INNOVA JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION 2
in preparation for General Certificate of Education Advanced Level
Higher 2

CANDIDATE NAME

CLASS IN DEX NUMBER

CHEMISTRY 9647/03

Paper 3 Free Response **14 September 2012**

2 hours

Candidates answer on separate paper.

Additional Materials: Writing Papers
Data booklet
Cover Page

READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work you hand in.
Write in dark blue or black pen on both sides of the 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.

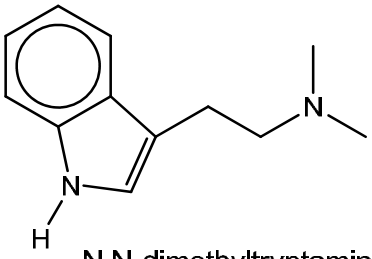
Answer **4 out of 5** questions.
Begin each answer on a fresh sheet of paper.

You are advised to show all working in calculations.
You are reminded of the need for good English and clear presentation in your answers.
You are reminded of the need for good handwriting.
Your final answers should be in 3 significant figures.

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

Answer **4 out of 5** questions.

1 **(a)** N,N-dimethyltryptamine is a psychoactive drug whose primary action is to alter cognition and perception. Depending on the dose and method of administration, its subjective effects can range from short-lived milder psychedelic states to powerful immersive experiences.



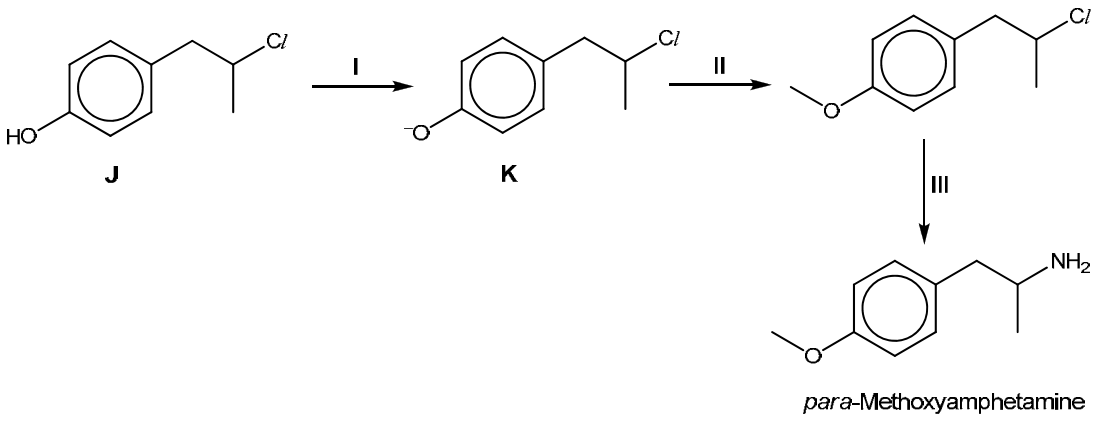
N,N-dimethyltryptamine

(i) Suggest a reason why N,N-dimethyltryptamine is soluble in acidic solutions.

(ii) Would you expect N,N-dimethyltryptamine to have a high or low melting point? Explain your answer in terms of structure and bonding.

[4]

(b) *para*-Methoxyamphetamine first came into circulation in the early 1970s and went by the street names of "Chicken Powder" and "Chicken Yellow" and was found to be the cause of a number of drug overdose deaths in the United States and Canada at that time. It can be synthesised by the following route.



J **K**

para-Methoxyamphetamine

(i) Suggest reagents and conditions for steps II and III.

(ii) What type of reaction is step II?

(iii) Suggest why compound **J** is converted into **K** before step **II** is carried out.

(iv) What type of stereoisomerism does *para*-methoxyamphetamine exhibits? Draw the structures of the stereoisomers of *para*-methoxyamphetamine.

[6]

(c) Propene is an important starting product in the petrochemical industry and is often used as the raw material for a wide variety of products.

(i) Name and describe the mechanism of the reaction between propene and hydrogen bromide.

(ii) The bromine atom in the product from **(i)** is very reactive towards nucleophilic reagents. The bromine atom in 1–bromopropene is unreactive towards nucleophilic reagents. Suggest an explanation for the unreactivity of the bromine atom in 1–bromopropene.

[5]

(d) Compound **P** is a neutral, sweet-smelling liquid with molecular formula $C_5H_8O_2$. It reacts with hot sulfuric acid to give a single compound **Q**, $C_5H_{10}O_3$. **Q** has two stereoisomers and gives a pale yellow precipitate with alkaline iodine and compound **R**. Deduce the structures of **P**, **Q** and **R**.

[5]

[Total:20]

2 **(a)** When a precipitate is formed, ΔG^{θ}_{ppt}, in kJ mol^{-1}, is given by the following expression.

$$\Delta G^{\theta}_{ppt} = \frac{2.303RT \log K_{sp}}{1000}$$

(i) Given that the K_{sp} value of BaF_2 is 1.70×10^{-6} at 298 K, calculate ΔG^{θ}_{ppt}, in kJ mol^{-1}, for BaF_2.

(ii) The standard enthalpy change of formation of BaF_2 is −858 kJ mol^{-1}. Use your answer in **(a)(i)** to calculate ΔS^{θ}_{ppt}, in J mol^{-1} K^{-1} for the formation of the precipitate at 298 K.

(iii) Explain the significance of the sign of your answer in **(ii)**.

(iv) Predict and explain whether the precipitation will be feasible at high or low temperature.

(v) Suggest how the magnitude of the lattice energy of BaF_2 might compare to that of $BaCl_2$. Explain your answer.

[7]

(b) In the past, chemical analysis was carried out by chemists using traditional laboratory apparatus. Many qualitative tests used depended on an application of the principles of solubility product.

(i) Write an expression for the K_{sp} of barium fluoride.

(ii) Predict whether precipitation occurs if 50.0 cm^3 of 0.150 mol dm^{-3} of $Ba(OH)_2$ solution is mixed with 50.0 cm^3 of 0.100 mol dm^{-3} of KF solution in the laboratory.
The K_{sp} of BaF_2 is 1.70×10^{-6} mol^3 dm^{-9}.

[3]

(c) Myrcene is a naturally occurring compound found in the leaves of bay trees. It is known to be a polyunsaturated hydrocarbon. It can react with hydrogen to produce a saturated hydrocarbon.

In a laboratory investigation, a 1.00 g sample of pure myrcene fully reacted with exactly 510 cm^3 of hydrogen gas measured at 20.0°C and 105.0 kPa. In this reaction, myrcene was converted to a saturated alkane with a molecular formula $C_{10}H_{22}$.

(i) What type of reaction has occurred between the myrcene and hydrogen?

(ii) Calculate the amount, in moles, of hydrogen reacting.

(iii) Calculate the mass of $C_{10}H_{22}$ produced in the reaction.

(iv) Determine the number of double bonds in each molecule of myrcene.

[6]

(d) In September 2009, the wholesale of weedkiller containing chlorate(V) ions was banned in various European countries.

Chlorate(V) ions can act as a strong oxidising agent in acid solution according to the following half equation:

$$ClO_3^-(aq) + 6H^+(aq) + 6e \rightarrow Cl^-(aq) + 3H_2O(l)$$

In an experiment, 25.0 cm^3 of a sample of sodium chlorate(V) solution reacted with an excess of sodium iodide, NaI. The iodine produced required 25.00 cm^3 of 1 mol dm^{-3} of sodium thiosulfate, $Na_2S_2O_3$, for complete reaction.

(i) Write a balanced equation between chlorate(V) ions and iodide ions in acidic medium.

(ii) Calculate the number of moles of iodine liberated by the chlorate(V) solution.

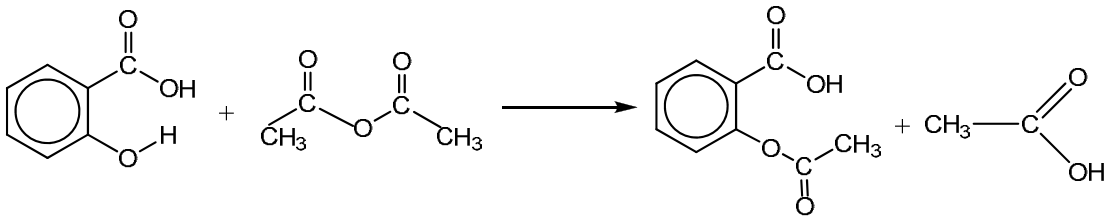
(iii) Calculate the concentration of sodium chlorate(V) in the solution.

[4]

[Total: 20]

3 **(a)** A sample of aspirin was prepared by reacting 2.20 g of salicylic acid with 4.20 cm^3 of ethanoic anhydride in a conical flask. After heating for 20 minutes the reaction mixture was cooled and white crystals precipitated. The crystals were then collected, dried to constant mass and weighed.

The equation for the reaction is:



salicyclic acid(s) ethanoic anhydride(*l*) aspirin(s)

The following results were obtained.

mass of salicylic acid	2.20 g
volume ethanoic anhydride	4.20 cm^3
mass of product	2.25 g

Use the following data to answer the questions below.

	molar mass (g mol^{-1})	**density (g cm^{-3})**
aspirin	180	–
ethanoic anhydride	102	1.08
salicyclic acid	138	–

(i) Calculate the initial amount, in moles, of salicylic acid used in this preparation.

(ii) What initial amount, in moles, of ethanoic anhydride was used?

(iii) What is the maximum mass of aspirin that can theoretically be produced from these reagents?

(iv) Determine the percentage yield in this preparation.

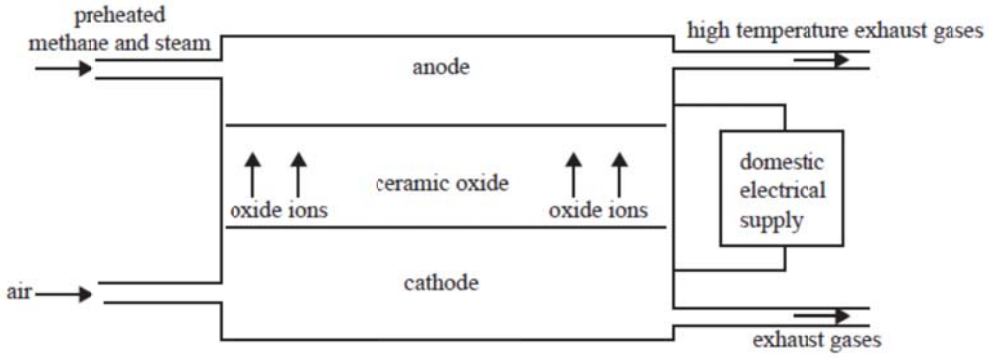
(v) To check whether the aspirin obtained is contaminated with salicyclic acid, a simple chemical test can be carried out. Suggest what reagent can be used and state the observation.

(vi) In carrying out the above preparation, the acid anhydride used must not contain moisture. Write an equation for the reaction between ethanoic anhydride with water.

(vii) Acid chlorides closely resemble the acid anhydrides in chemical reactions. They also react with nucleophilic reagents but at a faster rate and therefore more difficult to handle.
Suggest another reason why ethanoyl chloride is **not** used in the above preparation of aspirin.

[7]

(b) A company wish to manufacture solid oxide fuel cell for use in the home. These fuel cells uses natural gas to produce electricity through an electrochemical process summarised in the diagram below.



(i) Write an equation for the reaction at the cathode where atmospheric oxygen is converted to oxide ions.

(ii) A complex series of reactions takes place at the anode. These may be summarised by the half-equation:

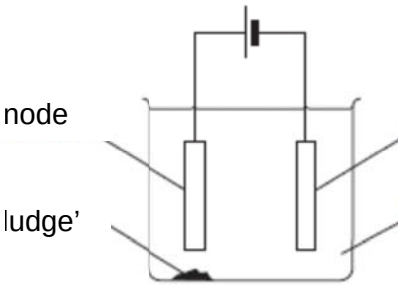
$$4O^{2-}(g) + CH_4(g) \longrightarrow CO_2(g) + 2H_2O(g) + 8e$$

Write an equation that represents the overall reaction that takes place in this fuel cell.

(iii) Suggest one way in which a fuel cell differs from other galvanic cells.

[3]

(c) The electrolytic purification of copper can be carried out in an apparatus similar to the one shown below.



Most of the current passed through the cell is used to dissolve the copper at the anode and precipitate pure copper onto the cathode. However, a small proportion of it is 'wasted' in dissolving the impurities at the anode which then remain in solution. When a current of 20.0 A was passed through the cell for 10.0 hours, it was found that 225 g of pure copper was deposited on the cathode.

Calculate the following, using appropriate data from the *Data Booklet*,

(i) number of moles of copper produced at the cathode

(ii) number of moles of electrons needed to produce this copper

(iii) number of moles of electrons that passed through the cell

(iv) Hence calculate the percentage of the current through the cell that has been 'wasted' in dissolving the impurities at the anode.

[4]

(d) **(i)** State what is meant by an *acidic buffer solution*.

(ii) Explain, using relevant equations, how a mixture of HC*l*O and NaC*l*O can regulate pH when relatively small amount of acid or base is added to the solution.

(iii) Explain why NaC*l*O exists as a solid whereas HC*l*O exists as a liquid under standard condition.

[6]

[Total: 20]

4 **(a)** By considering the likely mechanism of each reaction, suggest reasons why reaction **I** below must be heated for some time for it to occur, whereas reaction **II** takes place almost instantaneously at room temperature.

$CH_3CH_2CH_2Br(l) + NaOH(aq) \rightarrow CH_3CH_2CH_2OH(aq) + NaBr(aq)$ reaction **I**

$HBr(aq) + NaOH(aq) \rightarrow H_2O + NaBr(aq)$ reaction **II**

[2]

(b) How would the rate of reaction between $CH_3CH_2CH_2Cl(l)$ and NaOH(aq) compare to that of reaction **I**? Use appropriate data from the *Data Booklet* to explain your answer.

[2]

(c) In the presence of ethanolic potassium hydroxide, there is a competition between substitution and elimination of the bromoalkane. The data below shows some examples.

Formula of bromoalkane	Type of bromoalkane	Conditions	$\frac{\text{elimination}}{\text{substitution}}$ ratio
$(CH_3)_2CHBr$	Secondary	2 mol dm^{-3} OH^- in 60 % ethanol*	1.5
$(CH_3)_2CHBr$	Secondary	2 mol dm^{-3} OH^- in 80 % ethanol*	2.2
$(CH_3)_3CBr$	Tertiary	2 mol dm^{-3} OH^- in 100 % ethanol	13.0

* the remainder is water

Using the data given above, draw the structural formula of the major product of each of the following reactions:

(i) Heating $(CH_3)_2CHCH_2Br$ with NaOH(aq)

(ii) Heating $CH_3CH_2CHBrCH_2CH_3$ with NaOH in 100 % ethanol

(iii) Heating $(CH_3)_3CBr$ with NaOH in 100 % ethanol

[3]

(d) The rate constant for the reaction of $CH_3CH_2CHBrCH_3$ and KCN was measured at various temperatures and the results are shown below.

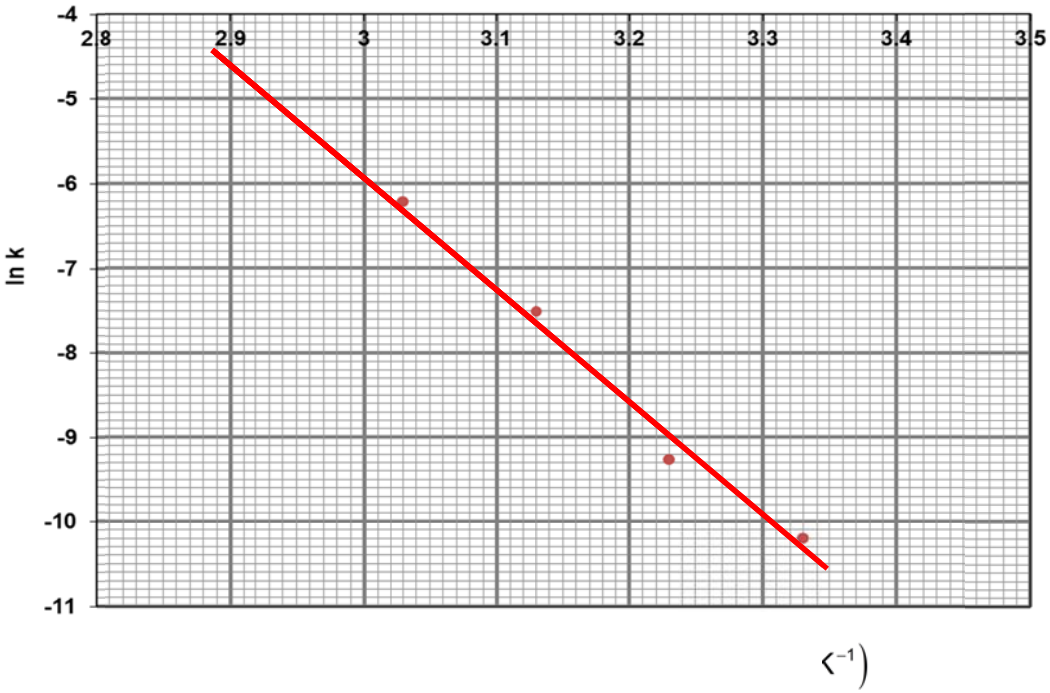
T/ K	300	310	320	330
***k*/ s^{-1}**	3.7×10^{-5}	9.4×10^{-5}	5.5×10^{-4}	2.0×10^{-3}

(i) Deduce the overall order of this reaction.

(ii) From the plotted graph given and by using the modified Arrhenius equation,

$$\ln k = \text{constant} - \frac{E_a}{RT}$$

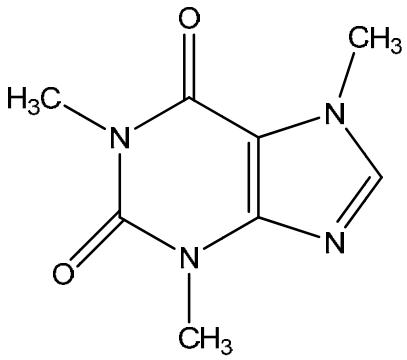
determine the activation energy, E_a, of the reaction.



(ii) Estimate the rate constant of the reaction at 340 K and hence calculate the half-life of the reaction at the same temperature.

[5]

(e) Caffeine is a stimulant found in coffee and tea. It is also added to cola drinks. The structure of caffeine is given below.



(i) Copy the above structure and label (with a *) all the carbon atoms with bond angles of 109 °.

(ii) On the structure that you have drawn, draw a circle round an amide group.

(iii) Decaffeinated coffee and tea are made by extracting the caffeine from solid coffee or tea using a solvent.

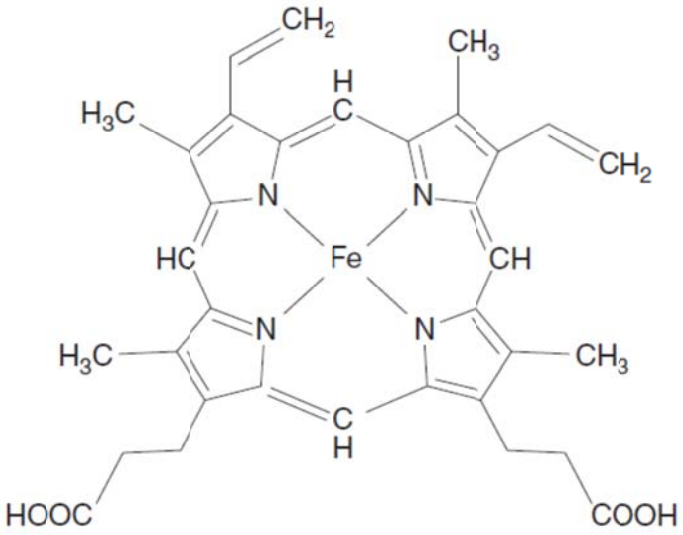
Suggest, with two reasons, which of the following industrial solvents would be the most suitable.

- Benzene
- A hydrocarbon, such as cyclohexane
- Liquid carbon dioxide

[5]

(f) Iron is an extremely important metal used in haemoglobin to transport oxygen molecules from the lungs to muscle cells and to carry carbon dioxide in the reverse direction.

One haemoglobin molecule contains four haem groups, each of which contains one iron atom. In the haem group four nitrogen atoms are in the same plane as the iron atom. The oxygen molecule is attached above this plane, and the iron atom is joined to a protein chain below this plane.



haem

(i) How many oxygen **atoms** could one haemoglobin molecule transport?

(ii) By what type of bonding is the oxygen molecule likely to be held to the iron atom in haem?

(iii) What is the geometry of bonding around the iron atom?

[3]

[Total:20]

5 **(a)** Bromine containing products, such as sodium bromate is frequently used in hair straightener and conditioning products.

(i) Write a balanced equation for the reaction that can make a solution that contains sodium bromate(I) under suitable condition in the laboratory.

(ii) Bromine can be obtained from the sodium bromide dissolved in sea water by the following step:

Blowing out the bromine with air and absorbing it in aqueous sodium carbonate.

This step produces a mixture of solution **Z** and sodium bromide in the molar ratio of 1:5. **Z** has the following composition by mass:

Na, 15.2%; Br, 52.9%; O, 31.8%

I. Calculate the empirical formula of **Z**.

II. Construct an equation for the formation of **Z** in the above step mentioned.

(iii) An acidified aqueous solution of **Z** reacts with hydrogen sulfide, H_2S, to give a precipitate of sulfur and an orange red solution. On shaking with trichloroethane, the colour is transferred to the organic layer.

I. State the role of H_2S and suggest an identity for the orange red solution.

II. Construct a balanced equation for the reaction.

(iv) When solid calcium fluoride reacts with concentrated sulfuric acid, gaseous hydrogen fluoride is produced. A similar reaction occurs with solid calcium chloride but with solid calcium bromide, bromine is formed.

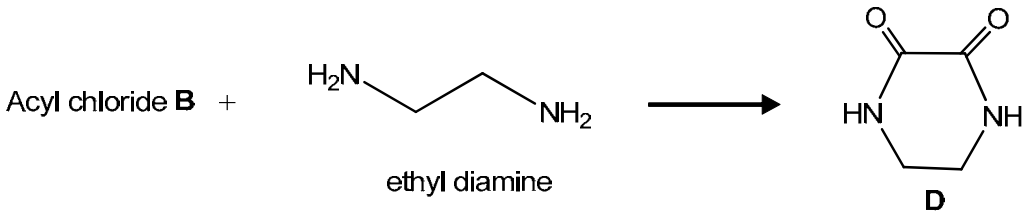
I. Write an equation for the reaction of solid calcium fluoride with concentrated sulfuric acid.

II. Explain why when reacted with concentrated sulfuric acid, solid calcium bromide form bromine whereas solid calcium chloride forms hydrogen chloride? Suggest a possible reaction product of the concentrated sulfuric acid in the reaction.

[9]

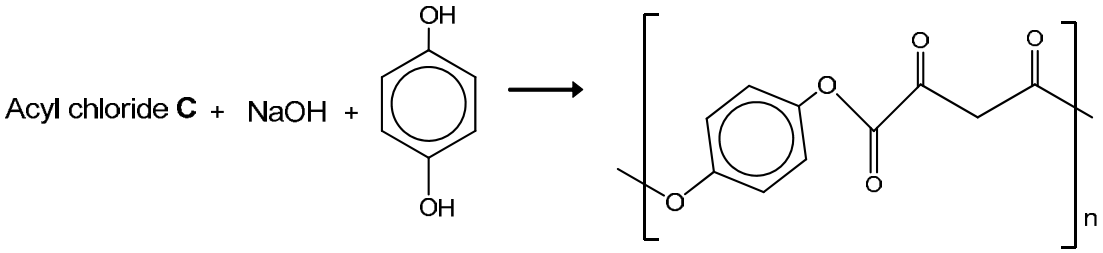
(b) Acyl chlorides are useful intermediates for making various acid derivatives. The following reaction shows two reactions of acyl chlorides.

Reaction scheme 1



D

Reaction scheme 2



E

(i) Suggest the structures of acyl chlorides **B** and **C** used in reaction scheme 1 and 2.

(ii) Suggest the type of polymer **E**.

(iii) Both compound **B** and compound **D** are soluble in water.

I. Write a balanced equation when compound **B** dissolves in water and describe the effect of the resulting solution on Universal Indicator solution.

II. Explain why compound **D** is soluble in water.

(iv) Suggest an observation for reaction scheme 2.

[7]

(c) "Ca^{2+} and Cl^- are isoelectronic but the radii of the ions are different".

(i) Explain the term 'isoelectronic'.

(ii) With the aid of the *Data Booklet*, explain the above observation as fully as you can.

(iii) State **two** ways in which the behaviour of Ca^{2+} ions in an electric field differs from that of Cl^- ions.

[4]

[Total:20]