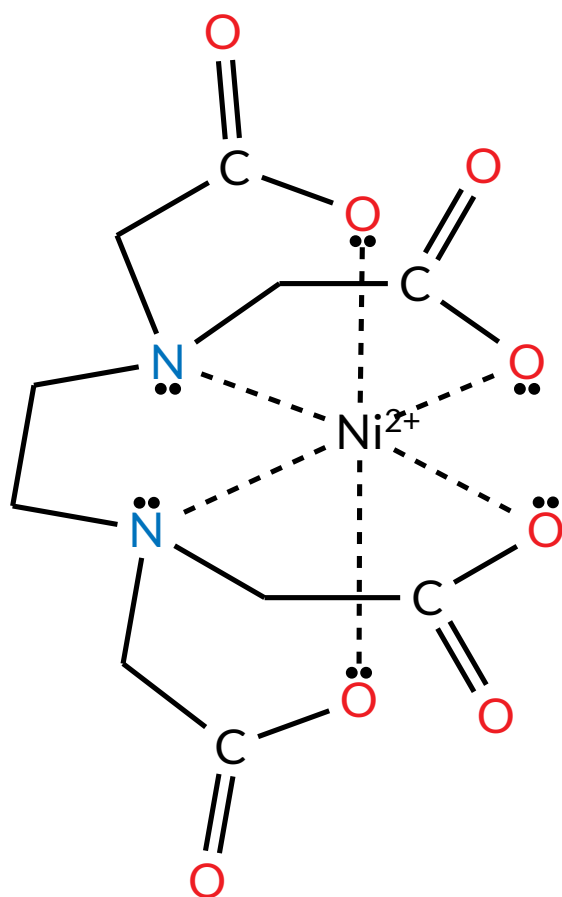


Inorganic Chemistry



Chapters 20 to 23

Contents

I. Group II

1. Overview	1
2. Physical Properties	1
2.1 Electronic Configuration	1
2.2 Ionic and Atomic Radii	1
2.3 Ionisation Energy	2
2.4 Melting and Boiling Points	2
2.4.1 General Trend	2
2.4.2 Comparison with Group I Metals	2
2.5 Solubility of Hydroxides and Sulphates	2
3. Chemical Properties of the Elements	3
3.1 Redox Reactivity	3
3.2 Reaction with Oxygen	3
3.3 Reaction with Water	4
4. Chemical Properties of the Oxides	4
4.1 Physical Properties	4
4.2 Reaction with Water	4
5. Thermal Stability of Group II Compounds	5
5.1 Overview	5
5.2 Mechanism of Action	5
5.2.1 Carbonates	6
5.2.2 Hydroxides	6
5.2.3 Nitrates	6
5.3 Comparison with Group I Metals	6
6. Beryllium Being Boneheaded	7
6.1 Non-reaction with Water and Oxygen	7
6.2 Amphoteric Nature	7
6.3 Formation of Be complexes	7
6.3.1 Hydrated Ions	7
6.3.2 Other Complexes	8
6.4 Acidity of Beryllium Salts	8

PART I

Group II

1 Overview

Group II metals are the *alkaline earth metals*, and have this name for two reasons; their oxides form alkaline solutions when dissolved in water, and some another mostly irrelevant and historical reason. Mainly the alkaline solution thing.

2 Physical Properties

2.1 Electronic Configuration

All compounds containing group II metals have them at a fixed oxidation state of +2, and all group II metals have a fully filled outermost *s* subshell:

Be: $1s^2 2s^2$

Mg: $1s^2 2s^2 2p^6 3s^2$

Ca: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$

Sr: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s^2$

Ba: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 6s^2$

Group II metals form +2 compounds two reasons; first, the 3rd ionisation energy (to get to a +3 state) is significantly greater than either the 1st or 2nd – this required energy cannot be sufficiently compensated for by an exothermic lattice energy.

Secondly, they do not exist in the +1 state because, in many cases, the lattice energy of compounds containing the metal in the +2 state is more exothermic, thus favouring the more stable MX_2 compound as opposed to the MX compound.

2.2 Ionic and Atomic Radii

Naturally, both the ionic and atomic radii of the group II metals *increase* down the group, due simply to the increasing number of quantum shells.

2.3 Ionisation Energy

As should be expected, the first and second ionisation energies of the elements in the group *decrease* progressively. This is due to the increasing number of electron shells between the nucleus and the valence electron shell. Thus, the shielding effect increases, the electrostatic force of attraction decreases, and less energy is required to remove the two valence electrons.

2.4 Melting and Boiling Points

2.4.1 General Trend

Generally speaking, the melting and boiling points decrease down the group, although there are rather large irregularities in the trend. The broad reason for decreasing melting and boiling points is the increasing cationic size down the group, leading to weaker electrostatic forces between the delocalised electron cloud and the ions – hence weaker metallic bonding.

There is unfortunately no simple explanation for the irregularity in the trend.

2.4.2 Comparison with Group I Metals

In the same period, group II metals have higher melting and boiling points than group I metals, primarily due to the increase in nuclear charge (+1 to +2), and more electrons in the delocalised cloud, leading to stronger metallic bonding.

2.5 Solubility of Hydroxides and Sulphates

The solubility of group II hydroxides *increases* down the group, while the solubility of the sulphates *decrease* down the group; $\text{Mg}(\text{OH})_2$ and BaSO_4 are insoluble, while MgSO_4 and $\text{Ba}(\text{OH})_2$ are soluble.

$$\Delta H_{\text{sol}} = -LE + \Delta H_{\text{hyd}}$$

$$LE \propto \frac{q_+ \times q_-}{r_+ + r_-} \qquad \Delta H_{\text{hyd}} \propto \frac{q_+}{r_+} + \frac{q_-}{r_-}$$

For the sulphates, the anionic radius is far larger than the cationic radius, hence the lattice energy remains relatively constant down the group. However, looking at the enthalpy change of hydration, the increasing cationic radius decreases the ΔH_{hyd} . Hence, the overall effect is that ΔH_{sol} increases down the group, becoming *less exothermic*, and hence solubility decreases.

For the hydroxides, the reverse is true; the anionic radius is small compared to the cation, so the lattice energy decreases down the group as the cationic radius has a greater effect. Thus, combined with the decreasing ΔH_{hyd} , solubility for the hydroxides increases down the group.

3 Chemical Properties of the Elements

3.1 Redox Reactivity

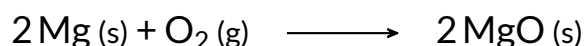
Due to the decrease in first two ionisation energies down the group, the group II metals are more easily oxidised down the group. Therefore, their strength as reducing agents also increases down the group.

Behold a table of E_{ox}^* values (lol you thought you had escaped them, didn't you):

Reaction	E_{ox}^*/V
$\text{Be (s)} \rightarrow \text{Be}^{2+} + 2 \text{e}^-$	+1.99
$\text{Mg (s)} \rightarrow \text{Mg}^{2+} + 2 \text{e}^-$	+2.37
$\text{Ca (s)} \rightarrow \text{Ca}^{2+} + 2 \text{e}^-$	+2.87
$\text{Sr (s)} \rightarrow \text{Sr}^{2+} + 2 \text{e}^-$	+2.89
$\text{Ba (s)} \rightarrow \text{Ba}^{2+} + 2 \text{e}^-$	+2.91

3.2 Reaction with Oxygen

The trend of the metals' reactions with oxygen is simply a product of their increasing reducing power down the group. They all tarnish in air (before exploding) without external agents, and the reactivity increases down the group.



Barium reacts at room temperature quickly, so it is stored under oil to prevent rapid tarnishing. Beryllium on the other hand needs to be burning before *any* reaction takes place; its curiosities will be explored later.

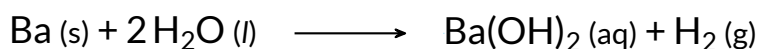
3.3 Reaction with Water

Again, the reactivity of the metals with water increase down the group; they reduce water to hydrogen gas. Note that beryllium does not react with water (or steam), even when heated.

All the metals form hydroxides with the exception of magnesium — when reacting with steam, it forms MgO directly, and reacts slowly with cold water otherwise to form Mg(OH)₂.



For the rest of the metals, hydroxides are formed directly, with increasing vigour down the group.



Note that the solubility of Ca(OH)₂ is an equilibrium, and exists as either slaked lime in the solid form, or limewater in the aqueous form. The latter is produced when reacted with excess water.

Finally, all the group II hydroxides are basic (duh), except for beryllium hydroxide (Be(OH)₂) which is amphoteric.

4 Chemical Properties of the Oxides

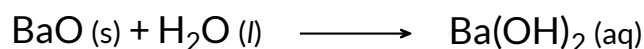
4.1 Physical Properties

Strictly does not belong in this section, but whatever. All group II oxides are solid at room temperature, are white, are basic, and have very high melting and boiling points. Melting and boiling points for the oxides decrease down the group, due to a decreasing lattice energy.

4.2 Reaction with Water

All group II oxides react with water to form their respective hydroxides (hence they are basic oxides), except BeO which is amphoteric, but does not react with water.

The vigour of the reaction increases down the group, since the magnitude of the lattice energy of the ionic oxide decreases.



5 Thermal Stability of Group II Compounds

5.1 Overview

All group II hydroxides, carbonates and nitrates thermally decompose at appropriate temperatures. The trend for all 3 is that the temperature required *increases* down the group, aka. the stability of these ionic compounds increases down the group.

The data for beryllium is generally sparse, so... it's not there. Oops.

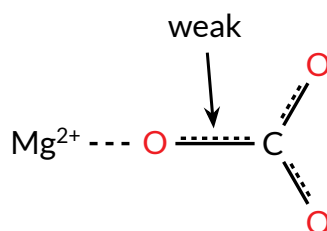
Element	MCO ₃	M(NO ₃) ₂	M(OH) ₂
Mg	400 °C	450 °C	300 °C
Ca	900 °C	575 °C	390 °C
Sr	1280 °C	635 °C	466 °C
Ba	1360 °C	675 °C	700 °C

The main factor affecting the thermal stability is the polarising power of the ion, which depends on charge density — this decreases down the group, leading to more stable ionic compounds.

5.2 Mechanism of Action

The decomposition of all 3 categories of ionic compounds follow the same principle. Given the relatively high charge density of the group II metals, they are able to *polarise* the covalent bonds *within the anion*, weakening them.

This weakening of the covalent bonds in the anion allows said bond to break when heat is applied, typically resulting in a metal oxide as the product.



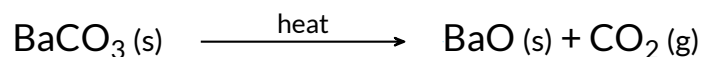
In this case, when heat is applied, the weak bond will be broken, leading to the formation of MO and CO₂. Generally speaking this is why metal oxides are usually formed.

As the polarising power of the metal ion decreases down the group (due to increasing radius but constant charge), the bond is weakened to a lesser degree, leading to a higher stability.

Clearly, only polyatomic anions can be decomposed; monatomic anions cannot be broken down further by heat.

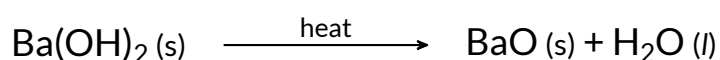
5.2.1 Carbonates

The thermal decomposition of group II carbonates generally produces the metal oxide, and carbon dioxide gas.



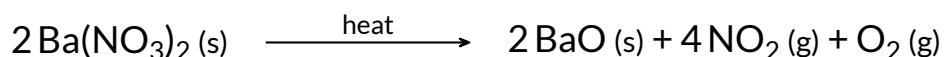
5.2.2 Hydroxides

Decomposing hydroxides produces the metal oxide and water.



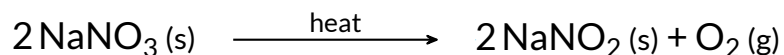
5.2.3 Nitrates

The thermal decomposition of nitrates generally yields the metal oxide, as well as nitrogen and oxygen gas.

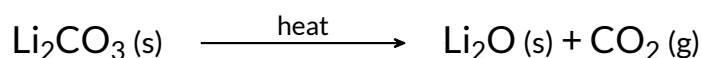


5.3 Comparison with Group I Metals

Most group I metals do not have sufficient charge density to polarise the carbonate anion, however they do polarise the nitrate ion enough for some decomposition:



Lithium is the exception to this rule – it has a sufficiently high charge density (due to its tiny ionic radius) to polarise nitrates fully to decompose in the same way as group 2 ions, and can also polarise carbonates.



6 Beryllium Being Boneheaded

Nice alliteration, eh?

The majority of the discrepancies with beryllium can be attributed to the highly covalent character of bonds formed with Be, partially due to its high charge density which can polarise the electron cloud of anions.

Compounds with large anions, such as BeCl_2 , are completely covalent.

6.1 Non-reaction with Water and Oxygen

Similar to magnesium but more extreme, beryllium forms an *impervious* oxide layer when exposed to oxygen – this reacts with neither water nor oxygen, leading to its unreactivity.

6.2 Amphoteric Nature

Beryllium oxides and hydroxides are amphoteric unlike its other group II compatriots, and this is due to the partially covalent nature of the bonds with Be.

- Acid: $\text{BeO} + 2 \text{NaOH} + \text{H}_2\text{O} \rightarrow \text{Na}_2[\text{Be}(\text{OH})_4]$
- Base: $\text{BeO} + \text{H}_2\text{SO}_4 \rightarrow \text{BeSO}_4 + \text{H}_2\text{O}$

Note the formation of the $[\text{Be}(\text{OH})_4]^{2-}$ complex, which will be discussed below.

6.3 Formation of Be complexes

6.3.1 Hydrated Ions

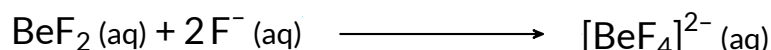
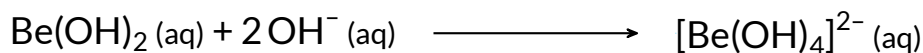
As will be discussed later, Mg^{2+} has sufficient charge density to form hydrated complex ions in water ($[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$). Thus, it is clear that Be should form these complexes as well, and it does – $[\text{Be}(\text{H}_2\text{O})_4]^{2+}$.

However, Be^{2+} is only 4-coordinate, due to the lack of vacant d-orbitals (there is no 2d subshell). Hence, by using the 2s and 2p orbitals, it can form 4 bonds with ligands. By contrast Mg^{2+} has a 3d subshell, allowing for more ligands.

6.3.2 Other Complexes

While Be^{2+} can form complexes, Be can also form complexes when bonded with other atoms, since it still has 2 vacant p-orbitals to fill with ligand bonds.

An example seen above is the formation of $[\text{Be}(\text{OH})_4]^{2-}$ when $\text{Be}(\text{OH})_2$ is exposed to more OH^- , and the formation of $[\text{BeF}_4]^{2-}$.



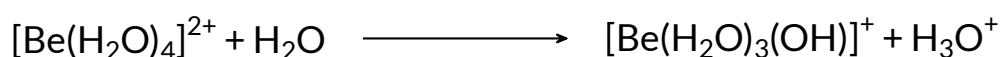
A point to note is that $[\text{Be}(\text{OH})_4]^{2-}$ is created from $\text{Be}(\text{OH})_2$, which is itself formed from the hydrolysis of a beryllium salt in water (since BeO does not react with water).

On adding a base (aka OH^-), the hydrated $[\text{Be}(\text{H}_2\text{O})_4]^{2+}$ complex acts as an acid, forming the $[\text{Be}(\text{OH})_4]^{2-}$ by losing 4 H^+ ions. This behaviour is conveniently discussed below.

6.4 Acidity of Beryllium Salts

Similar to other cations of high charge density like Al^{3+} , Fe^{3+} and Cr^{3+} (and to a certain extent Mg^{2+}), Be^{2+} forms a hydrated complex in water, $[\text{Be}(\text{H}_2\text{O})_4]^{2+}$, which was seen above.

Just like the other complexes, it can hydrolyse to give H_3O^+ , making it acidic in water.



Naturally it can undergo further hydrolysis to finally form $[\text{Be}(\text{OH})_4]^{2-}$. This behaviour is what enables beryllium to react with bases, and be amphoteric.