

## VICTORIA JUNIOR COLLEGE JC 2 PRELIMINARY EXAMINATION Higher 2

# CANDIDATE NAME .....

CT GROUP .....

### CHEMISTRY

Paper 2 Structured Questions

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

#### **READ THESE INSTRUCTIONS FIRST**

Write your name and CT group in the space at the top of this page. Write in dark blue or black pen. You may use a HB pencil for any diagrams or graphs. Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the space provided on the Question Paper. The use of an approved scientific calculator is expected, where appropriate.

A Data Booklet is provided.

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

For Examiner's Use		
1	/ 25	
2	/ 13	
3	/ 12	
4	/ 19	
5	/ 6	
Total	/ 75	

This document consists of 18 printed pages.

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2 hours

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- 1 (a) The most common oxidation states of iron are +2 and +3.
  - (i) Iron(II) and iron(III) both contain electrons in all five 3d orbitals.

Sketch and label the shape of the following two 3d orbitals:

- one 3d orbital from the lower energy level in an octahedral complex
- one 3d orbital from the higher energy level in an octahedral complex

Use the axes below.



lower energy level





Lower energy level (in between axes)



3d<sub>xv</sub>



Higher energy level (on the axes)



- (ii) Explain why  $Fe^{2+}(aq)$  ions are coloured, whereas  $Zn^{2+}(aq)$  ions are colourless.
- The degenerate 3d orbitals in Fe<sup>2+</sup> octahedral complex is split into 2 different energy levels due to the presence of water ligands.
- d-d transition took place whereby a 3d electron from the lower energy level is promoted to the upper energy level by absorbing energy from the visible region of the electromagnetic spectrum. The colour seen is the complement of the colour absorbed.
- Fe<sup>2+</sup> has a partially-filled d subshell but Zn<sup>2+</sup> has completely filled 3d subshell and so <u>d-d transition</u> whereby an electron is promoted from a lower energy level to a higher energy level is impossible.

(iii) Most naturally occurring samples of iron(II) oxide are found as the mineral wüstite. Wüstite has formula  $Fe_{20}O_x$ . It contains both  $Fe^{2+}$  and  $Fe^{3+}$  ions. 90% of the iron is present as  $Fe^{2+}$  and 10% is present as  $Fe^{3+}$ .

Deduce the value of *x*.

 $20 \times [0.9(+2) + 0.1(+3)] - 2x = 0$ • x = 21

When aqueous solutions of  $S_2O_8^{2-}$  and tartrate ions,  $C_4H_4O_6^{2-}$ , are mixed, the reaction proceeds very slowly. However, this reaction proceeds quickly in the presence of an Fe<sup>3+</sup>(aq) catalyst. The overall equation for this reaction is as shown.

$$C_4H_4O_6^{2-} + 3S_2O_8^{2-} + 2H_2O \rightarrow 2CO_2 + 2HCO_2^{-} + 6H^+ + 6SO_4^{2-}$$

(iv) State and explain the type of catalyst that Fe<sup>3+</sup>(aq) functions in the above reaction.

• Fe<sup>3+</sup>(aq) is a <u>homogeneous</u> catalyst in this reaction as it has the <u>same physical</u> <u>state (OR phase) as the reactants</u>.

[1]

[1]

- (v) Write two equations to show how  $Fe^{3+}(aq)$  functions as a catalyst in this reaction.
- $6Fe^{3+} + C_4H_4O_6^{2-} + 2H_2O \rightarrow 6Fe^{2+} + 2CO_2 + 2HCO_2^{-} + 6H^+$
- $2Fe^{2+} + S_2O_8^{2-} \rightarrow 2Fe^{3+} + 2SO_4^{2-}$

[2]

(b) (i) Complete the 'dot-and-cross' diagram below, drawing the outer electrons only, to show the bonding in methanoic acid, HCO<sub>2</sub>H. The two oxygen atoms in HCO<sub>2</sub>H are labelled O<sup>1</sup> and O<sup>2</sup> respectively.



[1]

- (ii) The carbon atom in  $HCO_2H$  is sp<sup>2</sup> hybridised. Explain what is meant by sp<sup>2</sup> hybridisation with reference to the carbon atom in  $HCO_2H$ .
- In sp<sup>2</sup> hybridisation, one 2s and two 2p orbitals of carbon are mixed to form three equivalent sp<sup>2</sup> hybrid orbitals that are arranged 120° apart.

[1]

(iii) Similar to carbon, oxygen atom can also undergo hybridisation. By considering the number of electron densities around oxygen atom labelled O<sup>1</sup>, suggest the type of hybridised orbitals for the oxygen atom labelled O<sup>1</sup>.

(iv) Sketch a diagram to show how two sp<sup>2</sup> hybridised orbitals can form a sigma bond.



- [1]
- (c) Cyclohexane is immiscible with water. Iodine,  $I_2$ , can dissolve in both water and cyclohexane. The expression and numerical value for the partition coefficient,  $K_{pc}$ , of iodine between cyclohexane and water are given below.

 $K_{pc} = \frac{\text{concentration of I}_2 \text{ in cyclohexane}}{\text{concentration of I}_2 \text{ in water}} = 93.8$ 

(i) 15.0 cm<sup>3</sup> of  $C_6H_{12}$  is shaken with 20.0 cm<sup>3</sup> of an aqueous solution containing  $I_2$  until no further change is seen. It is found that 0.390 g of  $I_2$  is extracted from water into the  $C_6H_{12}$ . Calculate the mass of  $I_2$  that remains in the aqueous layer. Show your working.

#### Let mass of I<sub>2</sub> that remains in the aqueous layer be *x* g.

 $K_{pc} = \frac{\text{concentration of } I_2 \text{ in cyclohexane}}{\text{concentration of } I_2 \text{ in water}}$   $93.8 = (0.390/15) \div (x/20)$   $x = 5.54 \times 10^{-3} \text{ g}$ 

- (ii) Suggest how the value of  $K_{pc}$  of  $I_2$  between hexa-2-one,  $CH_3(CH_2)_3COCH_3$ , and water would compare to the value given in (c). Explain your answer.
- $K_{pc}$  of I<sub>2</sub> between hexan-2-one and water would be <u>lower</u> than 93.8.
- lodine being <u>non-polar</u> would be <u>less soluble</u> in hexa-2-one which is a <u>polar solvent</u>. Hence <u>concentration of I<sub>2</sub></u> in hexa-2-one would be <u>lesser</u> than in cyclohexane in the presence of water.

(d) Some data relating to calcium and oxygen are listed in table 1.1.

Ta	ble	1	.1	
-		-		

process	value / kJ mol <sup>-1</sup>
first ionisation energy of oxygen	+1310
second ionisation energy of oxygen	+3390
first electron affinity of oxygen	-142
second electron affinity of oxygen	+844
enthalpy change for $\frac{1}{2}O_2(g) + 2e^- \rightarrow O^{2-}(g)$	+951
enthalpy change for $Ca(s) \rightarrow Ca^{2+}(g) + 2e^{-}$	+1933
lattice energy of CaO(s)	-3517

- (i) Suggest why the first electron affinity of oxygen is negative.
- First electron affinity of oxygen is negative (or exothermic) due to energy released from the <u>attraction between the nucleus (or protons)</u> of the gaseous oxygen atom <u>and</u> the incoming <u>electron</u>.

[1]

- (ii) Suggest why the second electron affinity of oxygen is positive.
- Second electron affinity of oxygen is positive (or endothermic) due to energy needed to overcome the <u>repulsion between the negatively charged O<sup>-</sup> ion and</u> the incoming <u>electron</u>.

[1]

(iii) Oxygen exists as O<sub>2</sub> molecules. Use relevant data from table 1.1 to calculate the bond energy of the O=O bond. Show your working.

- $\frac{1}{2}$ BE(O=O) -142 + (+844)= +951
- $\frac{1}{2}BE(O=O) = 249$ BE(O=O) = 498 kJ mol<sup>-1</sup>

[2]

(iv) Use relevant data from table 1.1 to calculate the enthalpy change of formation of calcium oxide, CaO(s). Show your working.



- $\Delta H_{\rm f} = +1933 + 951 3517$
- $\Delta H_{\rm f} = -633 \text{ kJ mol}^{-1}$

- (v) The lattice energy of lithium fluoride, LiF(s), is -1022 kJ mol<sup>-1</sup>. Identify the factor that causes the lattice energy of calcium oxide to be more exothermic than that of lithium fluoride. Explain why this factor causes the difference in lattice energies.
- It is the ionic charge of the ions causes the lattice energy of CaO to be more exothermic than that of LiF.
- $|\mathbf{LE}| \propto \left| \frac{\mathbf{q}_{+}\mathbf{q}_{-}}{\mathbf{r}_{+}+\mathbf{r}_{-}} \right|$

Since the <u>charge</u> of each ion in CaO is <u>twice</u> of that in LiF, the lattice energy of CaO is more exothermic than LiF.

[2]

[Total: 25]

- 2 (a) Chlorine can be manufactured using the electrolysis of NaC*l*(aq). At the cathode, H<sub>2</sub>(g) and OH<sup>-</sup>(aq) are produced. At the anode, the product mixture contains both C*l*<sub>2</sub>(g) and O<sub>2</sub>(g). The mole ratio of each gas depends on the concentration of NaCl(aq).
  - (i) The half-equation for the cathode reaction is as shown.

$$2H_2O(I) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$$

Starting from **neutral** NaC*l*(aq), write half-equations for the production of the following at the anode.

- O<sub>2</sub>(g),
- Cl<sub>2</sub>(g).
- $2H_2O \rightarrow 4H^+ + O_2 + 4e^-$
- $2Cl^- \rightarrow Cl_2 + 2e^-$

[2]

(ii) Explain why the  $Cl_2(g)$  :  $O_2(g)$  mole ratio increases as concentration of NaCl(aq) increases.

 $Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$  $E^{\circ}(O_2 \mid H_2O) = +1.23 V$   $E^{\circ}(Cl_2 | Cl^{-}) = +1.36 V;$ 

- The higher concentration of chloride ions will <u>shift</u> the <u>equilibrium position</u> to the <u>left</u>, making the <u>oxidation of Cl<sup>-</sup>(aq) to Cl<sub>2</sub>(g) to be more favourable</u>.
- Hence, the <u>electrode potential</u>, *E*(*Cl*<sub>2</sub> *Cl*<sup>-</sup>) will fall and more <u>*Cl*<sup>-</sup></u> will be oxidised to give *Cl*<sub>2</sub> thus the mole ratio of *Cl*<sub>2</sub>(g):O<sub>2</sub>(g) will increase.

(iii) Sodium chlorate(V) is prepared commercially by electrolysing NaC*l*(aq) in a cell that allows the electrolytes at cathode and anode to mix. The cathode reaction is the same as that described in (i). The equation for the anode reaction is as shown.

 $Cl^{-}(aq) + 6OH^{-}(aq) \rightarrow ClO_{3}^{-}(aq) + 3H_{2}O(l) + 6e^{-}$ 

Calculate the mass of  $NaClO_3$  that is produced when a current of 250 A is passed through the cell for 60 minutes.

Quantity of charge =  $250 \times 60 \times 60 = 9.00 \times 10^5$  C

- Amount of electrons transferred =  $\frac{9.00 \times 10^5}{96500}$  = 9.33 mol Amount of chlorate ions formed =  $\frac{9.33}{6}$  = 1.55 mol
- Mass of sodium chlorate formed = 1.55 × 106.5 = 166 g
- (b) Trimethylphosphine can act as a ligand, which can be represented as PR<sub>3</sub>. Chromium hexacarbonyl undergoes the following ligand exchange reaction with PR<sub>3</sub> as shown below.

$$Cr(CO)_6 + PR_3 \rightarrow Cr(CO)_5PR_3 + CO$$

Two separate experiments were carried out to study the rate of this reaction.

In the first experiment, the ligand  $PR_3$  was in a large excess and  $[Cr(CO)_6]$  was measured with time. The results are shown on the graph below whereby the y-axis represents the concentration of  $Cr(CO)_6$ .



In the second experiment,  $Cr(CO)_6$  was in a large excess, and  $[PR_3]$  was measured with time. Table 2.1 shows the results obtained.

time / s	$[PR_3]$ / mol dm <sup>-3</sup>
0	0.0100
120	0.0076
200	0.0060
360	0.0028

Table 2.1	
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- (i) Plot the data given in Table 2.1 on the graph above, using the same axis scales whereby the y-axis represents the concentration of PR<sub>3</sub>. Draw the best–fit line through your points.
- straight line from (0, 0.01) to point at (350, 0.0028) with all points on the line.
- (ii) Use the graphs to determine the order of reaction with respect to Cr(CO)<sub>6</sub> and PR<sub>3</sub>. Explain how you arrived at your answer.
- Order w.r.t. Cr(CO)<sub>6</sub> is <u>one</u> The graph for Cr(CO)<sub>6</sub> has a <u>constant half-life of 700</u>
- Order w.r.t. PR<sub>3</sub> is <u>zero.</u> The graph for PR<sub>3</sub> is a <u>straight line of constant gradient</u>, hence rate of reaction is <u>constant</u> at any concentration of PR<sub>3</sub>.

[2]

[1]

(iii) Define the term rate equation.

• The rate equation relates the rate of reaction to the concentration of the reactants and is determined experimentally

[1]

- (iv) Write the rate equation for the reaction and calculate the rate constant including its units.
- rate = k[Cr(CO)<sub>6</sub>] (ecf from (ii))
- $\mathbf{k} = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{700} = 9.90 \times 10^{-3} \text{ s}^{-1}$

[3]

[Total: 13]

- **3** (a) The chemistry of some period 3 elements and their compounds are discussed here.
  - (i) Explain why the first ionisation energy of aluminium is lower than that of magnesium.
  - The 3p electron to be removed from Al is at a <u>higher energy level</u> than the 3s electron to be removed from Mg. Hence <u>less energy is required to remove the 3p</u> <u>electron in Al</u> than the 3s electron in Mg and so the first ionisation energy of Al is lower than that of Mg

[1]

Table 3.1 shows some information regarding three oxides, E, F and G.

oxide	melting point / °C	electrical conductivity when molten	
E	1713	very poor	
F	24	nil	
G	2072	good	

- (ii) These three oxides, in no particular order, are  $Al_2O_3$ ,  $SiO_2$  and  $P_4O_6$ . Identify **E**, **F** and **G**.
- E: SiO<sub>2</sub> F: P<sub>4</sub>O<sub>6</sub> G: Al<sub>2</sub>O<sub>3</sub>

[1]

(iii) With reference to structure and bonding, account for your answer in (a)(ii).

- E is SiO<sub>2</sub> which has a <u>giant molecular structure with strong covalent bonds</u> <u>between its atoms</u> resulting in its high melting point. It conducts electricity poorly as there are <u>no charged particles</u> in the molten state.
- F is P<sub>4</sub>O<sub>6</sub> which is a <u>simple covalent molecule with weak intermolecular forces</u> of attraction resulting in its low melting point. It does not conduct electricity as there are <u>no charged particles</u> in the molten state.
- G is Al<sub>2</sub>O<sub>3</sub> which has <u>giant ionic lattice structure with strong electrostatic forces</u> of attraction between its cations and anions resulting in its high melting point. It conducts electricity in the molten state as its <u>ions become mobile</u>.

[3]

- (iv) Suggest the pH values of the mixture formed when **E**, **F** and **G** are added separately to water. Write balanced equations for each of these reactions, where appropriate.
- The pH values for solutions of E, F and G are 7, 2 3 and 7 respectively.
- $P_4O_6 + 6H_2O \rightarrow 4H_3PO_3$

[2]

- (v) Aluminium oxide is *amphoteric*. With the aid of equations, explain the meaning of the term *amphoteric*.
- Aluminium oxide is amphoteric as it can react with both acids and bases.
- $Al_2O_3 + 6H^+ \rightarrow 2Al^{3+} + 3H_2O$
- $Al_2O_3 + 2OH^- + 3H_2O \rightarrow 2[Al(OH)_4]^-$

(b) The nitrates of strontium and barium decompose on heating, forming the same gaseous products.

Explain whether strontium nitrate would decompose at a higher or lower temperature than barium nitrate.

- Although both ions have the <u>same charge</u> of +2, Sr<sup>2+</sup> ions have <u>higher charge</u> <u>density</u> than Ba<sup>2+</sup> ions due to its <u>smaller ionic radius</u>.
- Sr<sup>2+</sup> is able to polarise and <u>distort the electron cloud of NO<sub>3</sub><sup>-</sup> to a larger extent</u>, leading to lower thermal stability. Sr(NO<sub>3</sub>)<sub>2</sub> will decompose at <u>a lower temperature</u>.

[2]

- (c) Hydrogen chloride is stable to heat while hydrogen iodide decomposes to hydrogen and iodine when heated with a red-hot steel. Explain why this is so.
  - The <u>bond energy</u> of H–*Cl* is <u>higher</u> than that of H-I due to its <u>smaller atomic radius</u> compared with that of iodine. Hence it is difficult for HC*l* to undergo thermal decomposition.

[1]

[Total: 12]

- **4** Ibuprofen, C<sub>13</sub>H<sub>18</sub>O<sub>2</sub>, a non-steroidal anti-inflammatory drug, is used for the treatment of pain, fever and inflammation.
  - (a) The industrial synthesis of ibuprofen developed by BHC Company in the 1980s is shown below. This synthetic route proved to be highly successful in terms of its environmental friendliness.



An environmentally friendly chemical process is expected to have a high atom economy, indicating that a high proportion of the starting materials end up as part of the final product, hence reducing the amount of waste.

The atom economy of a process can be calculated using the formula:

atom economy =  $\frac{\text{molar mass of desired product}}{\text{sum of molar mass of all products}}$ 

- (i) Calculate the atom economy of the BHC Company process in the synthesis of ibuprofen.
- Molar mass of ibuprofen =  $12.0 \times 13 + 1.0 \times 18 + 16.0 \times 2 = 206$  g mol<sup>-1</sup> Molar mass of ethanoic acid = 60.0 g mol<sup>-1</sup>
- Atom economy =  $\frac{206}{206+60}$  = 0.774

[2]

[1]

- (ii) Suggest the type of reaction in step 1.
- Electrophilic substitution
- (iii) Outline a simple chemical test that could be carried out to distinguish compound A from ibuprofen.
- Add NaCO<sub>3</sub>(s) to both compounds.

• Only ibuprofen gives effervescence of CO<sub>2</sub> but compound A does not. OR

- Heat both compounds with K<sub>2</sub>Cr<sub>2</sub>O<sub>2</sub>, H<sub>2</sub>SO<sub>4</sub>(aq).
- Only compound A turns orange solution to green but ibuprofen does not. OR
- Warm both compounds with I<sub>2</sub> in NaOH(aq)
- Only compound A forms pale yellow precipitate but ibuprofen does not.

(iv) Ethanoic anhydride, (CH<sub>3</sub>CO)<sub>2</sub>O, used in step 1 could be regenerated by dehydrating ethanoic acid. In this reaction, 2 mol of ethanoic acid form 1 mol of ethanoic anhydride and 1 mol of water.

Determine the new atom economy if ethanoic acid formed in step 1 is reused in this synthesis.

For every two moles of ibuprofen formed, there are two moles of ethanoic acid formed.

2 mol of CH<sub>3</sub>CO<sub>2</sub>H will produce 1 mol of water.

• New atom economy would be  $\frac{206 \times 2}{206 \times 2 + 18} = 0.958$ 

[1]

(b) Instead of step 3 in (a), compound A formed during the BHC Company process can react with PCl<sub>5</sub> to give compound B which then undergoes further reactions to yield ibuprofen.



compound A

compound **B** 

The mechanism of converting compound **A** into compound **B** is thought to involve the following three steps.

- The initial nucleophilic attack on P by the lone pair of electrons on the oxygen atom in compound A to form a P-O bond together with a loss of Cl<sup>-</sup>.
- This is followed by  $Cl^{-}$  acting as a base to abstract a proton.
- The third step involves a nucleophilic attack on a carbon atom by another C*l*<sup>-</sup> ion together with simultaneous P=O bond formation and P−C*l* bond cleavage to form the products.
- (i) Use the information given above to draw out the three-step full mechanism for the reaction of compound **A** with  $PCl_5$ . Show relevant lone pairs and dipoles and use curly arrows to indicate the movement of electron pairs.

You may use R to represent the



- The high bond energy / strength of P=O bond that is formed makes the reaction highly exothermic.
- Hence,  $\Delta G$  of the reaction can be <u>very negative</u> leading to a <u>large  $K_c$  value</u> so the reaction I goes to completion.

[2]

(iii) Complete the reaction scheme to show how ibuprofen could be synthesised from compound **B** in two steps. Draw the structure of the intermediate and state the reagents and conditions for each step.



intermediate compound

reaction	reagents and conditions		
11	Ethanolic KCN, heat		
III	H <sub>2</sub> SO <sub>4</sub> (aq), heat		

[3]

(c) When Group 2 salts of carboxylic acids are heated, it gives the metal carbonate and a carbonyl compound. For example, when calcium ethanoate is heated, it produces propanone.

$$(CH_3CO_2)_2Ca \rightarrow CaCO_3 + (CH_3)_2CO$$

When this reaction is carried out by heating a 1:1 molar mixture of calcium ethanoate and calcium methanoate,  $(HCO_2)_2Ca$ , a mixture of three carbonyl compounds is formed, all having  $M_r < 60$ .

(i) Suggest the structures of the three carbonyl compounds and the ratio in which they might be produced.

Structure of carbonyl compound	НСНО	CH₃CHO	CH <sub>3</sub> COCH <sub>3</sub>
Ratio	1	2	1

[2]

(ii) Suggest **two** chemical tests that could be used to distinguish the three carbonyl compounds from each other. You should state what you would observe for each compound in each test.

Tests	observations			
	НСНО	CH <sub>3</sub> CHO	CH <sub>3</sub> COCH <sub>3</sub>	
Add Tollens' reagent and heat	Silver Mirror formed	Silver Mirror formed	No silver Mirror formed	
OR Add Fehling's reagent and heat	Brick-red ppt formed	Brick-red ppt formed	No brick-red ppt formed	
OR Add K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> (aq), H <sub>2</sub> SO <sub>4</sub> (aq) and heat	Orange solution turns green	Orange solution turns green	Orange solution did not turn green	
OR				
Add KMnO₄(aq), H₂SO₄(aq) and heat	Purple solution decolourised with effervescence of CO <sub>2</sub> which forms white ppt in limewater	Purple solution decolourised	Solution remains purple	
Add I₂(aq), NaOH(aq) and heat	No pale yellow ppt. formed	Pale yellow ppt. formed	Pale yellow ppt. formed	

[3]

[Total: 19]

5(a) Table 5.1 shows some information about the elements, calcium, iron and copper.

	calcium	iron	copper
Relative atomic mass	40.1	55.8	63.5
Atomic radius (metallic) / nm	0.197	0.126	0.128
Ionic radius (2+) / nm	0.099	0.076	0.069
Melting point / K	1112	1808	1358
Density / g cm <sup>-3</sup>	1.54	7.86	8.93

#### Table 5.1

(i) Describe the structure and bonding in calcium with the aid of a labelled diagram.



• Ca<sup>2+</sup> cations are arranged in a <u>giant metallic structure</u> held by <u>strong electrostatic</u> <u>forces of attraction between the delocalised electrons and the cations</u>.

[2]

- (ii) Suggest why the atomic radii of iron and copper are both smaller than that of calcium.
- The <u>nuclear charge</u> of both Fe and Cu are <u>higher</u> than that of Ca due to <u>greater</u> <u>number of protons</u>. Though Fe and Cu have greater number of inner electrons, the <u>shielding effect of d electrons in the penultimate subshells</u> of Fe and Cu is <u>not</u> as effective.
- Hence the <u>effective nuclear charge of Fe and Cu are higher</u>, leading to smaller atomic radii than that of Ca.

[2]

- (iii) Use information from Table 5.1 to explain why the densities of iron and copper are significantly greater than that of calcium. [No calculations are required.]
- Both Fe and Cu have <u>smaller atomic radius</u> than Ca, hence Fe and Cu can <u>be</u> <u>packed more closely together</u> in a metallic lattice.
- Fe and Cu also have <u>higher relative atomic mass</u> than Ca. This leads to a high mass per unit volume ratio (density).

[2]

[Total: 6]