table 5.2 and your answers in **(c)(i)**, predict using calculations what you would see at the beginning of the titration and at the end-point and explain why K_2CrO_4(aq) can be used as an indicator in this titration. **[4]**

[Total: 20]

- End of Paper –