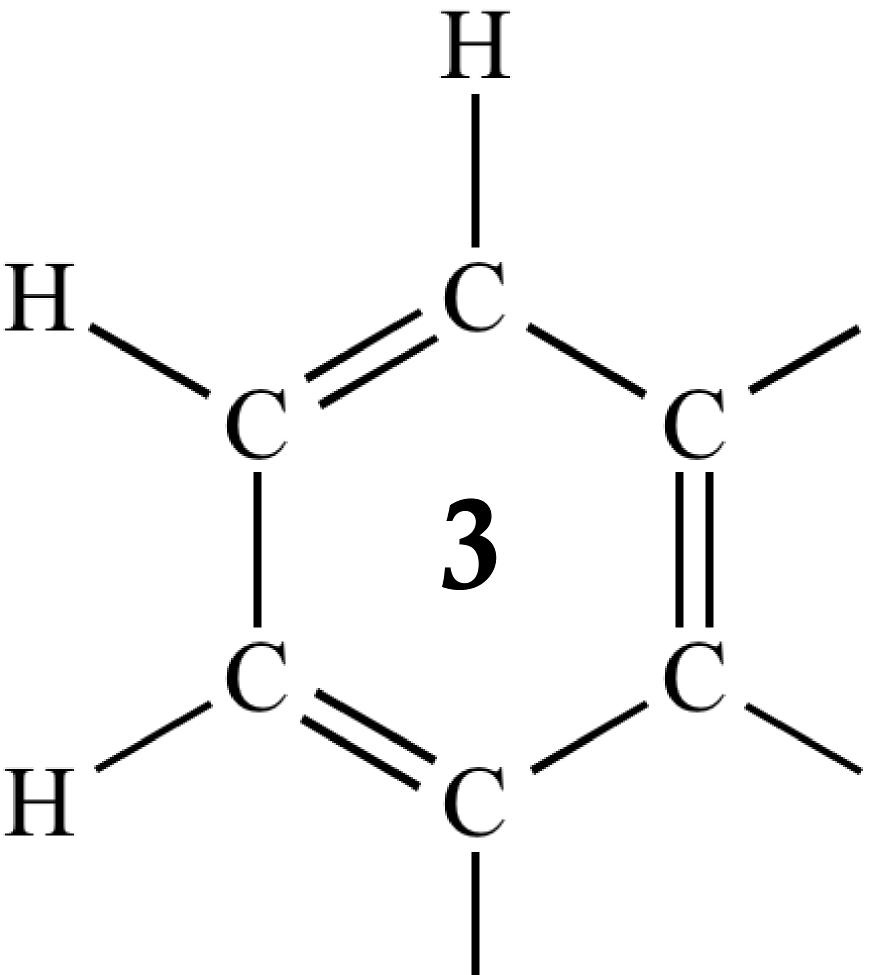
LONDON SCIENCE COLLEGE

OCR A2 CHEMISTRY

MODULE 5.4

THERMODYNAMICS



1 Calcium fluoride occurs naturally as the mineral fluorite, a very hard crystalline solid that is almost insoluble in water and is used as a gemstone.

Tables 1 and **2** contain thermodynamic data.

Table 1

Process	ΔH^{o} / kJ mol^{-1}
$Ca(s) \rightarrow Ca(g)$	+193
$Ca(g) \rightarrow Ca^{+}(g) + e^{-}$	+590
$Ca^{+}(g) \rightarrow Ca^{2+}(g) + e^{-}$	+1150
$F_2(g) \rightarrow 2F(g)$	+158
$F(g) + e^{-} \rightarrow F^{-}(g)$	–348

Table 2

Name of enthalpy change	ΔH^{o} / kJ mol^{-1}
Enthalpy of lattice dissociation for calcium fluoride	+2602
Enthalpy of lattice dissociation for calcium chloride	+2237
Enthalpy of hydration for F^{-} ions	–506
Enthalpy of hydration for Cl^{-} ions	–364
Enthalpy of hydration for Ca^{2+} ions	–1650

(a) Write an equation, including state symbols, for the process that occurs when the calcium fluoride lattice dissociates and for which the enthalpy change is equal to the lattice enthalpy.

....

(1)

(b) (i) Define the term *standard enthalpy of formation*.

....

....

....

....

(3)

(ii) Write an equation, including state symbols, for the process that has an enthalpy change equal to the standard enthalpy of formation of calcium fluoride.

....

(1)

(iii) Use data from the **Tables 1** and **2** to calculate the standard enthalpy of formation for calcium fluoride.

....

....

....

....

....

....

(3)

(c) Explain why the enthalpy of lattice dissociation for calcium fluoride is greater than that for calcium chloride.

....

....

....

....

(2)

(d) Calcium chloride dissolves in water. After a certain amount has dissolved, a saturated solution is formed and the following equilibrium is established.

$$CaCl_2(s) \rightleftharpoons Ca^{2+}(aq) + 2Cl^-(aq)$$

(i) Using data from **Table 2**, calculate the enthalpy change for this reaction.

....

....

....

....

....

....

(2)

(ii) Predict whether raising the temperature will increase, decrease or have no effect on the amount of solid calcium chloride that can dissolve in a fixed mass of water. Explain your prediction.
(If you have been unable to obtain an answer to part (d) (i), you may assume that the enthalpy change = –60 kJ mol^{-1}. This is **not** the correct answer.)

Effect on amount of solid that can dissolve ....

Explanation ....

....

....

....

(3)

(e) Calcium fluoride crystals absorb ultra-violet light. Some of the energy gained is given out as visible light. The name of this process, fluorescence, comes from the name of the mineral, fluorite.

Use your knowledge of the equation $\Delta E = h\nu$ to suggest what happens to the electrons in fluorite when ultra-violet light is absorbed and when visible light is given out.

....

....

....

....

(2)
(Total 17 marks)

2 The table below gives some values of standard enthalpy changes. Use these values to answer the questions.

Name of enthalpy change	**ΔH° /kJ mol^{-1}**
Enthalpy of atomisation of chlorine	+121
Electron affinity of chlorine	–364
Enthalpy of atomisation of silver	+289
First ionisation enthalpy of silver	+732
Enthalpy of formation of silver chloride	–127

(a) Calculate the bond enthalpy of a Cl–Cl bond.

....

(1)

(b) Explain why the bond enthalpy of a Cl–Cl bond is greater than that of a Br–Br bond.

....

....

....

....

(2)

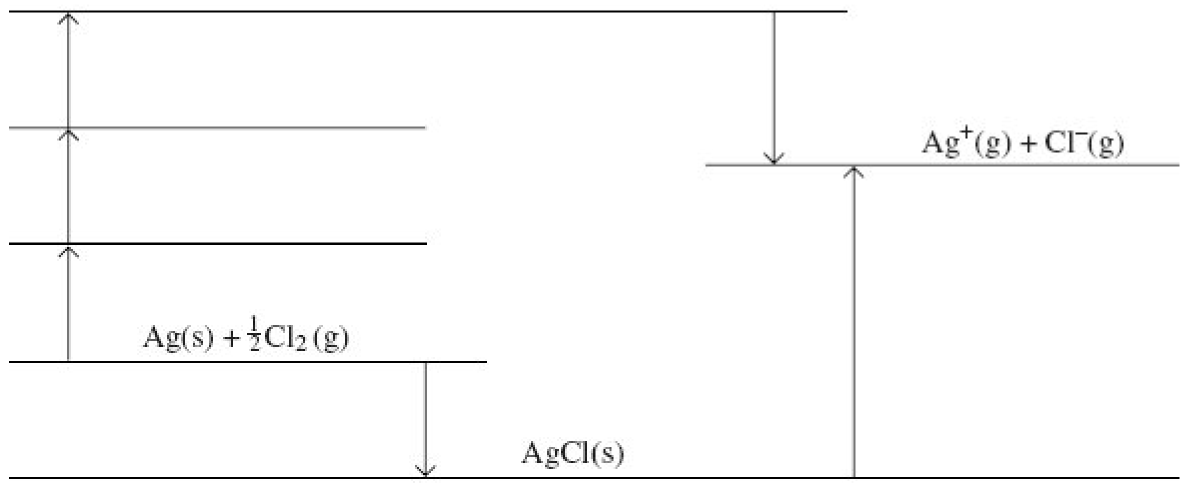
(c) Suggest why the electron affinity of chlorine is an exothermic change.

....

....

(1)

(d) The diagram below is an incomplete Born–Haber cycle for the formation of silver chloride. The diagram is not to scale.



(i) Complete the diagram by writing the appropriate chemical symbols, with state symbols, on each of the three blank lines.

(3)

(ii) Calculate a value for the enthalpy of lattice dissociation for silver chloride.

....

....

....

....

(2)

(e) The enthalpy of lattice dissociation for silver chloride can also be calculated theoretically assuming a perfect ionic model.

(i) Explain the meaning of the term *perfect ionic model*.

....

....

(1)

(ii) State whether you would expect the value of the theoretical enthalpy of lattice dissociation for silver chloride to be greater than, equal to or less than that for silver bromide. Explain your answer.

Theoretical lattice enthalpy for silver chloride ....

Explanation ....

....

....

(3)

(iii) Suggest why your answer to part (d) (ii) is greater than the theoretical value for the enthalpy of lattice dissociation for silver chloride.

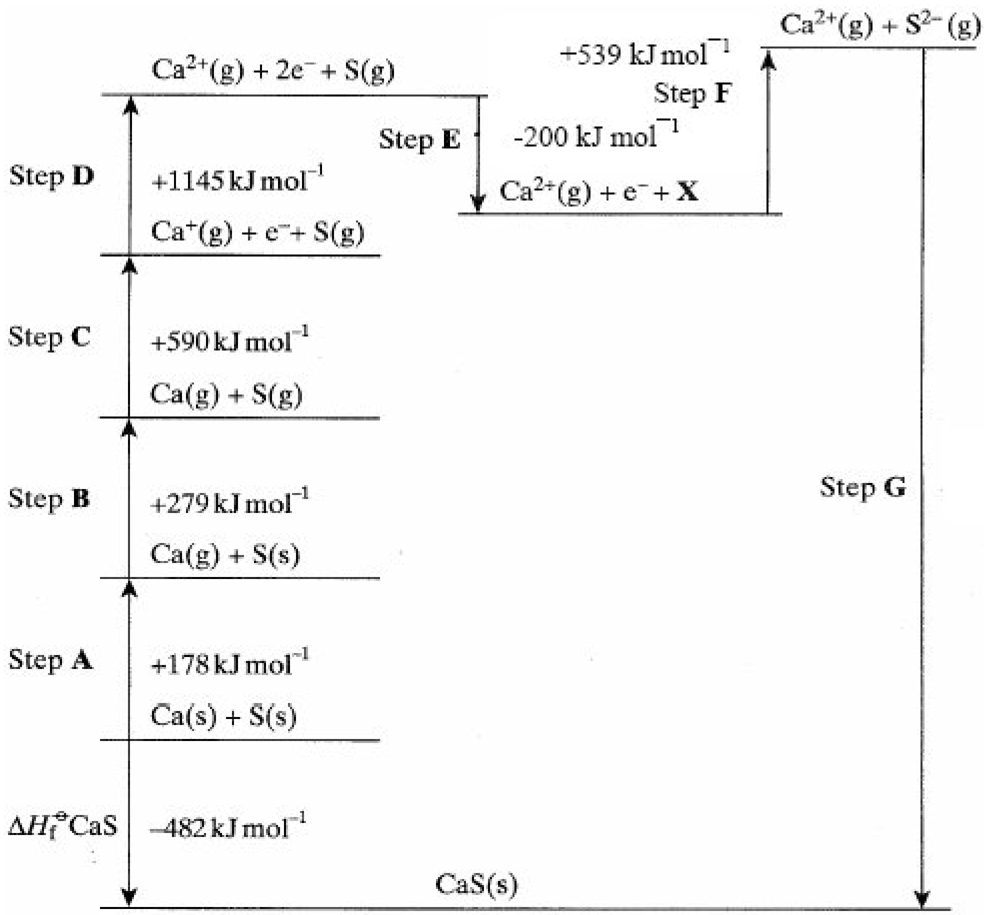
....

....

....

(2)
(Total 15 marks)

3 (a) A Born–Haber cycle for the formation of calcium sulphide is shown below. The cycle includes enthalpy changes for all steps except step **G**. (The cycle is not drawn to scale.)



(i) Give the full electronic configuration of the ion S^{2-}

....

(ii) Suggest why step **F** is an endothermic process.

....

....

(iii) Name the enthalpy changes in steps **B** and **D**.

*Step **B*** ....

*Step **D*** ....

(iv) Explain why the enthalpy change for step **D** is larger than that for step **C**.

....

....

(v) Use the data shown in the cycle to calculate a value for the enthalpy change for step **G**.

....

....

....

(9)

(b) Using a Born–Haber cycle, a value of –905 kJ mol^{-1} was determined for the lattice enthalpy of silver chloride. A value for the lattice enthalpy of silver chloride using the ionic model was –833 kJ mol^{-1}.

Explain what a scientist would be able to deduce from a comparison of these values.

....

....

....

....

(3)

(c) Some endothermic reactions occur spontaneously at room temperature. Some exothermic reactions do not occur if the reactants are heated together to a very high temperature.

In order to explain the following observations, another factor, the entropy change, ΔS, must be considered. The equation which relates ΔS to ΔH is given below.

$$\Delta G = \Delta H - T\Delta S$$

(i) Explain why the following reaction occurs at room temperature even though the reaction is endothermic.

$$NaHCO_3(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l) + CO_2(g)$$

....

....

....

....

(ii) Explain why the following reaction does not occur at very high temperatures even though the reaction is exothermic.

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

....

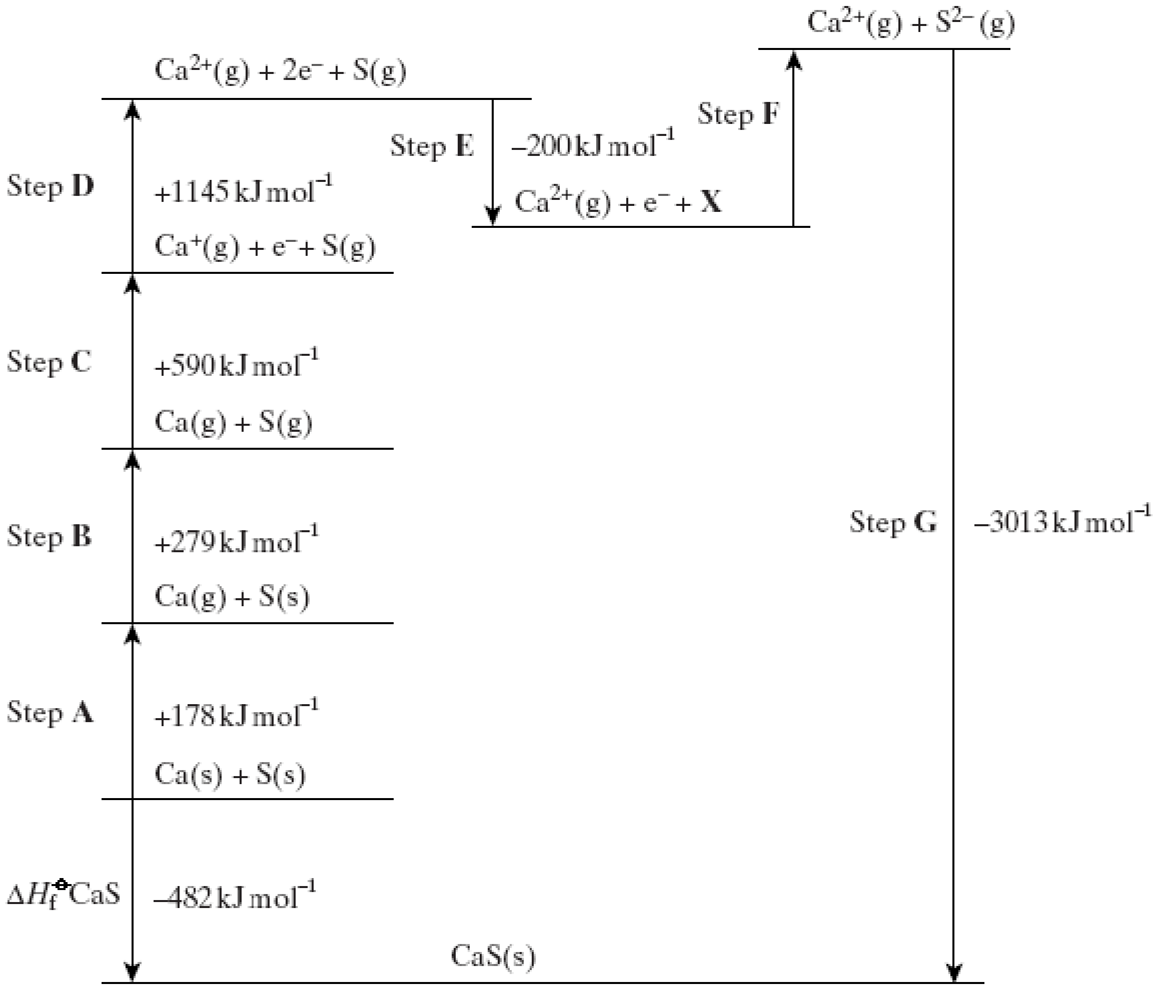
....

....

....

(6)
(Total 18 marks)

4 A Born–Haber cycle for the formation of calcium sulphide is shown below. The cycle includes enthalpy changes for all Steps except Step **F**. (The cycle is not drawn to scale.)



(a) Give the full electronic arrangement of the ion S^{2-}

....

(1)

(b) Identify the species **X** formed in Step **E**.

....

(1)

(c) Suggest why Step **F** is an endothermic process.

....

....

(2)

(d) Name the enthalpy change for each of the following steps.

(i) Step **B** ....

(ii) Step **D** ....

(iii) Step **F** ....

(3)

(e) Explain why the enthalpy change for Step **D** is larger than that for Step **C**.

....

....

(2)

(f) Use the data shown in the cycle to calculate a value for the enthalpy change for Step **F**.

....

....

....

(2)
(Total 11 marks)

5 Which one of the following statements is **not** correct?

A The first ionisation energy of iron is greater than its second ionisation energy.

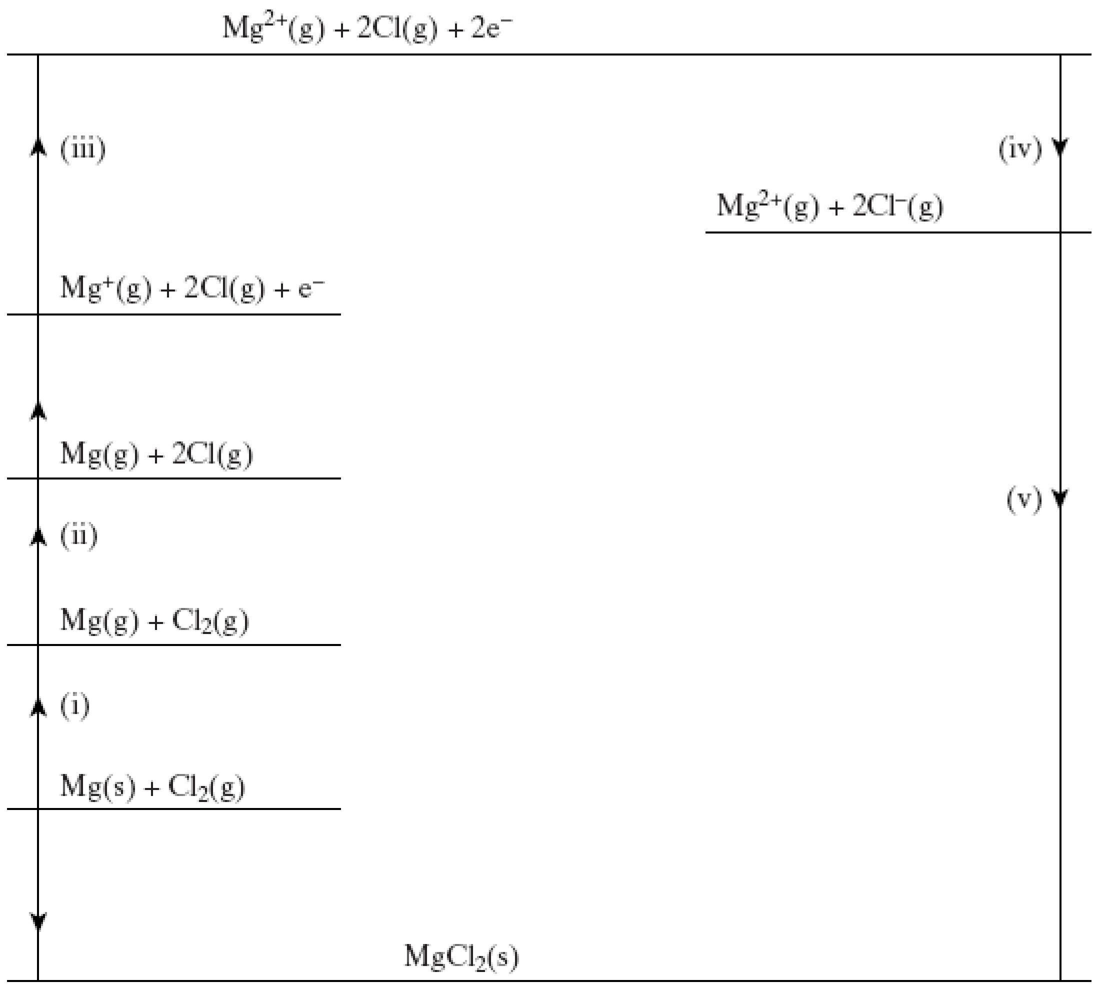
B The magnitude of the lattice enthalpy of magnesium oxide is greater than that of barium oxide.

C The oxidation state of iron in $[Fe(CN)_6]^{3-}$ is greater than the oxidation state of copper in $[CuCl_2]^-$

D The boiling point of C_3H_8 is lower than that of CH_3CH_2OH

(Total 1 mark)

6 (a) A Born–Haber cycle for the formation of magnesium(II) chloride is shown below.



Taking care to note the direction of the indicated enthalpy change and the number of moles of species involved, give each of the enthalpy changes (i) to (v) above.

Enthalpy change (i) ....

Enthalpy change (ii) ....

Enthalpy change (iii) ....

Enthalpy change (iv) ....

Enthalpy change (v) ....

(5)

(b) Write an equation for the decomposition of MgCl(s) into $MgCl_2$(s) and Mg(s) and use the following data to calculate a value for the enthalpy change of this reaction.

$\Delta H_f^{\ominus}$ MgCl(s) = –113 kJ mol^{-1}

$\Delta H_f^{\ominus}$ $MgCl_2$(s) = –653 kJ mol^{-1}

Equation ....

Calculation ....

....

....

....

(4)

(c) Use the data below to calculate a value for the molar enthalpy of a solution of $MgCl_2$(s).

Lattice formation enthalpy of $MgCl_2$(s)	= –2502 kJ mol^{-1}
$\Delta H^{\ominus}_{hydration}$ of Mg^{2+}(g)	= –1920 kJ mol^{-1}
$\Delta H^{\ominus}_{hydration}$ of Cl^{-}(g)	= –364 kJ mol^{-1}

....

....

....

....

....

....

(3)
(Total 12 marks)

7 (a) (i) Draw a fully-labelled Born–Haber cycle for the formation of solid barium chloride, $BaCl_2$, from its elements. Include state symbols for all species involved.

(ii) Use your Born–Haber cycle and the standard enthalpy data given below to calculate a value for the electron affinity of chlorine.

Enthalpy of atomisation of barium	+180 kJ mol^{-1}
Enthalpy of atomisation of chlorine	+122 kJ mol^{-1}
Enthalpy of formation of barium chloride	–859 kJ mol^{-1}
First ionisation enthalpy of barium	+503 kJ mol^{-1}
Second ionisation enthalpy of barium	+965 kJ mol^{-1}
Lattice formation enthalpy of barium chloride	–2056 kJ mol^{-1}

....

....

....

....

(9)

(b) Use data from part (a)(ii) and the entropy data given below to calculate the lowest temperature at which the following reaction becomes feasible.

$BaCl_2(s) \rightarrow Ba(s) + Cl_2(g)$

	$BaCl_2(s)$	Ba(s)	$Cl_2(g)$
$S^\ominus$ / J K^{-1} mol^{-1}	124	63	223

....

....

....

....

....

(4)
(Total 13 marks)

8 Which one of the following has the most covalent character?

A MgF_2

B $MgBr_2$

C AlF_3

D $AlBr_3$

(Total 1 mark)

9 Which one of the following has the most covalent character?

A MgF_2

B $MgBr_2$

C AlF_3

D $AlBr_3$

(Total 1 mark)