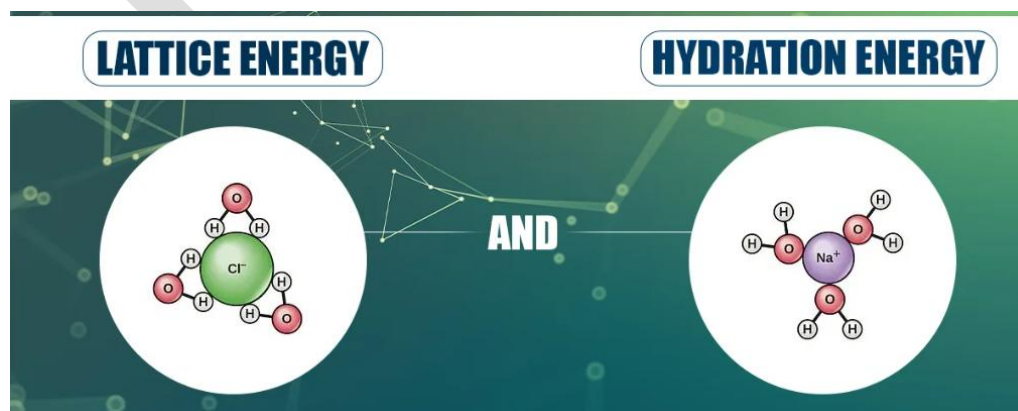


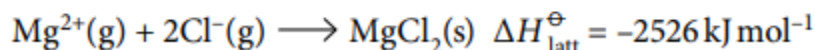
Cambridge
A2 level
Chemistry
CODE: (9701)
Chapter 19
Lattice Energy



Defining lattice energy

The **lattice energy** is released when opposite-charge ions form a crystalline lattice, a highly exothermic reaction. $\Delta H^{\ominus}_{\text{latt}}$. Equations describing sodium chloride's and magnesium chloride's lattice energy are shown here.

Lattice energy is the enthalpy change when 1 mole of an ionic compound is formed from its gaseous ions under standard conditions



Note that:

- it is the gaseous ions that combine to form the ionic solid
- the lattice energy is always exothermic: the value of $\Delta H^{\ominus}_{\text{latt}}$ is always negative because the definition specifies the bonding together of ions, not the separation of ions.

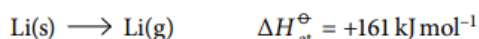
Lattice **energy**, or lattice enthalpy, is the internal energy change when 1 mole of an ionic compound forms from its gaseous ions at OK, closely corresponding to lattice enthalpy values.

Enthalpy change of atomization and electron affinity

Enthalpy changes in atomization

The standard enthalpy changes of atomization, $\Delta H^{\ominus}_{\text{at}}$, is the enthalpy change when 1 mole of gaseous atoms is formed from its element under standard conditions

The standard enthalpy change of atomisation of lithium relates to the equation:



The standard enthalpy change of atomisation of chlorine relates to the equation:



Electron affinity

The energy change occurs when a gaseous non-metal Atom accepts one electron is called **electron affinity**. The symbol for electron affinity is $\Delta H^{\ominus}_{\text{ea}}$.

The first electron affinity, $\Delta H^{\ominus}_{\text{ea1}}$, is the enthalpy change when 1 mole of electrons is added to 1 mole of gaseous atoms to form 1 mole of gaseous 1- ions under standard conditions.

Equations representing the first electron affinity of chlorine and sulfur are:

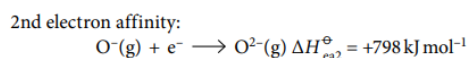
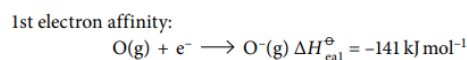


Note that:

- the change is from gaseous atoms to gaseous 1- ions
- the enthalpy change for the first electron affinity, $\Delta H^{\ominus}_{\text{ea1}}$ is generally exothermic: $\Delta H^{\ominus}_{\text{ea}}$ is negative.

The **second electron affinity**, $\Delta H^{\ominus}_{\text{ea2}}$, is the enthalpy change when 1 mole of electrons is added to 1 mole of gaseous 1- ions to form 1 mole of gaseous 2- ions under standard conditions.

The equations representing the 1st and 2nd electron affinities of oxygen are:



Born–Haber cycles

Components of the Born–Haber cycle

A Born–Haber cycle is a particular type of enthalpy cycle to calculate lattice energy. In simple terms, it can be represented by Figure 19.2

We can determine the lattice energy of a compound if we know:

- Its enthalpy changes of formation, ΔH_f^\ominus
- The enthalpy changes involved in changing the elements from their standard states to their gaseous ions, ΔH_1^\ominus

According to Hess's law, Figure 19.2 shows that:

$$\Delta H_1^\ominus + \Delta H_{\text{latt}}^\ominus = \Delta H_f^\ominus$$

Rearranging this equation we get:

$$\Delta H_{\text{latt}}^\ominus = \Delta H_f^\ominus - \Delta H_1^\ominus$$

The enthalpy changes ΔH_1^\ominus involve several steps. Taking lithium fluoride as an example, the relevant enthalpy cycle can be written to show these steps (Figure 19.3).

Calculating lattice energies

Calculating lattice energies Applying Hess's law to find the lattice energy of lithium fluoride:

Note: take care to account for the signs of the enthalpy changes. The values of the enthalpy changes of formation and the electron affinity may be negative or positive.

$$\Delta H_{\text{latt}}^\ominus = \Delta H_f^\ominus - \Delta H_1^\ominus$$

We know that:

$$\Delta H_1^\ominus = \Delta H_{\text{at}}^\ominus [\text{Li}] + \Delta H_{\text{il}}^\ominus [\text{Li}] + \Delta H_{\text{at}}^\ominus [\text{F}] + \Delta H_{\text{ea1}}^\ominus [\text{F}]$$

So

$$\Delta H_{\text{latt}}^\ominus = \Delta H_f^\ominus - \{\Delta H_{\text{at}}^\ominus [\text{Li}] + \Delta H_{\text{il}}^\ominus [\text{Li}] + \Delta H_{\text{at}}^\ominus [\text{F}] + \Delta H_{\text{ea1}}^\ominus [\text{F}]\}$$

Putting in the figures:

$$\Delta H_{\text{latt}}^\ominus = (-617) - \{(+161) + (+520) + (+79) + (-328)\}$$

= +432

$$\Delta H_{\text{latt}}^\ominus = (-617) - (+432) = -1049 \text{ kJ mol}^{-1}$$

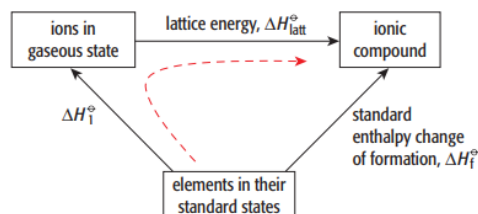


Figure 19.2 A simple enthalpy cycle that can be used to calculate lattice energy. The dashed line shows the two-step route: using Hess's law, $\Delta H_1^\ominus + \Delta H_{\text{latt}}^\ominus = \Delta H_f^\ominus$.

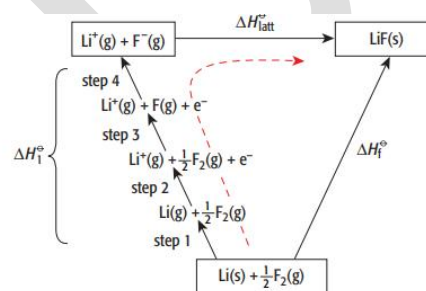


Figure 19.3 An enthalpy cycle that can be used to calculate the lattice energy of lithium fluoride. The dashed line shows the two-step route.

The Born–Haber cycle as an energy level diagram

We can show the Born–Haber cycle as an energy level diagram (Figure 19.4). This is the best, and clearest, type of diagram for a Born–Haber cycle. You should therefore choose to draw this type of diagram to show a Born–Haber cycle.

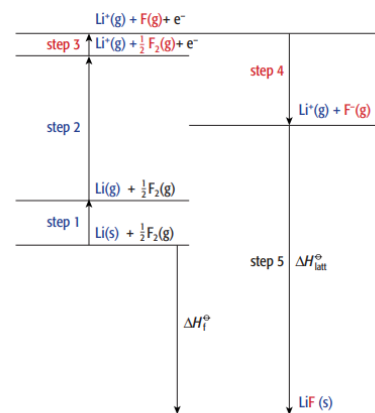


Figure 19.4 Born–Haber cycle for lithium fluoride.

To draw the cycle, you:

- Start by putting down the elements in their standard state on the left-hand side
- Add the other enthalpy changes in the order of steps 1 to 4 shown in Figure 19.4
- Complete the cycle by adding the enthalpy change of formation and lattice energy

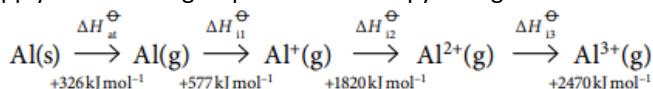
The Born–Haber cycle for magnesium chloride

The Born–Haber cycle for magnesium chloride is shown in Figure 19.5

Constructing a Born–Haber cycle for aluminium oxide

Aluminium oxide, Al_2O_3 , contains two aluminium ions (Al^{3+}) and three oxide ions (O^{2-}).

■ In order to form 1 mole of gaseous Al^{3+} ions from 1 mole of $\text{Al}(\text{s})$, we apply the following sequence of enthalpy changes:



■ To form 1 mole of gaseous O^{2-} ions from oxygen molecules, we apply the following sequence of enthalpy changes:

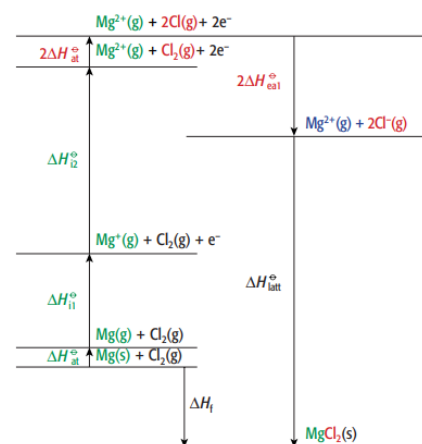
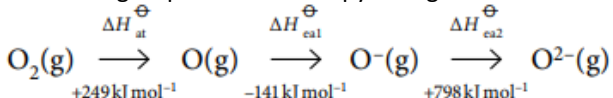


Figure 19.5 Born–Haber cycle for magnesium chloride.

Factors affecting the value of lattice energy

Lattice energy is generated by the electrostatic attraction of oppositely charged ions during crystalline lattice formation, with the size and charge of these ions influencing the value.

Lattice energy and ion size

As the size of the ion increases, the lattice energy becomes less exothermic. This applies to both anions and cations. Figure 19.6 shows that:

■ For any given anion, e.g. F^- , the lattice energy gets less exothermic as the size of the cation increases from Li^+ to Cs^+

■ For any given cation, e.g. Li^+ , the lattice energy gets less exothermic as the size of the anion increases from F^- to I^-

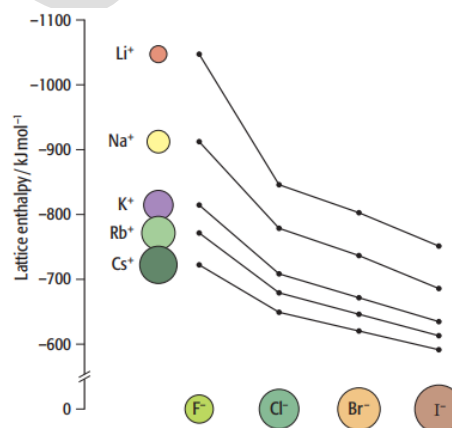


Figure 19.6 Lattice enthalpies of the Group 1 halides.

Lattice energy and charge on the ions

The lattice energy of lithium fluoride (LiF) and magnesium oxide (MgO) increases as the ionic charge increases, demonstrating the similar arrangement of ions in their lattice structure.

The anions F^- and O^{2-} are similar in size (although they are much larger than the cations). The major physical difference between LiF and MgO are ionic charges. This affects the lattice energy:

$$\Delta H_{\text{latt}}^{\ominus} [\text{LiF}] = -1049 \text{ kJ mol}^{-1}$$

$$\Delta H_{\text{latt}}^{\ominus} [\text{MgO}] = -3923 \text{ kJ mol}^{-1}$$

Magnesium oxide has higher lattice energy and stronger ionic bonds due to its doubly charged Mg^{2+} and O^{2-} ions attracting each other more strongly than LiF .

Ion polarization

The ionic lattice model assumes ions are spherical, but this is not always the case. A positive charge on a cation can attract electrons, causing **ion polarization**, which distorts the electron cloud of the anion, and is known as the **polarizing power** of the cation.

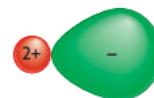


Figure 19.7 Ion polarisation. A small highly charged cation can distort the shape of the anion.

Factors affecting ion polarization

The degree of polarization of an anion depends on:

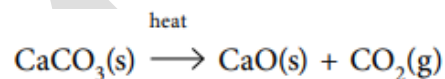
- The charge density of the cation
- The ease with which the anion can be polarized – its polarizability.

An anion is more likely to be polarized if:

- the cation is small
- the cation has a charge of 2^+ or 3^+
- the anion is large
- the anion has a charge of 2^- or 3^-

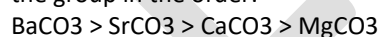
The thermal stability of Group 2 carbonates and nitrates

The Group 2 carbonates decompose their oxides and carbon dioxide on heating. For example: Table 19.1 shows the decomposition temperature and enthalpy change of reaction, ΔH^\ominus_r , for some Group 2 carbonates.



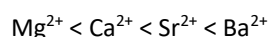
The stability of carbonate relative to oxide and carbon dioxide is determined by the enthalpy changes of reaction and the decomposition temperatures, with higher temperatures required further down the group.

So, the relative stabilities of these carbonates increase down the group in the order:



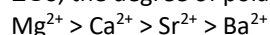
We can explain this trend using ideas about ion polarization:

- The carbonate ion has a relatively large ionic radius, so it is easily polarized by a small highly charged cation
- The Group 2 cations increase in ionic radius down the group



- The smaller the ionic radius of the cation, the better it is at polarizing the carbonate ion (Figure 19.8)

- So, the degree of polarization of the carbonate ion by the Group 2 cation follows the order.



- The greater the polarization of the carbonate ion, the easier it is to weaken a carbon-oxygen bond in the carbonate and form carbon dioxide and the oxide on heating

Group 2 carbonate	Decomposition temperature / °C	Enthalpy change of reaction / kJ mol ⁻¹
magnesium carbonate	540	+117
calcium carbonate	900	+176
strontium carbonate	1280	+238
barium carbonate	1360	+268

Table 19.1 Enthalpy change of reaction values for the decomposition of some Group 2 carbonates.

Enthalpy changes in solution

The ionic solid dissolves in water, breaking the crystal lattice and separating ions, requiring significant energy to overcome attractive forces.

Enthalpy changes of solution

The enthalpy changes of the solution, $\Delta H^\ominus_{\text{sol}}$ is the energy absorbed or released when 1 mole of an ionic solid dissolves in sufficient water to form a very dilute solution

Note that:

- The symbol for the enthalpy changes of the solution is $\Delta H^\ominus_{\text{sol}}$
- The symbol 'aq' represents the very large amount of water used
- Enthalpy changes in solution can be positive (endothermic) or negative (exothermic)
- A compound is likely to be soluble in water only if $\Delta H^\ominus_{\text{sol}}$ is negative or has a small positive value; substances with large positive values of $\Delta H^\ominus_{\text{sol}}$ are relatively insoluble.

Enthalpy changes in hydration

The lattice energy for sodium chloride is -788 kJ mol^{-1} . This means that we need to supply (at least) $+788 \text{ kJ mol}^{-1}$ to overcome the forces of attraction between the ions. But $\Delta H^\ominus_{\text{sol}} [\text{NaCl}]$ is only $+3.9 \text{ kJ mol}^{-1}$. Where does the energy needed to separate the ions come from? The answer is that it comes from the strong attraction between the ions and the water molecules.

Ion-dipole bonds form between water molecules and ions when an ionic solid dissolves in water. Water molecules attract δ^- oxygen and δ^+ hydrogen atoms to the ions.

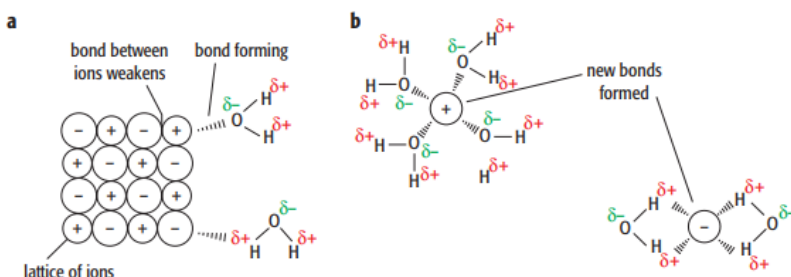
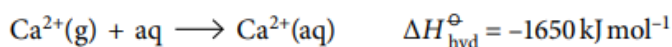


Figure 19.9 a Water molecules forming ion-dipole bonds with an ionic compound. b Hydrated ions in solution.

The enthalpy change of hydration is the energy released when gaseous ions dissolve in water, compensating for the energy required to separate anions and cations in the crystal lattice.

The enthalpy changes of hydration, $\Delta H^\ominus_{\text{hyd}}$, is the enthalpy change when 1 mole of a specified gaseous ion dissolves in sufficient water to form a very dilute solution.

The enthalpy changes of hydration for calcium ions and chloride ions are described by the equations below:



Note that:

- the symbol for enthalpy change of hydration is $\Delta H^\ominus_{\text{hyd}}$
- the enthalpy change of hydration is always exothermic
- the value of $\Delta H^\ominus_{\text{hyd}}$ is more exothermic for ions with the same charge but smaller ionic radii, e.g. $\Delta H^\ominus_{\text{hyd}}$ is more exothermic for Li^{+} than for Na^{+}
- the value of $\Delta H^\ominus_{\text{hyd}}$ is more exothermic for ions with the same radii but a larger charge, e.g. $\Delta H^\ominus_{\text{hyd}}$ is more exothermic for Mg^{2+} than for Li^{+} .

Calculating enthalpy changes in solution

We can calculate the enthalpy change of the Solution or the enthalpy changes of hydration by constructing an enthalpy cycle and using Hess's law (Figure 19.10).

We can see from this enthalpy cycle that:

$$\Delta H_{\text{latt}}^{\ominus} + \Delta H_{\text{sol}}^{\ominus} = \Delta H_{\text{hyd}}^{\ominus}$$

Note that the $\Delta H_{\text{hyd}}^{\ominus}$ values for both anions and cations are added together to get the total value of $\Delta H_{\text{hyd}}^{\ominus}$.

We can use this energy cycle to calculate:

- the value of $\Delta H_{\text{sol}}^{\ominus}$
- the value of $\Delta H_{\text{hyd}}^{\ominus}$

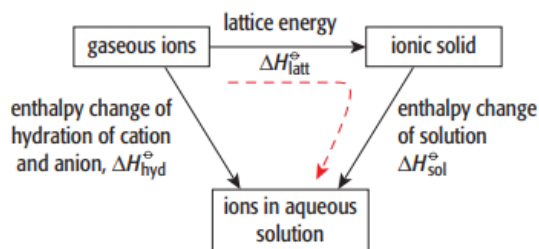


Figure 19.10 An enthalpy cycle involving lattice energy, enthalpy change of hydration and enthalpy change of solution.

The solubility of Group 2 sulfates

Table 19.2 shows the solubility in water of some Group 2 sulfates. The solubility decreases as the radius of the metal ion increases. We can explain this variation in solubility in terms of the relative values of enthalpy change of hydration and the corresponding lattice energy.

Change in hydration enthalpy down the group

- Smaller ions (with the same charge) have Greater enthalpy changes in hydration
- So, the enthalpy changes of hydration decreases (gets less exothermic) in the order $\text{Mg}^{2+} > \text{Ca}^{2+} > \text{Sr}^{2+} > \text{Ba}^{2+}$
- This decrease is relatively large down the group and it depends entirely on the increase in the size of the cation, as the anion is unchanged (it is the sulfate ion in every case).

Compound	Solubility / mol dm ⁻³
magnesium sulfate	1.83
calcium sulfate	4.66×10^{-2}
strontium sulfate	7.11×10^{-4}
barium sulfate	9.43×10^{-6}

Table 19.2 Solubilities in water of some Group 2 sulfates.

Change in lattice energy down the group

- Lattice energy is greater if the ions (with the same charge) forming the lattice are small
- So, the lattice energy decreases in the order $\text{Mg}^{2+} > \text{Ca}^{2+} > \text{Sr}^{2+} > \text{Ba}^{2+}$
- The lattice energy is also inversely proportional to the sum of the radii of the anion and cation
- The sulfate ion is much larger than the group 2 cations
- So, the sulfate ion contributes a relatively greater part to the change in the lattice energy down the group
- So, the decrease in lattice energy is relatively smaller down the group and it is determined more by the size of the large sulfate ion than the size of the cations.

Difference in enthalpy change of solution of Group 2 sulfates

On page 265 we saw that substances that have a very low solubility in water are likely to have $\Delta H_{\text{sol}}^{\ominus}$ with a high positive (endothermic) value. As a rough guide, the higher the positive value of $\Delta H_{\text{sol}}^{\ominus}$ the less soluble the salt.

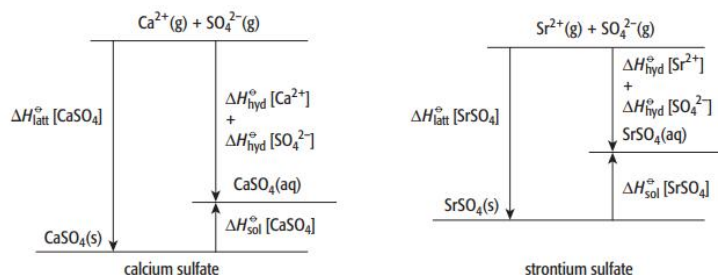


Figure 19.14 Enthalpy cycles comparing the enthalpy change of solution of calcium sulfate and strontium sulfate.

Revision questions

1) Magnesium is used extensively in the form of alloys as a constructional material due to its low density (1.7 g cm³, compared to 7.8 g cm⁻³ for iron). It is usually prepared by the electrolysis of magnesium chloride, MgCl₂, at a temperature a little above its melting point of 715°C.

- Suggest the half-equation that represents the production of magnesium at the cathode during the electrolysis.
- What will be the product at the other electrode?
- Suggest two properties of its atoms that could explain why magnesium is less dense than iron.

One of the reasons the melting point of magnesium chloride is quite high is that it has a high lattice energy.

- Explain the term lattice energy.
 - Write a balanced equation including state symbols to represent the lattice energy of magnesium chloride.
- Suggest, with an explanation in each case, how the lattice energy of magnesium chloride might compare with that of
 - sodium chloride, NaCl,
 - calcium chloride, CaCl₂

c) Use the following data to calculate a value for the lattice energy of sodium chloride.

$\Delta H_f(\text{NaCl})$	=	-411 kJ mol ⁻¹
$\Delta H_{\text{at}}(\text{Na})$	=	107 kJ mol ⁻¹
$\Delta H_{\text{at}}(\text{Cl})$	=	122 kJ mol ⁻¹
first ionisation energy of Na	=	494 kJ mol ⁻¹
electron affinity of Cl	=	-349 kJ mol ⁻¹

3) Limestone is an important raw material, used in building, steel making and agriculture.

The first stage in using limestone is often to heat it in a kiln.

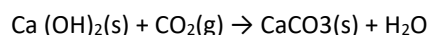


Water is then added to the 'quicklime' produced in the kiln, to make 'slaked lime'.



- Suggest two reasons why reaction 1 needs heating to a high temperature.
 - Explain whether MgCO₃ would require a higher or a lower temperature than CaCO₃ for its decomposition.

Before the widespread use of cement, bricks and stones used for buildings were bonded together with a mixture of slaked lime, sand and water, known as lime mortar. On exposure to the air, the lime mortar gradually set hard due to the following reaction.



- Use the data given above to calculate the enthalpy change for this reaction.
- One of the major ores of magnesium is the mixed carbonate called dolomite, CaMg(CO₃)₂

Calculate the percentage loss in mass that would be observed when a sample of dolomite is heated at a high temperature until the reaction has finished.

4) Use the following data, together with relevant data from the Data Booklet, to construct a Born-Haber cycle and calculate a value for the lattice energy of zinc chloride.

standard enthalpy change of formation of ZnCl_2	-415 kJ mol^{-1}
standard enthalpy change of atomisation of Zn(s)	$+131 \text{ kJ mol}^{-1}$
electron affinity per mole of chlorine atoms	-349 kJ mol^{-1}

5) (a) Describe and explain how the solubilities of the sulfates of the Group II elements vary down the group.

(b) The following table lists some enthalpy changes for magnesium and strontium compounds.

enthalpy change	value for magnesium / kJ mol^{-1}	value for strontium / kJ mol^{-1}
lattice enthalpy of M(OH)_2	-2993	-2467
enthalpy change of hydration of $\text{M}^{2+}(\text{g})$	-1890	-1414
enthalpy change of hydration of $\text{OH}^-(\text{g})$	-550	-550

(i) Use the above data to calculate values of $\Delta H^\circ_{\text{sol}}$ for Mg(OH)_2 and for Sr(OH)_2

(ii) Use your results in (i) to suggest whether Sr(OH)_2 is more soluble in water than Mg(OH)_2 . State any assumptions you make.

(iii) Suggest whether Sr(OH)_2 would be more soluble in hot water than in cold. Explain your reasoning.

(c) Calcium hydroxide, Ca(OH)_2 , is slightly soluble in water.

(i) Write an expression for K_{sp} for calcium hydroxide and state its units.

(ii) 25.0 cm³ of a saturated solution of Ca(OH)_2 required 21.0 cm³ of 0.0500 mol dm⁻³ HCl for complete neutralization.

Calculate the $[\text{OH}^-(\text{aq})]$ and the $[\text{Ca}^{2+}(\text{aq})]$ in the saturated solution, and hence calculate a value for K_{sp}

(iii) How would the solubility of Ca(OH)_2 in 0.1 mol dm⁻³ NaOH compare with that in water? Explain your answer.

6) Taken together, nitrogen and oxygen make up 99% of the air. Oxygen is by far the more reactive of the two gases, and most of the substances that react with air combine with the oxygen rather than with the nitrogen.

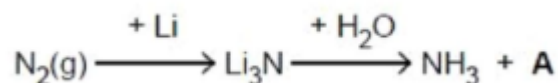
(a) State one reason why the molecule of nitrogen, N_2 , is so unreactive.

Despite the apparent lack of reactivity of N_2 , nitrogen atoms have been found to form bonds with almost all the elements in the Periodic Table. Lithium metal reacts with nitrogen gas at room temperature to give lithium nitride, Li_3N . Magnesium produces magnesium nitride, Mg_3N_2 , as well as magnesium oxide when heated in air.

(b) Calculate the lattice energy of magnesium nitride using the following data, in addition to relevant data from the Data Booklet.

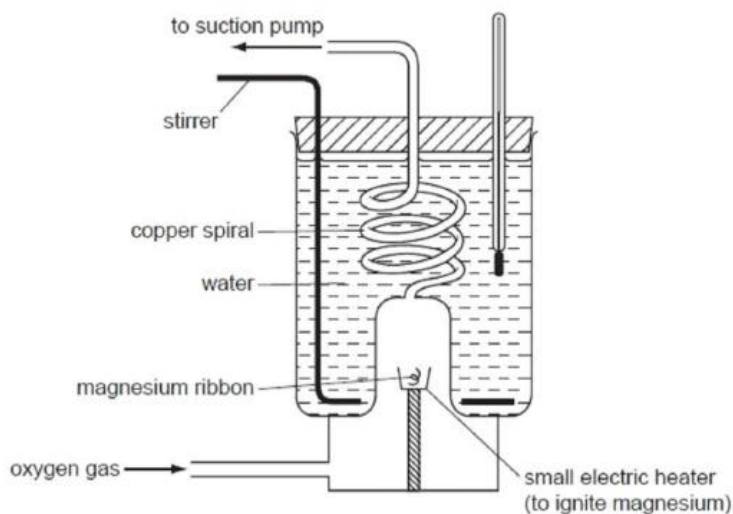
enthalpy change	value/ kJ mol^{-1}
atomisation of Mg(s)	+148
total of electron affinities for the change $\text{N(g)} \rightarrow \text{N}^{3-}(\text{g})$	+2148
enthalpy of formation of $\text{Mg}_3\text{N}_2(\text{s})$	-461

(c) Lithium reacts readily with nitrogen, and because of this LiN has been considered as a possible intermediate in the 'fixing' of nitrogen to make ammonia-based fertilizers.



- (i) Construct an equation for the reaction between LiN and H₂O, and hence identify compound A.
 (ii) Using your knowledge of the Haber process, consider one advantage and one disadvantage of using lithium as a means of fixing nitrogen, rather than the Haber process.

- 7)(a) (i) What is meant by the term lattice energy?
 (ii) Write an equation to represent the lattice energy of MgO.
 (b) The apparatus shown in the diagram can be used to measure the enthalpy change of formation of magnesium oxide, $\Delta H_f^\circ(\text{MgO})$.



List the measurements you would need to make using this apparatus to calculate $\Delta H_f^\circ(\text{MgO})$.

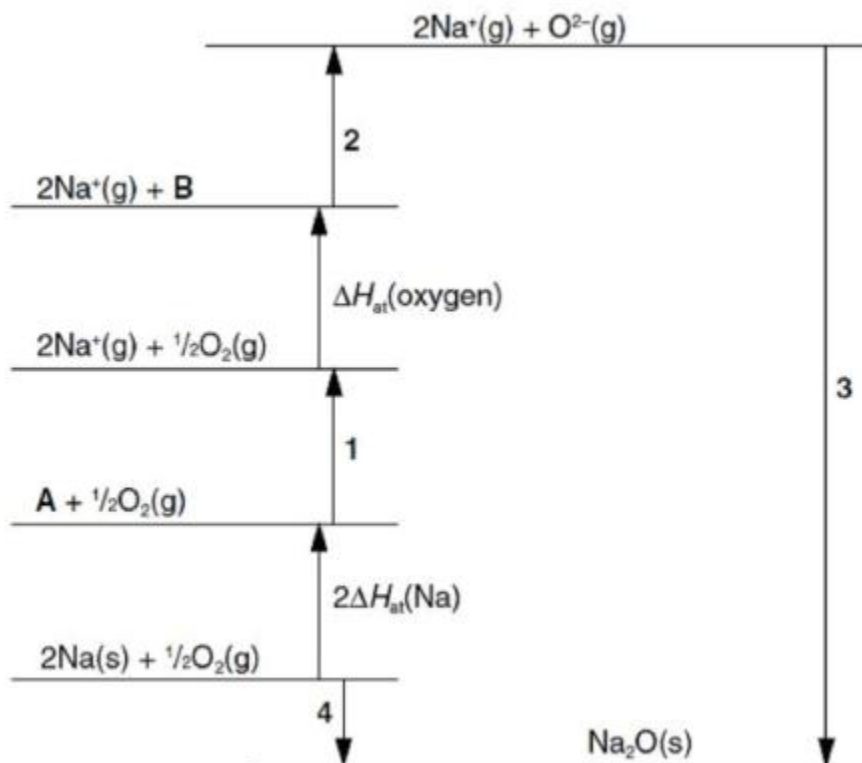
c) Use the following data, together with appropriate data from the Data Booklet, to calculate a value of $\Delta H_f^\circ(\text{MgO})$.

lattice energy of MgO(s)	=	-3791 kJ mol ⁻¹
enthalpy change of atomisation of Mg	=	+148 kJ mol ⁻¹
electron affinity of the oxygen atom	=	-141 kJ mol ⁻¹
electron affinity of the oxygen anion, O ⁻	=	+798 kJ mol ⁻¹

(d) Write equations, including state symbols, for the reactions, if any, of the following two oxides with water. Suggest values for the pH of the resulting solutions.

oxide	equation	pH of resulting solution
Na ₂ O		
MgO		

- 8)(a) Write an equation to represent the lattice energy of sodium oxide, Na₂O.
 (b) The Born-Haber cycle shown may be used to calculate the lattice energy of sodium oxide.



- (i) In the spaces below, identify the species A and B in the cycle, including the appropriate state symbols.
 (ii) Identify the enthalpy changes labelled by the numbers 1 to 4 in the cycle.

Use your cycle, the following data, and further data from the Data Booklet to calculate a value for the lattice energy of sodium oxide.

Data:	enthalpy change of atomisation for Na(s)	+107 kJ mol ⁻¹
	first electron affinity of oxygen	-141 kJ mol ⁻¹
	second electron affinity of oxygen	+798 kJ mol ⁻¹
	enthalpy change of formation of Na ₂ O(s)	-414 kJ mol ⁻¹
	enthalpy change of atomisation for oxygen = half the bond energy for O ₂ .	

- (d) (i) How would you expect the magnitude of the lattice energy of magnesium oxide to compare with that of sodium oxide? Explain your reasoning.
 (ii) State the use of magnesium oxide and explain how the use relates to your answer in part (d) (i).

9) Calcium sulphate is a major by-product of flue gas desulphurization, which is an important method of decreasing the emission of acid-rain gases from power stations. It is used extensively in plaster and cement. Both magnesium sulphate and barium sulphate find uses in medicine.

Describe and explain the variation in the solubilities of the Group II sulphates in water.

Focus