Examiner only

SECTION A

Answer **all** *the questions in the spaces provided.*

1. *(a)* Magnesium carbonate decomposes on heating.

$$MgCO_3(s) \rightarrow MgO(s) + CO_2(g)$$

(i) Given the enthalpy change of formation, $\Delta H_f^{\ominus}$, values below, calculate the enthalpy change, $\Delta H^{\ominus}$, for the decomposition of magnesium carbonate. [1]

Species	Enthalpy change of formation $\Delta H_f^{\ominus}$ / kJ mol^{-1}
$CO_2(g)$	–393.5
$MgCO_3(s)$	–1095.8
$MgO(s)$	–601.7

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(ii) The entropy change, $\Delta S^{\ominus}$, for the decomposition is 174.8 J mol^{-1}K^{-1}. Explain why there is an increase in entropy for this reaction. [1]

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(iii) Convert the value of $\Delta S^{\ominus}$ into units of kJ mol^{-1}K^{-1}. [1]

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(iv) Using your answers to *(a)*(i) and (iii), determine, in degrees K, the temperature above which magnesium carbonate would decompose spontaneously. [3]

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(b) The solution of ionic compounds such as magnesium carbonate or sodium carbonate in water at 20 °C (room temperature) can be represented by the equations

$$MgCO_3(s) \rightleftharpoons Mg^{2+}(aq) + CO_3^{2-}(aq)$$

$$Na_2CO_3(s) \rightleftharpoons 2Na^+(aq) + CO_3^{2-}(aq)$$

Use the free energy change, ΔG, values in the table to comment on the solubilities of magnesium carbonate and sodium carbonate in water. [2]

Solution	Free Energy Change ΔG / kJ mol^{-1}
$MgCO_3(s) \rightleftharpoons Mg^{2+}(aq) + CO_3^{2-}(aq)$	+28.2
$Na_2CO_3(s) \rightleftharpoons 2Na^+(aq) + CO_3^{2-}(aq)$	–4.3

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(c) As solids do not affect the position of equilibrium, for the solution equilibrium

$$MgCO_3(s) \rightleftharpoons Mg^{2+}(aq) + CO_3^{2-}(aq)$$

the simplest expression for the equilibrium constant, K_c, can be written

$$K_c = [Mg^{2+}(aq)][CO_3^{2-}(aq)]$$

(i) Given that the solubility of $MgCO_3$ at 20 °C is 3.16×10^{-3} mol dm^{-3}, state the molar concentrations of magnesium ions, $Mg^{2+}(aq)$, and carbonate ions, $CO_3^{2-}(aq)$, in a saturated $MgCO_3$ solution. [1]

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(ii) Hence calculate the value of K_c at 20 °C. [1]

....

....

(iii) Giving your reasons, state whether the value of K_c is consistent with the value of the free energy change, ΔG, given for this reaction in *(b)*. [1]

....

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(iv) By applying Le Chatelier's Principle to the chemical equation above, and giving your reasons, state the effect on the solubility of magnesium carbonate of adding sodium carbonate to the solution. [1]

....

....

Total [12]

(b) A different fuel for use in fuel cells is methanol, CH_3OH, which would undergo the following reaction with oxygen.

$$CH_3OH(l) \; + \; 1\tfrac{1}{2}O_2(g) \longrightarrow CO_2(g) \; + \; 2H_2O(l)$$

Compound	Standard enthalpy change of formation, $\Delta H_f^{\ominus}$ / kJ mol^{-1}
CH_3OH	–239
CO_2	–394
H_2O	–286

(i) Calculate the standard enthalpy change of combustion for methanol. [2]

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(ii) The entropy change of this reaction is calculated as follows.

ΔS = (Sum of all entropies for products) – (Sum of all entropies for reactants)

$$\Delta S = 354 - 435$$

$$\Delta S = -81 \text{ J K}^{-1} \text{ mol}^{-1}$$

The reaction was repeated using gaseous methanol, $CH_3OH(g)$, in place of the liquid methanol, $CH_3OH(l)$, used above. What effect, if any, would this have on the value of the entropy change ΔS given above? Explain your answer. [2]

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(iii) Use the values in parts (i) and (ii) of this question to calculate the value of the Gibbs free energy, ΔG, for this reaction at 298K and state what information this gives about the feasibility of the reaction. [2]

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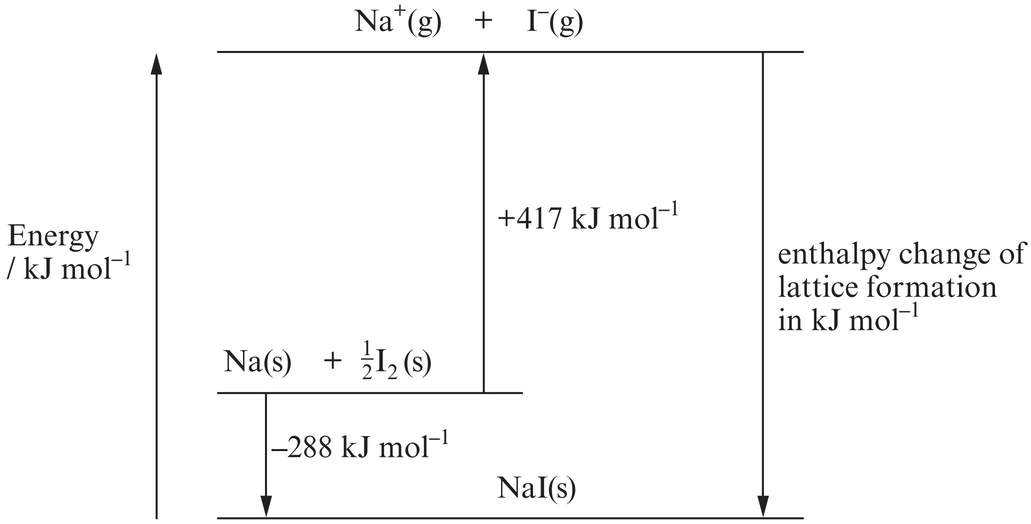
Total [11]

2. *(a)* The diagram shows an outline of the Born-Haber cycle for the formation of sodium iodide (NaI) from its elements.



Use the information given to calculate the enthalpy change of lattice formation (in kJ mol^{-1}) of sodium iodide. [2]

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(b) Sodium iodide is very soluble in water at room temperature.

(i) Complete the sentence below using the relevant enthalpy terms.

For a compound to be very soluble in water the value of the enthalpy of

.... will be greater than the enthalpy of .... [1]

(ii) Aqueous solutions of sodium iodide become yellow in the presence of oxygen due to the slow production of iodine.
One suggested reason for this is that a low concentration of hydrogen ions in the solution produces iodine according to the equation below.

$$4H^+(aq) + 4I^-(aq) + O_2(aq) \rightleftharpoons 2I_2(aq) + 2H_2O(l)$$

Use Le Chatelier's principle to suggest a reagent that you could add, apart from water, to decrease the amount of yellow iodine present. Explain your choice. [2]

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1095 010005

3. *Read the passage below and then answer the questions (a) to (e) in the spaces provided.*

Copper – an essential element

There is an ever-increasing world demand for copper and this has driven its cost upwards. This has led to the extraction of copper from sources once thought to be uneconomic. One such source of copper is the spoil heaps from old mines. The spoil heap material is crushed and then sprayed with acidified water in the presence of the bacterium *Thiobacillus ferrooxidans*. These bacteria convert any iron present to aqueous iron(III) ions, which then oxidise sulfide ions to aqueous sulfate(VI) ions, SO_4^{2-}. A solution containing copper(II) sulfate is produced that is then treated with iron to leave copper.

$$Cu^{2+}(aq) \quad + \quad Fe(s) \longrightarrow Cu(s) \quad + \quad Fe^{2+}(aq)$$

The concentration of copper in this copper(II) sulfate solution can be found by a variety of methods, which include

- precipitating the copper and weighing it
- reacting the solution with an excess of iodide ions and titrating the liberated iodine with aqueous sodium thiosulfate
- titrating the copper(II) ions with ethylenediaminetetra-acetic acid (EDTA)
- using instrumental methods such as atomic absorption and X- ray fluorescence spectroscopy

Copper(II) sulfate continues to be a familiar and commonly used substance in schools and colleges and its reactions are typical of many transition metal compounds. For example, in aqueous solution the copper ions are present as the complex cation, $[Cu(H_2O)_6]^{2+}$. The water molecules in this complex ion can be replaced by other ligands.

$$[CuCl_4]^{2-} \xleftarrow{\text{excess } Cl^-(aq)} [Cu(H_2O)_6]^{2+} \xrightarrow{\text{excess } NH_3(aq)} [Cu(NH_3)_4(H_2O)_2]^{2+}$$

$$[Cu(H_2O)_6]^{2+} \xrightarrow{\text{excess } OH^-(aq)} \text{‘}Cu(OH)_2(H_2O)_4\text{’}$$

copper(II) hydroxide

$$\text{‘}Cu(OH)_2(H_2O)_4\text{’} \xrightarrow{\text{heat}} CuO$$

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(iv) The mass of the copper-containing sample was 11.56 g. All the copper in this sample was present in a solution of volume 1.00 dm^3.
Calculate the percentage of copper in the sample. [1]

....

....

(b) Both copper and zinc are d-block elements. Explain, using electron configurations, why copper is described as a transition metal and zinc (whose compounds contain Zn^{2+} ions) is not. [2]
(QWC) [1]

....

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(c) The passage shows the formulae of some copper-containing species formed by ligand exchange *(line 20)*.
Complete the table below, stating the approximate shape and colour of the complex ions shown. [2]

Complex ion	Shape	Colour
$[CuCl_4]^{2-}$		
$[Cu(NH_3)_4(H_2O)_2]^{2+}$		

(d) Standard enthalpy of formation values, $\Delta H_f^{\ominus}$, can be used to calculate enthalpy changes, such as the reduction of copper(II) oxide by magnesium, described in the article *(line 27)*.
Some $\Delta H_f^{\ominus}$ values are given in the table below.

Metal oxide	$\Delta H_f^{\ominus}$ / kJ mol^{-1}
CuO	–157
PbO	–217

State and explain how the $\Delta H_f^{\ominus}$ values for these two oxides give an indication of their relative stability. [2]

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SECTION B

Answer **both** *questions in the separate answer book provided.*

4. *(a)* In the reaction below carbon monoxide is acting as a reducing agent.

$$5CO \ + \ I_2O_5 \longrightarrow 5CO_2 \ + \ I_2$$

Use oxidation states (numbers) to show that carbon monoxide is acting as a reducing agent in this reaction. [2]

(b) State how the stabilities of the +II and +IV oxidation states vary down Group 4. [1]

(c) You are given two solutions. One contains aqueous aluminium ions, Al^{3+}, and the other contains aqueous lead(II) ions, Pb^{2+}.

(i) Describe a reaction to show that both of these ions exhibit amphoteric behaviour. Your answer should state the reagent(s) used, the names of any precipitates and any relevant observations. *Chemical equations are not required.* [4]
QWC [1]

(ii) Describe what is **seen** when iodide ions are added to an aqueous solution of Pb^{2+} ions. Give the **ionic** equation for the reaction that occurs. [2]

(d) Monomeric aluminium chloride is described as containing an electron-deficient species.

(i) Explain, using monomeric covalent aluminium chloride, what is meant by *electron deficient* and why this leads to the ready formation of the Al_2Cl_6 dimer.
You should show the structure of this dimer as part of your answer. [3]

(ii) The electron-deficient nature of the aluminium chloride monomer results in the compound having an affinity for chlorine-containing species. This is important in catalysis and also in the production of specialised solvents.
Give **one** example of the use of the monomer in either of these ways. [1]

(iii) On heating, gaseous dimeric aluminium chloride molecules dissociate into the monomer.

$$Al_2Cl_6(g) \ \rightleftharpoons \ 2AlCl_3(g)$$

I State **one** reason why the entropy of this gaseous system is increasing. [1]

II Use the equation

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

to calculate the temperature at which the dissociation of gaseous Al_2Cl_6 molecules into gaseous $AlCl_3$ molecules just occurs spontaneously.
The entropy change for this reaction, ΔS, is 88 $J\,mol^{-1}\,K^{-1}$ and the enthalpy change, ΔH, is 60 $kJ\,mol^{-1}$. [2]

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SECTION A

Answer **all** *questions in the spaces provided.*

1. Halogens and their compounds take part in a wide variety of reactions.

(a) Give the chemical name of a chlorine-containing compound of commercial or industrial importance. State the use made of this compound. [1]

....

....

(b) Hydrogen reacts with iodine in a reversible reaction.

$$H_2(g) \quad + \quad I_2(g) \quad \rightleftharpoons \quad 2HI(g)$$

An equilibrium was established at 300 K, in a vessel of volume 1 dm^3, and it was found that 0.311 mol of hydrogen, 0.311 mol of iodine and 0.011 mol of hydrogen iodide were present.

(i) Write the expression for the equilibrium constant in terms of concentration, K_c. [1]

(ii) Calculate the value of K_c at 300 K. [1]

K_c = ...

(iii) What are the units of K_c, if any? [1]

....

(iv) Equilibria of H_2, I_2 and HI were set up at 500 K and 1000 K and it was found that the numerical values of K_c were 6.25×10^{-3} and 18.5×10^{-3} respectively.

Use these data to deduce the sign of ΔH for the forward reaction. Explain your reasoning. [3]

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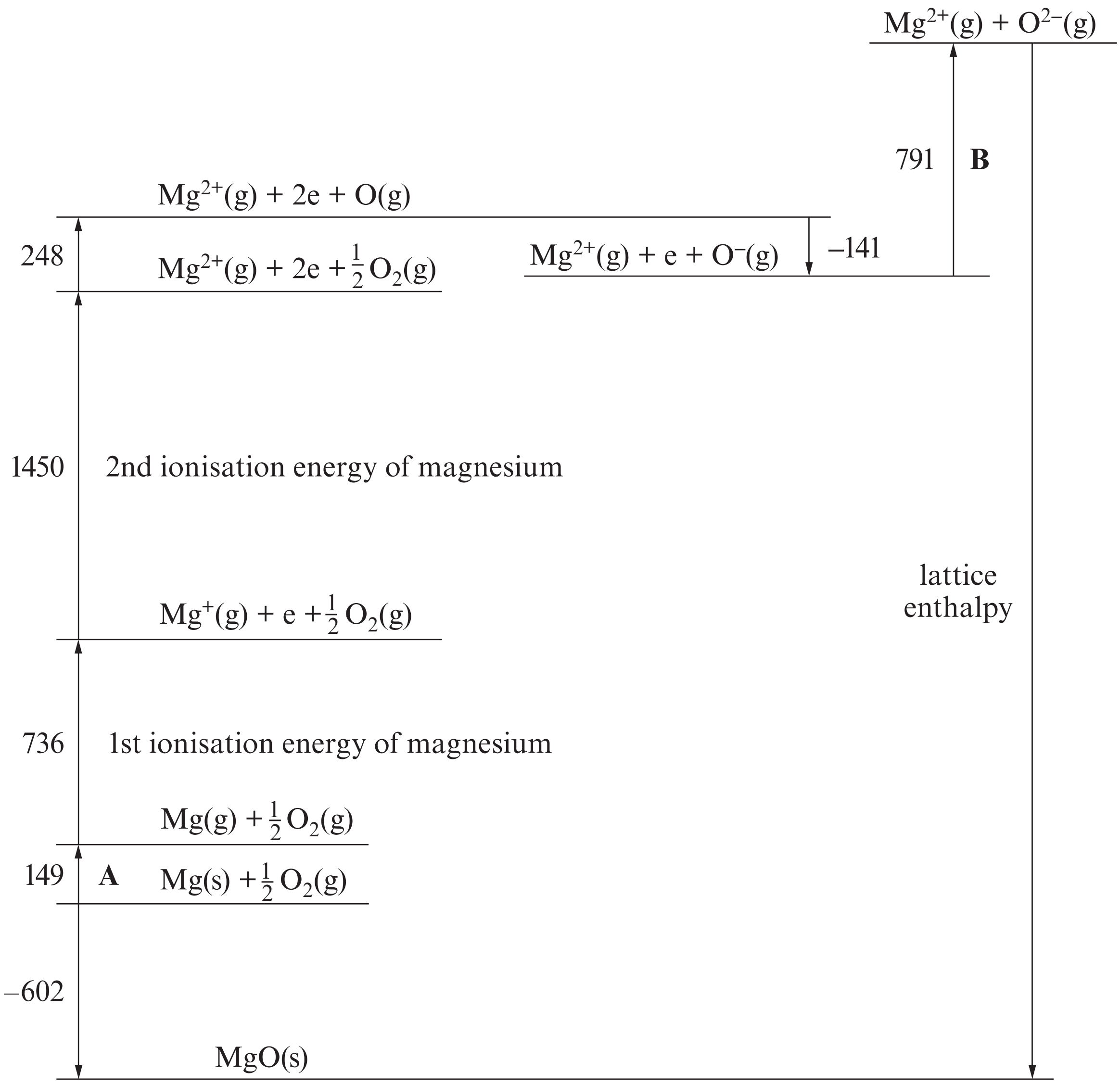
5. Magnesium oxide, MgO, is a white solid with a very high melting temperature and it is used as the refractory lining in furnaces.

(a) The following Born-Haber cycle shows the enthalpy changes involved in the formation of magnesium oxide.

All enthalpy changes are in kJ mol^{-1}. The cycle is not drawn to scale.



(i) What is the name given to the enthalpy change labelled **A**? [1]

(ii) State why the second ionisation energy of magnesium is greater than its first ionisation energy. [1]

(iii) Suggest why the second electron affinity of oxygen, labelled **B**, is positive. [1]

(iv) Calculate the value of the lattice enthalpy for magnesium oxide. [2]

(b) Many metal oxides can be reduced to the metal by carbon monoxide. The equation for the reduction of magnesium oxide is given below.

$$MgO(s) + CO(g) \longrightarrow Mg(s) + CO_2(g)$$

The conditions under which reactions will occur can be predicted using enthalpy and entropy changes. The entropies of the substances involved in this reaction are shown in the table.

Substance	MgO(s)	CO(g)	Mg(s)	CO_2(g)
Entropy / $JK^{-1}mol^{-1}$	26.9	197.7	32.7	213.7

(i) Suggest a reason why the entropies of carbon monoxide and carbon dioxide are much higher than those of magnesium and magnesium oxide. [1]

(ii) Calculate the entropy change in this reaction. [1]

(iii) The enthalpy change, ΔH, for the reduction of magnesium oxide is 318.0 kJ mol^{-1}. Calculate the minimum temperature at which this reduction could occur. [3]

(c) Magnesium oxide, MgO, lead(II) oxide, PbO, and aluminium oxide, Al_2O_3, all react with dilute acids to form aqueous ions – Mg^{2+}(aq), Pb^{2+}(aq) and Al^{3+}(aq).

Suggest tests that would enable you to distinguish between solutions containing one of each of these ions. You should include the expected result for **each** test and are advised to record your tests and expected results in a table. [5]

QWC [2]

(d) Aluminium chloride, $AlCl_3$, can be used to produce compounds including the chloroaluminate(III) ion, $AlCl_4^-$.

(i) Draw a dot and cross diagram to show the electron arrangement in the $AlCl_4^-$ ion. You should show outer electrons only. [1]

(ii) Give **one** industrially important use in which the $AlCl_4^-$ ion is involved. State the role of the ion in this use. [2]

Total [20]

Total Section B [40]

END OF PAPER

(b) Carbon is the first element in Group 4. Two of its allotropes are diamond and graphite. A compound that forms structures corresponding to diamond and graphite is boron nitride.

(i) Describe the structure of graphite and explain why **hexagonal** boron nitride can adopt the same structure yet have different electrical conductivity properties. [4]
QWC [1]

(ii) State **one** use for the **cubic** boron nitride structure. [1]

(c) Another element in Group 4 is tin. At low temperatures tin exists as its grey form. At higher temperatures the white form is stable. The change can be represented by the equation:

$$Sn_{(grey)} \longrightarrow Sn_{(white)} \qquad \Delta H^{\ominus} = 1.92\,kJ\,mol^{-1}$$

The standard entropy values are $44.8\,J\,K^{-1}\,mol^{-1}$ for grey tin and $51.5\,J\,K^{-1}\,mol^{-1}$ for white tin.

(i) Calculate the minimum temperature needed to cause grey tin to change to white tin. [3]

(ii) During Napoleon's disastrous campaign in Russia from June to December in 1812 the tin buttons on his infantry's uniforms disintegrated. Suggest a reason why this might have happened. [1]

(d) An important technological development in recent years has been the hydrogen fuel cell. This uses electrochemical methods to get energy from hydrogen.

(i) Write the half-equations for the processes occurring at the electrodes and an equation for the overall reaction. [3]

(ii) Give **one** disadvantage of using hydrogen fuel cells to power vehicles. [1]

Total [20]

5. *(a)* Chlorine reacts with aqueous sodium hydroxide in one of two ways, depending on the temperature used.

(i) Write the equation for the reaction of chlorine with

I cold aqueous sodium hydroxide, [1]

II hot aqueous sodium hydroxide. [1]

(ii) Classify this type of redox reaction. [1]

(b) Chlorine reacts with many elements to form chlorides. Explain why phosphorus forms two chlorides, PCl_3 and PCl_5, but nitrogen only forms NCl_3. [2]

(c) Most ionic chlorides, e.g. sodium chloride, are soluble in water. However some, e.g. silver chloride, are insoluble.

The enthalpy change of solution of an ionic compound and its solubility depend on the balance between two enthalpy changes. Name these enthalpy changes and state if they are endothermic or exothermic. Explain how the enthalpy change of solution of a compound and its solubility depend on the balance between them. [4]
QWC [1]

(d) Some standard electrode potentials, $E^{\ominus}$, are given below.

System	$E^{\ominus}$/V
$\frac{1}{2}I_2(s) + e^- \rightleftharpoons I^-(aq)$	+0.54
$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$	+0.77
$\frac{1}{2}Br_2(l) + e^- \rightleftharpoons Br^-(aq)$	+1.09
$\frac{1}{2}Cl_2(g) + e^- \rightleftharpoons Cl^-(aq)$	+1.36
$Ce^{4+}(aq) + e^- \rightleftharpoons Ce^{3+}(aq)$	+1.45

(i) Using the information from the table, state which of the **halides** will reduce Fe^{3+} to Fe^{2+}. Give a reason for your answer. [2]

(ii) Write the cell diagram of the cell formed by combining the $Fe^{3+}(aq)$, $Fe^{2+}(aq)$ and $Ce^{4+}(aq)$, $Ce^{3+}(aq)$ half cells and calculate the standard e.m.f. of this cell. [2]

QUESTION 5 CONTINUES ON PAGE 12