

PIONEER JUNIOR COLLEGE
H2 CHEMISTRY (9647)
Group II

References:

- Hill and Holman – Chemistry In Context
- Peter Cann and Peter Hughes – Chemistry For Advanced Level

Syllabus Content:

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

Learning Outcomes:

Candidates should be able to:

- describe the reactions of the elements with oxygen and water
- describe the behaviour of the oxides with water
- 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
- interpret, and make predictions from, the trends in physical and chemical properties of the elements and their compounds

1. Introduction

Group II metals are also known as **alkaline earth metals** as many of their compounds exist as minerals in rocks e.g. limestone rock (mainly CaCO_3) and dolomite (mixed carbonate of CaCO_3 and MgCO_3) and they generally react with water to form alkalis.

Elements of Group II have a valence electronic configuration **ns^2** :

Element	Proton No.	Electronic Configuration	Shortened form
Be	4	$1s^2 2s^2$	$[\text{He}] 2s^2$
Mg	12	$1s^2 2s^2 2p^6 3s^2$	$[\text{Ne}] 3s^2$
Ca	20	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$	$[\text{Ar}] 4s^2$
Sr	38	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s^2$	$[\text{Kr}] 5s^2$
Ba	56	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 6s^2$	$[\text{Xe}] 6s^2$
Ra	88	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} 6s^2 6p^6 7s^2$	$[\text{Rn}] 7s^2$

Group II metals shows only **one oxidation state of +2** in their compounds, which are mostly ionic (except for beryllium which shows a tendency to form covalent compounds e.g. BeCl_2 .)

2. Physical Properties of Group II Metals

	Atomic radius/nm	1 st I.E. / kJ mol ⁻¹	2 nd I.E. / kJ mol ⁻¹	3 rd I.E. / kJ mol ⁻¹	Melting point/°C	Boiling point/°C	$\Delta H^{\circ}_{\text{at}}$ / kJ mol ⁻¹	Density / g cm ⁻³
Mg	0.160	736	1450	7740	650	1110	148	1.74
Ca	0.197	590	1150	4940	838	1440	178	1.55
Sr	0.215	548	1060	4120	768	1380	164	2.54
Ba	0.217	502	966	3390	714	1640	180	3.59

2.1 Atomic (Metallic) Radius

- Down a group, the number of filled quantum shells increases.
- Due to the additional filled shell of electrons, valence electron is further away from nucleus, resulting in a decreased attraction between the nucleus and outermost electron.
- Thus, atomic radius increases down the group.

2.2 First Ionisation Energy

1st IE decreases down the group because:

- Down a group, the number of filled quantum shells increases.
- Due to the additional filled shell of electrons, valence electron is further away from nucleus, resulting in a decreased attraction between the nucleus and outermost electron.
- Less energy is required to remove the outermost electron.
- Thus, I.E. decreases down the the group.

Worked example 1

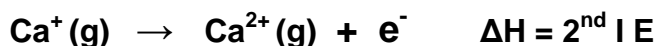
Explain why :

- (a) the Ca²⁺ ionic radius is smaller than the metallic radius of calcium.



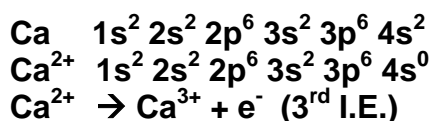
The loss of the 4s subshell makes the calcium ion smaller than the calcium atom.

- (b) the second ionisation energy of calcium is greater than its first ionization energy.



The second electron is harder to remove than the first because it is being removed from an ion that is already positively charged, rather than from a neutral atom

- (c) the third ionisation energy of calcium is **much** greater than its second ionisation energy.



The 3rd IE of calcium involves the removal of an electron from an inner principal quantum shell (3p subshell), which is closer to nucleus/ lower in energy than the 4s subshell.

The energy required to remove an electron from inner quantum shell is therefore greater than that required to remove an electron from the 4s subshell.

2.3 Melting Point / Boiling Point

- No regular trend down the group, due to different crystal structures of the elements.
- Higher melting point / boiling point than corresponding Group I metals as they form stronger metallic bonds due to the smaller cationic radii and the use of (more electrons) two electrons per atom for metallic bonding.
- A larger amount of energy is required to break the stronger metallic bonds within the giant metallic lattice.

2.4 $\Delta H_{\text{at}}^{\theta}$

- No regular trend down the Group due to different crystal structures of the elements.
- $\text{M(s)} \longrightarrow \text{M(g)} \quad \Delta H_{\text{at}}^{\theta}$
 $\text{M(g)} \longrightarrow \text{M(s)} \quad \text{Lattice energy of a metal}$
 Thus, $\Delta H_{\text{at}}^{\theta} = - \text{Lattice energy of a metal}$ (\propto metallic bond strength).
 Higher $\Delta H_{\text{at}}^{\theta}$ than corresponding Group I metals due to stronger metallic bonds.

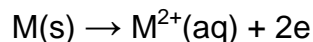
[Note also that $\text{M(s)} \longrightarrow \text{M(l)} \longrightarrow \text{M(g)}$ implies $\Delta H_{\text{at}}^{\theta} = \Delta H_{\text{fusion}}^{\theta} + \Delta H_{\text{vapourisation}}^{\theta}$]

2.5 Density

- No regular trend down the Group due to different crystal structures of the elements.
- Denser than corresponding Group I metals due to stronger metallic bonds and more closely packed structures. Their atoms have relatively smaller atomic radii compared to Group I elements.

3. Chemical Properties of Group II Metals

Group II metals tend to lose electrons (**become** oxidised) to form M^{2+} ions and are thus reducing agents.



All Group II metals have large **negative** standard electrode potential (E^0) values (**E^0 studied next year in JC2**), indicating that they are good reducing agents.

	Standard electrode potential, E^0 / V	<div style="display: flex; align-items: center;"> <div style="width: 10px; height: 100px; border-left: 1px solid black; margin-right: 5px;"></div> <div style="writing-mode: vertical-rl; transform: rotate(180deg);">Increasing power of reducing agent</div> </div>
$Mg^{2+}(aq) + 2e \rightarrow Mg(s)$	-2.38	
$Ca^{2+}(aq) + 2e \rightarrow Ca(s)$	-2.87	
$Sr^{2+}(aq) + 2e \rightarrow Sr(s)$	-2.89	
$Ba^{2+}(aq) + 2e \rightarrow Ba(s)$	-2.90	

The more negative the E^0 value, the stronger the metal is acting as a reducing agent.

Explain why the reducing power of Group II metals increases down the group. (i.e., Explain why the metals become more reactive down the group.)

This trend follows the trend in ionisation energies (1^{st} and 2^{nd}).

- Down the group, the valence electrons are more easily removed due to the weaker attraction to the nucleus, (I.E. decreases down the group).
- Thus, the metal M is more easily oxidised to form M^{2+} ions, thus the strength of the **reducing ability of metal M increases down the group.**
- The metals thus become more reactive on descending the group.

The reactions of Group II metals with oxygen and water are examples of redox reactions in which the metal is the reducing agent.

3.1 Reactions of Group II Metals with Oxygen

- Group II metals exist as hard, grey metals which tarnish readily when exposed to atmospheric oxygen.
- They burn when heated directly to form **oxides (white ionic solids)**. The redox reaction is **highly exothermic** and **intense white flame** is seen.
- **Reactivity increases down the group.**

General equation: $2M(s) + O_2(g) \rightarrow 2MO(s)$	
Mg	Ignites above melting point. White dazzling flame seen.
Ca	Ignites on heating.
Sr	White dazzling flame (with tinge of red at the end).
Ba	Ignites spontaneously. White dazzling flame (with tinge of green at the end).

- The more reactive Group II metals may form peroxides when reacted with oxygen.
e.g. $\text{Ba(s)} + \text{O}_2\text{(g)} \rightarrow \text{BaO}_2\text{(s)}$
- Due to their reactivity, the more reactive Group II metals such as Ca and Ba must be stored under oil to prevent exposure to oxygen and water vapour.

3.2 Reactions of Group II Metals with Water

Group II metals are generally reactive towards water and reduce water to hydrogen gas. The reactivity towards water increases down the group.

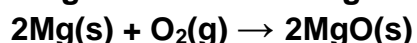
General Equation: $\text{M(s)} + 2\text{H}_2\text{O(l)} \rightarrow \text{M(OH)}_2\text{(s, aq)} + \text{H}_2\text{(g)}$ Trend in solubility : $\text{Mg(OH)}_2 < \text{Ca(OH)}_2 < \text{Sr(OH)}_2 < \text{Ba(OH)}_2$	
Mg	Very slow (no reaction) with cold water but reacts slowly with hot water. $\text{Mg(s)} + 2\text{H}_2\text{O(l)} \rightarrow \text{Mg(OH)}_2\text{(s)} + \text{H}_2\text{(g)}$ <p style="text-align: center;">white suspension</p> $\text{Mg(OH)}_2\text{(s)} + \text{aq} \rightleftharpoons \text{Mg}^{2+}\text{(aq)} + \text{OH}^-\text{(aq)}$ <p>Mg(OH)_2 is slightly soluble to form a weakly <u>alkaline</u> solution</p> <p>With steam, an oxide is formed.</p> $\text{Mg(s)} + 2\text{H}_2\text{O(g)} \rightarrow \text{MgO(s)} + \text{H}_2\text{(g)}$
Ca	Reacts with cold water, with increasing vigour. $\text{Ca(s)} + 2\text{H}_2\text{O(l)} \rightarrow \text{Ca(OH)}_2\text{(s)} + \text{H}_2\text{(g)}$ <p style="text-align: center;">white suspension</p>
Sr	
Ba	
	$\text{Ba(s)} + 2\text{H}_2\text{O(l)} \rightarrow \text{Ba(OH)}_2\text{(aq)} + \text{H}_2\text{(g)}$

Worked example 2

Describe what you would see when:

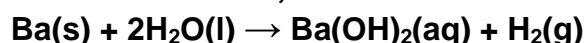
- (a) magnesium burns in oxygen

Burns with a bright white flame to give a white solid.



- (b) magnesium and barium reacts separately with water containing universal indicator. Write equations, where appropriate.

Magnesium reacts very slowly (almost no reaction) with water. Barium reacts with water vigorously to give an alkaline solution (pH13 or 14) and turns the green solution violet, with effervescence of a colourless gas, H_2 .



3.3 Reactions of Group II Oxides with Water

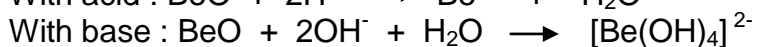
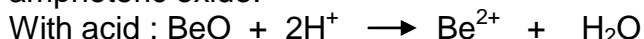
Oxides of Group II metals react with water to form an aqueous solution of hydroxides.

Oxide	Nature of oxide	General Equation: $\text{MO(s)} + \text{H}_2\text{O(l)} \rightarrow \text{M(OH)}_2\text{(s, aq)}$ Trend in solubility : $\text{MgO} < \text{CaO} < \text{SrO} < \text{BaO}$	pH of aq. solution
BeO*	Amphoteric	No reaction. BeO insoluble in water	-
MgO*	Ionic and basic	Slow reaction. Reacts only very slightly to form a weakly alkaline solution $\text{MgO(s)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{Mg(OH)}_2\text{(s)}$ $\text{Mg(OH)}_2\text{(s)} + \text{aq} \rightleftharpoons \text{Mg}^{2+}\text{(aq)} + \text{OH}^-\text{(aq)}$	≈ 9
CaO		Reacts exothermically to form an alkaline solution: $\text{CaO(s)} + \text{H}_2\text{O(l)} \rightarrow \text{Ca(OH)}_2\text{(aq)}$ White solid swells and crumbles to a white powder and steamy fumes seen (heat given off). Hissing sound as water turns into steam. With excess water, the powder dissolves to form a colourless solution.	≈ 10 - 13

* 2 factors to explain the low solubility of BeO / MgO :

- The high charge density of the Be^{2+} / Mg^{2+} ion makes the bonding in BeO / MgO slightly covalent.
- The large magnitude of the lattice energy of BeO / MgO.

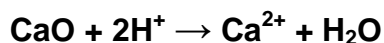
The greater degree of covalency in BeO (compared to MgO) also makes it an amphoteric oxide.



Worked example 3

Volcanic soil, although rich in nutrients, is generally too acidic for growing plants. Farmers often use calcium oxide to reduce the acidity of the soil.

(a) Write an equation to show how calcium oxide removes the acidity.



(b) Suggest a reason why magnesium oxide is not used.

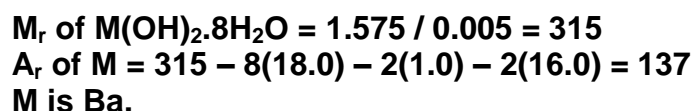
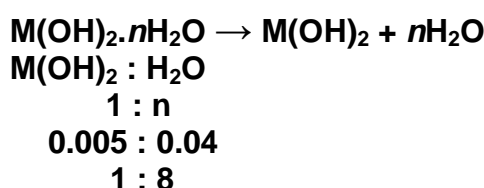
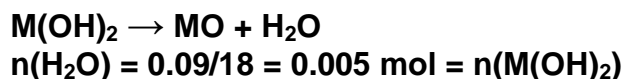
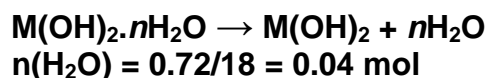
Low solubility of MgO in water.

Worked example 4

Group II hydroxides and nitrates decompose to give the same solid residues but different gaseous products.

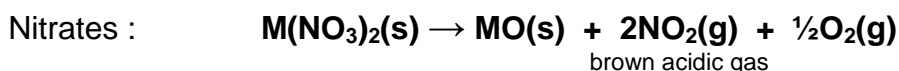
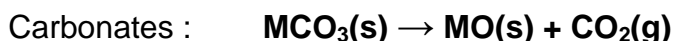
A Group II hydroxide exists as a hydrate, $M(OH)_2 \cdot nH_2O$. When a 1.575 g sample of this hydrate was heated, the mass of the sample decreased by 0.720 g. Subsequent heating to constant mass produced a further mass loss of 0.090 g.

Calculate the value of n , and deduce the identity of the metal M .



3.4 Thermal Decomposition of Group II Carbonates and Nitrates

Group II carbonates and nitrates tend to decompose on heating.



Thermal stability of the carbonates and nitrates increases down the group.

Carbonates	Decomposition Temperature / °C	Nitrates	Decomposition Temperature / °C
MgCO ₃	540	Mg(NO ₃) ₂	129
CaCO ₃	900	Ca(NO ₃) ₂	560
SrCO ₃	1290	Sr(NO ₃) ₂	570
BaCO ₃	1350	Ba(NO ₃) ₂	592

Increasing thermal stability

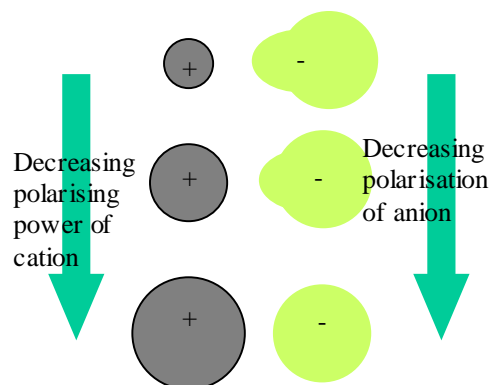
On descending the group of carbonates and nitrates, note that:

- the temperature for decomposition increases.
- it is more difficult to decompose (ease of thermal decomposition decreases).
- thermal stability increases**

The thermal stability of Group II carbonates and nitrates depends on the polarizing power of the cation.

On descending the group,

- Size of cation increases.
- Charge density of cation decreases.
- Polarising power of cation decreases
- Anion becomes less polarised and C-O bonds (in CO_3^{2-}) or N-O bonds (in NO_3^-) is weakened to lesser extent.
- Thermal stability increases.

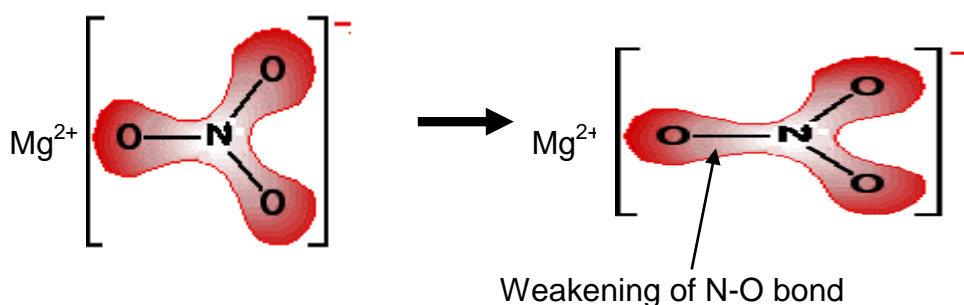


$$\text{Polarising power of cation} \propto \text{Charge density} \\ = \frac{\text{ionic charge}}{\text{ionic radius}}$$

Terminologies

- **Polarising power of cation refers to its ability to distort electron cloud of anion.**
- **The lesser the polarising power of the cation, the lesser the distortion of the electron cloud of the anion, hence the anion becomes less polarised.**

- Mg^{2+} is a **small cation** and thus has a **high charge density**.
- Thus, Mg^{2+} with high charge density has high polarizing power and is able to **polarise the large NO_3^- anion electron cloud** to a large extent that the **N-O bond in NO_3^- weakens and breaks**, forming the decomposition products (MgO , O_2 and NO_2).



Worked example 5

Dolomite is a double carbonate of calcium and magnesium, and has the formula $\text{CaMg}(\text{CO}_3)_2$. Both carbonates will decompose on heating. State and explain which of the carbonates will decompose first on heating.

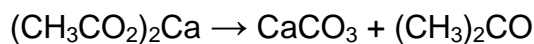
MgCO_3 decomposes first. Compared to Ca^{2+} , Mg^{2+} has

- **smaller cationic radii**
- **higher charge density and polarising power**
- **greater ease of polarising, weakening and breaking the C-O bond**

MgCO_3 has lower thermal stability and decomposition temperature.

Worked example 6

In 1834, the French chemist Eugene Peligot investigated the action of heat on Group II salts of ethanoic acid such as calcium ethanoate and barium ethanoate.



Compare the decomposition temperature required for calcium ethanoate and barium ethanoate to decompose. Explain your answer.

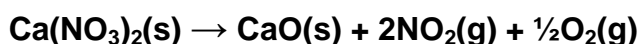
$(\text{CH}_3\text{CO}_2)_2\text{Ba}$ decomposes at a higher temperature. Compared to Ca^{2+} , Ba^{2+} has:

- larger cationic radii
- lower charge density and polarising power
- lower ease of polarising, weakening and breaking the covalent bonds in the anion

$(\text{CH}_3\text{CO}_2)_2\text{Ba}$ has higher thermal stability and decomposition temperature.

Worked example 7

What would you expect to observe when calcium nitrate is heated?

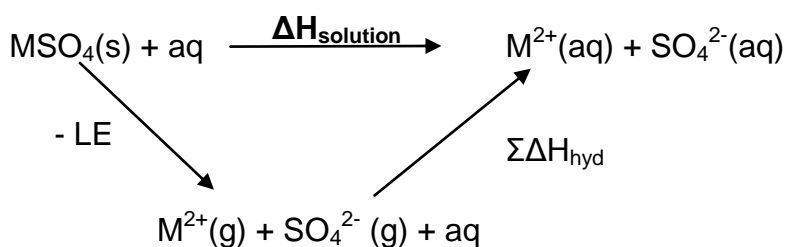


On heating, the white solid first appears to 'melt' as it dissolves in its water of crystallisation. A white solid remains. Brown gas seen. A colourless gas that reignites a glowing splint is also produced.

3.5 Solubility of Group II Sulfates

The solubility of Group II sulfates decreases down the group.

	Solubility in water
MgSO₄	Soluble
CaSO₄	Sparingly soluble
SrSO₄	Insoluble
BaSO₄	Insoluble



By Hess' Law, $\Delta H_{\text{solution}} = -\text{LE} + \Sigma \Delta H_{\text{hyd}} = -\text{LE} + \Delta H_{\text{hyd}}(\text{M}^{2+}) + \Delta H_{\text{hyd}}(\text{SO}_4^{2-})$

Going down the group:

- Size of cation increases, and both the magnitude of lattice energy $|L.E|$ and the sum of hydration energies expected to become smaller (less exothermic).

$$\text{(Recall: } |LE| \propto \frac{q_+q_-}{r^+ + r^-} \text{ and } |\Delta H_{\text{hyd}}| \propto \frac{q}{r} \text{)}$$

- $|\Sigma \Delta H_{\text{hyd}}|$ **decreases much more than $|LE|$** since $|LE|$ remains almost **constant** due to the large size of the sulfate ion ($|LE| \propto |q_+q_-|/r$ since $r_- \gg r_+$). Thus, $\Delta H_{\text{solution}}$ becomes less exothermic.
- The less exothermic the $\Delta H_{\text{solution}}$, the less soluble the sulfate. Thus, solubility of sulfates decreases down the group.

4. Prediction of Physical and Chemical Properties of Group II Metals

Trends which are observed for Group II metals can be used to predict the physical and chemical properties of other Group II metals and its compounds.

E.g. Several predictions can be made for radium. Compared to Ba, it would

- have larger atomic radius.
- have smaller 1st ionisation energy.
- ignite more spontaneously with O₂.
- be a more thermally stable nitrate.

5. Uses of Group II Compounds

Compound	Properties	Uses
MgO	Giant ionic structure, strong ionic bonds. High melting point.	Refractory lining material in furnace
Mg(OH) ₂	Weakly alkaline	Used in antacids and toothpaste
MgSO ₄ (anhydrous)	Highly exothermic ΔH_{hyd} as Mg ²⁺ has a high charge density.	Drying agent in organic synthesis and anti-inflammatory agent (also able to draw out water from boils)
CaO (quicklime) Ca(OH) ₂ (slaked lime) CaCO ₃ (limestone)	Basic	Reduce acidity in soils
CaSO ₄	Setting property (hardens) after hydration as it loses water of crystallisation	CaSO ₄ ·½H ₂ O used to make plaster for setting broken bones, casts for toys, statues, etc
BaSO ₄	Insoluble and will not be harmful when ingested by users	Used as 'barium meal' in X-ray diagnostic work to detect stomach ulcers

