

Q1. This question is about magnesium oxide. Use data from the table below, where appropriate, to answer the following questions.

	$\Delta H^\ominus / \text{kJ mol}^{-1}$
First electron affinity of oxygen (formation of $\text{O}^-(\text{g})$ from $\text{O}(\text{g})$)	-142
Second electron affinity of oxygen (formation of $\text{O}^{2-}(\text{g})$ from $\text{O}^-(\text{g})$)	+844
Atomisation enthalpy of oxygen	+248

(a) Define the term *enthalpy of lattice dissociation*.

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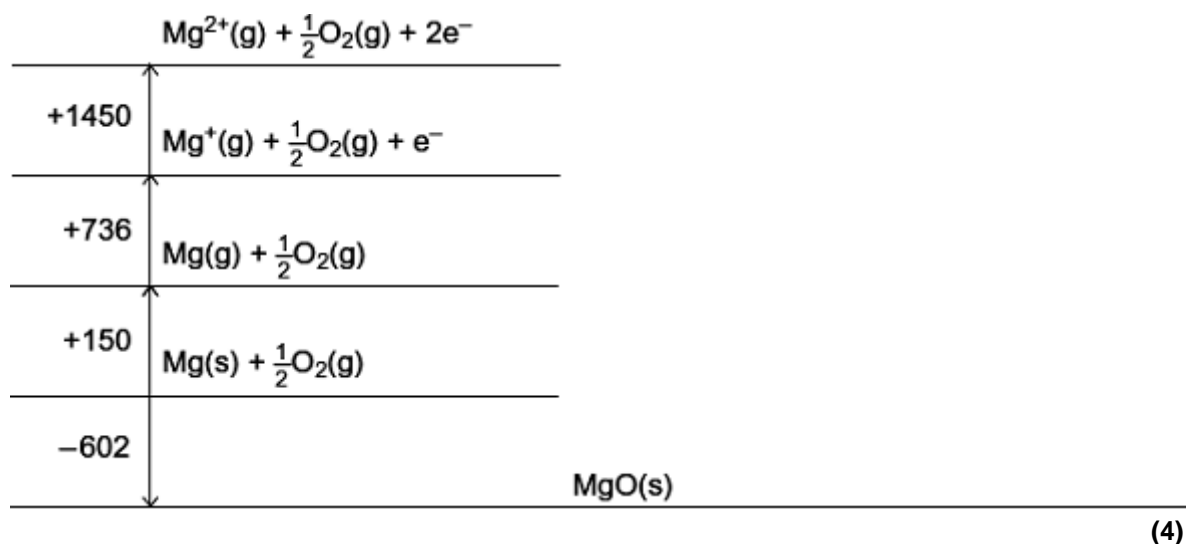
(3)

(b) In terms of the forces acting on particles, suggest **one** reason why the first electron affinity of oxygen is an exothermic process.

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(1)

(c) Complete the Born–Haber cycle for magnesium oxide by drawing the missing energy levels, symbols and arrows.
The standard enthalpy change values are given in kJ mol^{-1} .



(d) Use your Born–Haber cycle from part (c) to calculate a value for the enthalpy of lattice dissociation for magnesium oxide.

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(2)

(e) The standard free-energy change for the formation of magnesium oxide from magnesium and oxygen, $\Delta G_f^\ominus = -570 \text{ kJ mol}^{-1}$. Suggest **one** reason why a sample of magnesium appears to be stable in air at room temperature, despite this negative value for ΔG_f^\ominus .

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(1)

(f) Use the value of ΔG_f^\ominus given in part (e) and the value of ΔH_f^\ominus from part (c) to calculate a value for the entropy change ΔS^\ominus when one mole of magnesium oxide is formed from magnesium and oxygen at 298 K. Give the units of ΔS^\ominus .

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(3)

(g) In terms of the reactants and products and their physical states, account for the sign of the entropy change that you calculated in part (f).

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(Total 16 marks)

Q2. Thermodynamics can be used to investigate the changes that occur when substances such as calcium fluoride dissolve in water.

(a) Give the meaning of each of the following terms.

(i) enthalpy of lattice formation for calcium fluoride

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(ii) enthalpy of hydration for fluoride ions

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(1)

(b) Explain the interactions between water molecules and fluoride ions when the fluoride ions become hydrated.

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(c) Consider the following data.

	$\Delta H^\ominus / \text{kJ mol}^{-1}$
Enthalpy of lattice formation for CaF_2	-2611
Enthalpy of hydration for Ca^{2+} ions	-1650
Enthalpy of hydration for F^- ions	-506

Use these data to calculate a value for the enthalpy of solution for CaF_2

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(2)

(Total 7 marks)

Q3. Comparison of lattice enthalpies from Born-Haber cycles with lattice enthalpies from calculations based on a perfect ionic model are used to provide information about bonding in crystals.

(a) Define the terms *enthalpy of atomisation* and *lattice dissociation enthalpy*.

Enthalpy of atomisation

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Lattice dissociation enthalpy

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(4)

(b) Use the following data to calculate a value for the lattice dissociation enthalpy of sodium chloride.

	$\Delta H^\ominus / \text{kJ mol}^{-1}$
Na(s) \longrightarrow Na(g)	+109
Na(g) \longrightarrow Na ⁺ (g) + e ⁻	+494
Cl ₂ (g) \longrightarrow 2Cl(g)	+242
Cl(g) + e ⁻ \longrightarrow Cl ⁻ (g)	-364
Na(s) + $\frac{1}{2}$ Cl ₂ (g) \longrightarrow NaCl(s)	-411

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(3)

(c) Consider the following lattice dissociation enthalpy (ΔH_L^\ominus) data.

	NaBr	AgBr
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$\Delta H_{\text{L}}^{\circ}$ (experimental)/kJ mol ⁻¹	+733	+890
$\Delta H_{\text{L}}^{\circ}$ (theoretical)/kJ mol ⁻¹	+732	+758

The values of $\Delta H_{\text{L}}^{\circ}$ (experimental) have been determined from Born–Haber cycles.

The values of $\Delta H_{\text{L}}^{\circ}$ (theoretical) have been determined by calculation using a perfect ionic model.

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

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- (ii) State what you can deduce about the bonding in NaBr from the data in the table.

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- (iii) State what you can deduce about the bonding in AgBr from the data in the table.

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(1)

(Total 11 marks)

Q4. 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	$\Delta H^\ominus / \text{kJ mol}^{-1}$
$\text{Ca(s)} \rightarrow \text{Ca(g)}$	+193
$\text{Ca(g)} \rightarrow \text{Ca}^+(\text{g}) + \text{e}^-$	+590
$\text{Ca}^+(\text{g}) \rightarrow \text{Ca}^{2+}(\text{g}) + \text{e}^-$	+1150
$\text{F}_2(\text{g}) \rightarrow 2\text{F}(\text{g})$	+158
$\text{F}(\text{g}) + \text{e}^- \rightarrow \text{F}^-(\text{g})$	-348

Table 2

Name of enthalpy change	$\Delta H^\ominus / \text{kJ mol}^{-1}$
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.

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(1)

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

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(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.

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(1)

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

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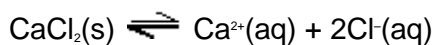
(3)

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

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



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

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(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

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- (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.

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(2)

(Total 17 marks)