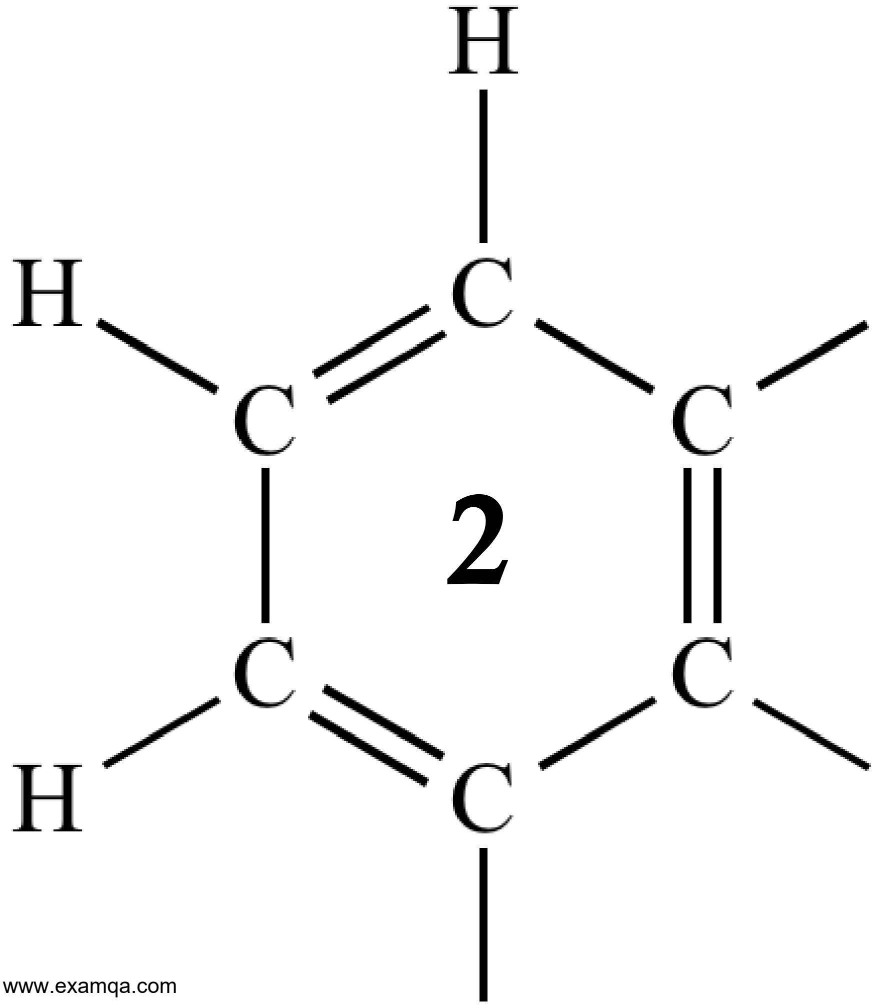
OCR A2 CHEMISTRY

MODULE 5.4

THERMODYNAMICS



1 The enthalpy of hydration for the chloride ion is −364 kJ mol^{-1} and that for the bromide ion is −335 kJ mol^{-1}.

(a) By describing the nature of the attractive forces involved, explain why the value for the enthalpy of hydration for the chloride ion is more negative than that for the bromide ion.

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(3)

(b) The enthalpy of hydration for the potassium ion is −322 kJ mol^{-1}. The lattice enthalpy of dissociation for potassium bromide is +670 kJ mol^{-1}.

Calculate the enthalpy of solution for potassium bromide.

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(2)

(c) The enthalpy of solution for potassium chloride is +17.2 kJ mol^{-1}.

(i) Explain why the free-energy change for the dissolving of potassium chloride in water is negative, even though the enthalpy change is positive.

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(Extra space) ....

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(3)

(ii) A solution is formed when 5.00 g of potassium chloride are dissolved in 20.0 g of water. The initial temperature of the water is 298 K.

Calculate the final temperature of the solution.

In your calculation, assume that only the 20.0 g of water changes in temperature and that the specific heat capacity of water is 4.18 J K^{-1} g^{-1}.

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(5)
(Total 13 marks)

2 This table contains some values of lattice dissociation enthalpies.

Compound	$MgCl_2$	$CaCl_2$	MgO
Lattice dissociation enthalpy / kJ mol^{-1}	2493	2237	3889

(a) Write an equation, including state symbols, for the reaction that has an enthalpy change equal to the lattice dissociation enthalpy of magnesium chloride.

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(1)

(b) Explain why the lattice dissociation enthalpy of magnesium chloride is greater than that of calcium chloride.

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(Extra space) ....

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(2)

(c) Explain why the lattice dissociation enthalpy of magnesium oxide is greater than that of magnesium chloride.

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(Extra space) ....

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(2)

(d) When magnesium chloride dissolves in water, the enthalpy of solution is −155 kJ mol^{-1}.
The enthalpy of hydration of chloride ions is −364 kJ mol^{-1}.

Calculate the enthalpy of hydration of magnesium ions.

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(Extra space) ....

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(3)

(e) Energy is released when a magnesium ion is hydrated because magnesium ions attract water molecules.

Explain why magnesium ions attract water molecules.
You may use a labelled diagram to illustrate your answer.

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(2)

(f) Suggest why a value for the enthalpy of solution of magnesium oxide is **not** found in any data books.

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(1)
(Total 11 marks)

3 Some thermodynamic data for fluorine and chlorine are shown in the table.
In the table, X represents the halogen F or Cl.

	Fluorine	**Chlorine**
Electronegativity	4.0	3.0
Electron affinity / kJ mol^{-1}	–348	–364
Enthalpy of atomisation / kJ mol^{-1}	+79	+121
Enthalpy of hydration of $X^{-}(g)$ / kJ mol^{-1}	–506	–364

(a) Explain the meaning of the term *electron affinity*.

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(2)

(b) Explain why the electronegativity of fluorine is greater than the electronegativity of chlorine.

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(Extra space) ....

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(2)

(c) Explain why the hydration enthalpy of the fluoride ion is more negative than the hydration enthalpy of the chloride ion.

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(2)

(d) The enthalpy of solution for silver fluoride in water is –20 kJ mol^{-1}.

The hydration enthalpy for silver ions is –464 kJ mol^{-1}.

(i) Use these data and data from the table to calculate a value for the lattice enthalpy of dissociation of silver fluoride.

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(ii) Suggest why the entropy change for dissolving silver fluoride in water has a positive value.

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(iii) Explain why the dissolving of silver fluoride in water is always a spontaneous process.

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(2)
(Total 12 marks)

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

	$\Delta H^{\ominus}$ / kJ mol^{-1}
First electron affinity of oxygen (formation of O^-(g) from O(g))	–142
Second electron affinity of oxygen (formation of O^{2-}(g) from O^-(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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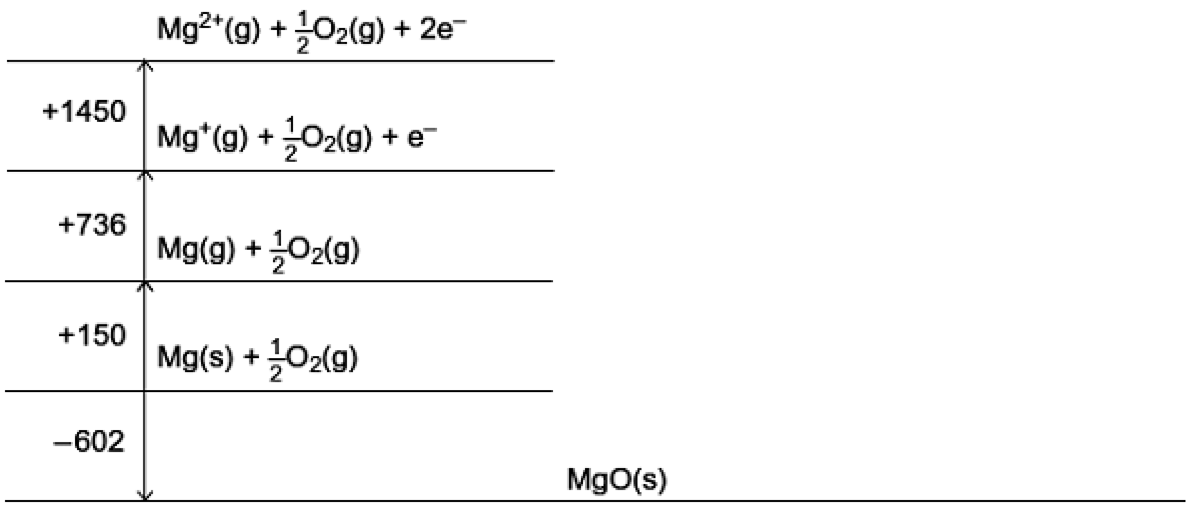
(1)

(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}.



(4)

(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 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 $\Delta G_f^{\ominus}$.

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(Extra space) ....

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(1)

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

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(Extra space) ....

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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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(2)
(Total 16 marks)

5 Consider the following process that represents the melting of ice.

$H_2O(s) \longrightarrow H_2O(l)$ $\Delta H^\ominus = +6.03$ kJ mol^{-1}, $\Delta S^\ominus = +22.1$ J K^{-1} mol^{-1}

(a) State the meaning of the symbol $^\ominus$ in $\Delta H^\ominus$.

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(1)

(b) Use your knowledge of bonding to explain why $\Delta H^{\ominus}$ is positive for this process.

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(c) Calculate the temperature at which $\Delta G^{\ominus} = 0$ for this process. Show your working.

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(3)

(d) The freezing of water is an exothermic process. Give **one** reason why the temperature of a sample of water can stay at a constant value of 0 °C when it freezes.

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(1)

(e) Pure ice can look pale blue when illuminated by white light. Suggest an explanation for this observation.

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(2)
(Total 9 marks)

6 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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(2)

(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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(2)

(c) Consider the following data.

	$\Delta H^{\ominus}$/ 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)

7 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.

	$\Delta H^\ominus$/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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(c) Consider the following lattice dissociation enthalpy ($\Delta H_L^\ominus$) data.

	NaBr	AgBr
$\Delta H_L^\ominus$(experimental)/kJ mol^{-1}	+733	+890
$\Delta H_L^\ominus$(theoretical)/kJ mol^{-1}	+732	+758

The values of $\Delta H_L^\ominus$ (experimental) have been determined from Born–Haber cycles.

The values of $\Delta H_L^\ominus$ (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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(2)

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

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(1)

(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)