

Content

9.2.1 Similarities and trends in the properties of the Group II metals magnesium to barium and their compounds

Learning Outcomes

Candidates should be able to:

- (a) describe the reactions of the elements with oxygen and water
- (b) describe the behaviour of the oxides with water
- (c) interpret and explain qualitatively the trend in the thermal stability of the nitrates in terms of the charge density of the cation and the polarisability of the large anion
- (d) interpret, and make predictions from, the trends in physical and chemical properties of the elements and their compounds

9.2.1 Similarities and trends in the properties of Group II metals magnesium to barium and their compounds

Define

s-block element

An s-block element is any element in Groups I and II of the Periodic Table.

- Group I elements are commonly known as alkali metals while Group II elements are commonly known as alkali earth metals.
- Group I elements have <u>one</u> valence electron (oxidation state +1) while Group II elements have <u>two</u> valence electrons (oxidation state +2).
- \bigcirc Outershell configuration: ns^2
- Group II metals are <u>reactive</u> with <u>low</u> electronegativity. They form <u>stable</u> ions with an oxidation state of +2 since its two outer s electrons are <u>easily</u> lost.
- *They seldom* form complexes, and form <u>basic</u> oxides and hydroxides.

Example

• Barium and magnesium are examples of Group II elements.

Variations in the physical properties of alkali earth metals

Atomic and ionic radii 🤞

- *I* Down the group, the atomic and ionic radii <u>increase</u>.
- Each element has progressively one <u>more</u> electron shell, thus the outer electrons are <u>further</u> from the nucleus.

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Electronegativity

- *I* Down the group, the <u>electronegativity</u> of the elements <u>decreases</u>.
- The atomic <u>size</u> of the elements <u>increase</u> down the group, thus the nuclear charge effect <u>decreases</u>. Additional electrons are <u>not</u> held as <u>strongly</u> by the nucleus.

Melting and boiling points 🖗

- *I* Down the group, the melting and boiling points <u>decrease</u>.
- As the atomic size of the elements <u>increase</u> down the group, the <u>attraction</u> of the ions for the electron cloud <u>decreases</u>, thus <u>weakening</u> the metallic bonds.

Ionisation energy 🖗

- \mathcal{I} Down the group, the ionization energy of the elements <u>decreases</u>.
- The atomic size of the elements <u>increase</u> down the group, thus the screening effect <u>increases</u>. <u>Less</u> energy is required to remove an electron.

Hardness 🖗

- \mathcal{J} Down the group, the hardness of the metals <u>decreases</u>.
- *The strength* of the metallic bonding <u>decreases</u> down the group.

Variations in the chemical properties of alkali earth metals

- All the alkali earth metals are <u>strong</u> reducing agents with <u>low</u> ionization energy, <u>low</u> electronegativity and negative electrode potentials.
- The reactivity and reducing power of the elements <u>increases</u> down the group as it is <u>easier</u> to remove the outermost electrons.

Reaction with air or oxygen

All the alkali earth metals burn <u>brilliantly</u> to form a mixture of *metal monoxide* and *nitride*.

Assuming X is the metal atom, the general equation is:

 $\begin{array}{l} 2X\left(s\right)+O_{2}\left(g\right)\rightarrow2XO\left(s\right)\\ 3X\left(s\right)+N_{2}\left(g\right)\rightarrow X_{3}N_{2}\left(s\right)\end{array}$

- Going down the group, the <u>rate</u> of reaction and the <u>proportion</u> of nitride formed <u>increases</u>.
- Group II elements can be <u>identified</u> through the *flame test* whereby the mixture of the metal salt and concentrated hydrochloric acid is heated in a non-luminous Bunsen flame on the tip of a nichrome wire. Each element burns with a <u>different</u> coloured flame. For example, Mg²⁺ gives a bright white flame and Ca²⁺ gives a brick-red flame.

Example

• The equation for the reaction of calcium with air is as follows:

 $\begin{aligned} & 2\text{Ca}~(\text{s}) + \text{O}_2~(\text{g}) \rightarrow 2\text{CaO}~(\text{s}) \\ & 3\text{Ca}~(\text{s}) + \text{N}_2~(\text{g}) \rightarrow \text{Ca}_3\text{N}_2~(\text{s}) \end{aligned}$

Reaction with water

All Group II elements (except beryllium) react with water to form metal hydroxides and hydrogen gas.

 $M(s) + 2H_2O(g) \rightarrow M(OH)_2(aq) + H_2(g)$

- Add Magnesium reacts <u>readily</u> with <u>steam</u> to form magnesium oxide. It does <u>not</u> react with cold water. Magnesium oxide will <u>dissolve</u> in water to give an alkaline solution of magnesium hydroxide.
- Calcium, strontium and barium react <u>vigorously</u> with cold water to form hydroxides.
- $\hat{\mathcal{T}}$ The <u>solubility</u> of Group II hydroxides <u>increases</u> down the group.
- Group II metals <u>must</u> be stored under oil to <u>prevent</u> reaction with oxygen and water vapour in the air.
- Exceptions to this are beryllium and magnesium as they form protective oxide layers and prevent the metals from corrosion.

Example

• The equation for the reaction of magnesium with steam is as follows:

 $Mg (s) + H_2O (I) \rightarrow MgO (s) + H_2 (g)$

2 The equation for the reaction of calcium with cold water is as follows:

 $Ca (s) + H_2O (I) \rightarrow Ca(OH)_2 (s) + H_2 (g)$

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Reaction with acids

All Group II elements react with acids to form the corresponding salts and hydrogen gas.

 $\mathsf{M}\left(\mathsf{s}\right)+\mathsf{2H}^{\scriptscriptstyle +}\left(\mathsf{aq}\right)\to\mathsf{M}^{\mathsf{2+}}\left(\mathsf{aq}\right)+\mathsf{H}_{\mathsf{2}}\left(\mathsf{g}\right)$

- Beryllium does <u>not</u> react with acids at <u>room</u> temperature. It reacts <u>slowly</u> at higher temperatures.
- Agnesium, calcium, strontium and barium react vigorously with acids to form the corresponding ion and hydrogen gas.
- *G* Group II metals should <u>not</u> be placed in dilute acids as explosions are likely.
- *reactivity with acids increases down the Group.*

Example

• The equation for the reaction of barium with acid is as follows:

$$Ba (s) + 2H^{+} (aq) \rightarrow Ba^{2+} (aq) + H_{2} (g)$$

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Variations in the chemical properties of oxides of alkali earth metals

- With the <u>exception</u> of beryllium oxide, which is amphoteric, the other oxides are <u>basic</u> oxides. They react with acids to give salts and water.
- Beryllium oxide is <u>amphoteric</u> as its bonding has some degree of <u>covalency</u>, contributing to its acidic nature. It reacts with <u>both</u> acids and bases.
- Going down the group, the solubility of the oxides <u>increases</u> as the lattice energy <u>decreases</u>.
 - Beryllium oxide is virtually <u>insoluble</u>.
 - Magnesium oxide is <u>slightly</u> soluble and forms an insoluble hydroxide.
 - The other oxides all dissolve rapidly to produce <u>alkaline</u> solutions.

XO (s) + H₂O (l) \rightarrow X²⁺ (g) + 2OH⁻ (aq) where X is the metal atom

XO (s) + 2HCl (aq) \rightarrow XCl₂ (aq) + H₂O (l) where X is the metal atom.

Deing amphoteric, beryllium oxide reacts with alkalis to form beryllates.

Examples

• The equation for the reaction of magnesium oxide with water is as follows:

MgO (s) + $H_2O(I) \rightarrow Mg(OH)_2$ (aq)

• The equation for the reaction of calcium oxide with dilute hydrochloric acid is as follows:

CaO (s) + 2HCl (aq) \rightarrow CaCl₂ (aq) + H₂O (I)

• The equation for the reaction of beryllium oxide with sodium hydroxide is as follows:

BeO (s) + 2NaOH (aq) + $H_2O(I) \rightarrow Na_2Be(OH)_4$ (aq)

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Relative thermal stabilities of the alkali earth salts

- \mathcal{I} The thermal <u>stability</u> of the salts <u>increases</u> down the group.
 - This is due to the <u>increasing</u> cation size, which <u>decreases</u> the polarizing power of the cation.
 - The cations of the elements lower in the group <u>distort</u> the anion clouds to a <u>smaller</u> extent than the cations of the elements higher in the group.
 - Since anions which have <u>highly</u> distorted electron clouds are <u>more</u> readily decomposed by heat, the thermal stability <u>increases</u> down the group.
- Group II salts are <u>less</u> stable than the Group I salts as the polarizing effect of the Group II ions is <u>greater</u>, thus distorting the anion cloud to a <u>greater</u> extent.
- Group II nitrates <u>decompose</u> on heating to form the corresponding oxides, nitrogen dioxide gas and oxygen gas.

 $M(NO_3)_2$ (s) \rightarrow MO (s) + 2NO₂ (g) + $\frac{1}{2}O_2$ (g)

Group II carbonates <u>decompose</u> on heating to form the *corresponding* oxides and carbon dioxide gas.

 MCO_3 (s) $\rightarrow MO$ (s) + CO_2 (g)

 Group II hydroxides <u>decompose</u> on heating to form the *corresponding oxides* and *water*.

 $M(OH)_2$ (s) $\rightarrow MO$ (s) + H_2O (g)



The oxides are more stable than the nitrates, carbonates and hydroxides as they form stronger lattices, and the smaller oxide anion is less polarisable.

Comparison with Group I salts

- All Group I nitrates <u>decompose</u> on heating to produce the nitrite salt and oxygen gas. Lithium nitrate decomposes in a similar manner as the Group II nitrates due to the <u>high</u> charge density of the lithium ion.
- Only lithium carbonate decomposes on heating to produce lithium oxide and carbon dioxide. All other carbonates are quite <u>stable</u> to heat.
- $rightarrow \frac{Only}{D}$ lithium hydroxide decomposes on heating (650°C) to produce lithium oxide and water. All other carbonates are quite <u>stable</u> to heat.

Relative solubility of the sulphates

- Beryllium and magnesium sulphates are <u>soluble</u> in water, and calcium sulphate is <u>sparingly</u> soluble. The other Group II sulphates are <u>insoluble</u> in water.
- *The solubility* of the Group II sulphates <u>decreases</u> down the Group.
 - Down the group, the cationic size <u>increases</u>, leading to <u>less</u> exothermic lattice and hydration energies.
 - Enthalpy change of solution = hydration energy + lattice energy
 - The hydration energy decreases <u>more</u> than the lattice energy, causing the enthalpy change of solution to become <u>less</u> exothermic.
- Barium sulphate can be swallowed as it is <u>insoluble</u> and only small traces can be found in the bloodstream.
- \checkmark Barium carbonate is capable of <u>reacting</u> with stomach acid to form a <u>soluble</u> barium salt, and thus is <u>more</u> poisonous than barium sulphate.

Relative solubility of the hydroxides

- *I* <u>Solubility</u> of the Group II hydroxides <u>increases</u> down the group.
 - Down the group, the cationic size <u>increases</u>, leading to <u>less</u> exothermic lattice and hydration energies. The hydroxide ion is much <u>smaller</u> than the sulphate ion.
 - The lattice energy <u>decreases</u> more than the hydration energy, causing the enthalpy change of solution to become more exothermic.
- Due to the presence of the hydroxide ions, solutions of hydroxides are <u>alkaline</u>.

- Barium hydroxide is more soluble in water as compared to magnesium and calcium hydroxide which are sparingly soluble in water.
- All Group I hydroxides are soluble in water producing strongly alkaline solutions.

Uses of some Group II compounds

- Calcium carbonate, calcium hydroxide and calcium oxide fertilizer for correcting acidity (liming)
- Calcium sulphate making plaster; constituent of concrete, cement and in road surfacing; blackboard chalk
- Calcium carbonate building material; used in blast furnace in iron extraction
- An Magnesium oxide refractory lining material
- Anhydrous magnesium sulphate anti-inflammatory agent; drying agent
- And A Magnesium sulphate fertilizer; astringent; laxative
- Darium sulphate swallowed as "barium metal" in X-ray diagnostic work
- Barium carbonate rat poison

Worked Examples

Example 1

State and explain whether magnesium nitrate or barium nitrate is more susceptible to thermal decomposition.

Solution:

The thermal stability of the nitrates increases down the group. This is due to the increasing cation size, which decreases the polarizing power of the cation. The cations of the elements lower in the group distort the anion clouds to a smaller extent than the cations of the elements higher in the group. Since anions which have highly distorted electron clouds are more readily decomposed by heat, the thermal stability increases down the group.

Thus magnesium nitrate is more susceptible to thermal decomposition. (ans)

Group II nitrates decompose on heating to form the corresponding oxides, nitrogen dioxide gas and oxygen gas.

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Calcium is in Group II of the Periodic Table.

- (a) Write a balanced equation to show the action of heat on calcium nitrate.
- (b) Compare the thermal stability of calcium nitrate with barium nitrate.

Solution:

- (a) $2Ca(NO_3)_2$ (s) $\rightarrow 2CaO$ (s) $+ 4NO_2$ (g) $+ O_2$ (g) (ans)
- (b) Calcium nitrate is expected to have a lower thermal stability than barium nitrate. It has a smaller cation than barium, which increases the polarizing action of the cation and the anion is distorted to a greater extent than in barium nitrate. Since anions which have highly distorted electron clouds are more readily decomposed by heat, calcium nitrate is more susceptible to heat. (ans)

Example 3

- (a) Explain why magnesium nitride is formed in addition to magnesium oxide when magnesium is burned in air.
- (b) Magnesium nitride contains about 73% of magnesium by mass. Calculate the empirical formula of magnesium nitride.
- (c) Write a balanced equation to show what happens when water is added to magnesium nitride.

Solution:

- (a) Magnesium is very reactive. Thus nitrogen is also reduced by magnesium to form magnesium nitride at high temperatures, especially when the oxygen has been used up. This only occurs at high temperatures as the triple bond between the nitrogen atoms requires a large amount of energy for the reaction to occur. (ans)
- (b) Assuming there is 100 g of magnesium nitride,

	Mg	N
Mass/g	73	27
Molar mass/ g mol ⁻¹	24.3	14
Amount/mol	3.00	1.93
Simplest ratio	3	2

Thus the empirical formula is Mg₃N₂. (ans)

(c) $Mg_3N_2(s) + 6H_2O(l) \rightarrow 2Mg(OH)_2(s) + 2NH_3(g)$ (ans)

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Worked Problems

Example 1

Calcium is the fifth most common element in the Earth's crust. Calcium compounds occur in bones and teeth and also in many minerals.

Some reactions of calcium and its compounds are shown in the reaction scheme below.



- (a) State the formula of each of the calcium compounds U to Y. [5]
- (b) Compound Y may be converted into compound V.

Outline how this reaction would be carried out in a school or college laboratory using a small sample of Y.

(c) (i) Construct balanced equations for the following reactions.

calcium to compound U compound V to compound W compound U to compound Y

- (ii) Construct a balanced equation for the effect of heat on solid compound W.
- (d) Suggest the formula of an aqueous reagent, other than an acid, for reaction1. [1]
- (e) What would be observed when each of the following reactions is carried out in a test tube?

the formation of X from Ca(s) the formation of X from V

> [2] [Total: 13]

[1]

[4]

Solution:

- (a) U $CaCl_2$
 - V CaO
 - W $Ca(NO_3)_2$
 - X Ca(OH)₂
 - Y CaCO₃



- (b) heat strongly in a test-tube or a boiling tube do not allow 'heat gently' or 'reflux'.
- (c) (i) Ca to U Ca + 2HC $l \rightarrow$ CaC l_2 + H₂ V to W CaO + 2HNO₃ \rightarrow Ca(NO₃)₂ + H₂O U to Y CaC l_2 + Na₂CO₃ \rightarrow CaCO₃ + 2NaCl
 - (ii) $2Ca(NO_3)_2 \rightarrow 2CaO + 4NO_2 + O_2$
- (d) Na₂SO₄(aq)
- (e) (i) Ca to X colourless gas formed
 - (ii) vigorous reaction

© Mark Scheme							
	(a)	U V W X Y	$CaCI_2$ CaO Ca(NO ₃) ₂ Ca(OH) ₂ CaCO ₃	(1) (1) (1) (1) (1)	[5]		
	(b)	hea do	it strongly in a test-tube or a boiling tube not allow 'heat gently' or 'reflux'	(1)	[1]		
	(c)	(i)	Ca to U Ca + 2HC $l \rightarrow CaCl_2 + H_2$ V to W	(1)			
			$CaO + 2HNO_3 \rightarrow Ca(NO_3)_2 + H_2O$ U to Y	(1)			
			$CaCl_2 + Na_2CO_3 \rightarrow CaCO_3 + 2NaCl$	(1)			
		(ii)	$2Ca(NO_3)_2 \rightarrow 2CaO + 4NO_2 + O_2$	(1)	[4]		
	(d)	Na ₂	$SO_4(aq)/K_2SO_4(aq)$ or formula of any soluble sulfate	(1)	[1]		
	(e)	 (i) Ca to X colourless gas formed/fizzing/effervescence/bubbles or Ca dissolves or 					
		(ii)	white precipitate/suspension formed strongly exothermic/vigorous reaction or steam formed/steamy fumes or	(1)			
			surface crumbles	(1)	[2]		
			do not allow white ppt.	(-	[2]		
	[Total:]				al: 13]		

Exam Report

This question tested candidates' knowledge of the reactions of calcium and its compounds. There were many good answers but a significant number of candidates did not check their work carefully and gave answers with incorrect formulae and/or unbalanced equations.

- (a) This was well answered with many candidates being awarded full credit for this part. However, other candidates gave answers in which the oxidation number of calcium varied from compound to compound and were penalised.
- (b) Candidates were expected to state that Y needed heating which some candidates confused with burning or combustion.
- (c) (i) These reactions were usually well known with only occasional slips in balancing the equations.
 - (ii) The products of the thermal decomposition of calcium nitrate were less well known, oxygen often being omitted, or calcium a product.
- (d) The formula of a soluble sulphate was needed. Barium sulphate was a common wrong answer while many answers contained an anion other than sulphate.
- (e) Most candidates knew that in forming X, calcium dissolves with effervescence, leaving a white precipitate.

However, answers suggested that candidates had little experience of the second reaction – the formation of X from V – as an observation from the previous answer was often simply repeated.

The vigorous and exothermic nature of the reaction was rarely stated.