The s-block Metals

<table>
<thead>
<tr>
<th>Group 1: alkali metals</th>
<th>Atomic number</th>
<th>Flame colour</th>
<th>Group 2: alkaline earth metals</th>
<th>Atomic number</th>
<th>Flame colour</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lithium (Li)</td>
<td>3</td>
<td>Deep red ▲</td>
<td>Beryllium (Be)</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>Sodium (Na)</td>
<td>11</td>
<td>Yellow ▲</td>
<td>Magnesium (Mg)</td>
<td>12</td>
<td>Brilliant white</td>
</tr>
<tr>
<td>Potassium (K)</td>
<td>19</td>
<td>Lilac ▲</td>
<td>Calcium (Ca)</td>
<td>20</td>
<td>Brick red ▲</td>
</tr>
<tr>
<td>Rubidium (Rb)</td>
<td>37</td>
<td>Bluish red ▲</td>
<td>Strontium (Sr)</td>
<td>38</td>
<td>Blood red ▲</td>
</tr>
<tr>
<td>Caesium (Cs)</td>
<td>55</td>
<td>Blue ▲</td>
<td>Barium (Ba)</td>
<td>56</td>
<td>Apple green ▲</td>
</tr>
<tr>
<td>Francium (Fr)</td>
<td>87</td>
<td>?</td>
<td>Radium (Ra)</td>
<td>88</td>
<td></td>
</tr>
</tbody>
</table>

Table 1: The s-block elements, their atomic numbers and flame colours.

The s-block elements are characterised by their high electronegativity (low electronegativity) and the relative ease with which they lose their outer shell s-electron(s) to form positive ions (low ionisation energies). Group 1 metals, the alkali metals, have a single s-electron in their outer shell and this is easily lost to form M\(^+\) ions, e.g. Na\(^+\), whilst Group 2 metals, the alkaline earth metals, have 2 outermost s-electrons which they tend to lose to form M\(^{2+}\) ions, e.g. Ca\(^{2+}\). These are the only stable ions formed by these metals under normal conditions. The elements are strong reducing agents (due to their tendency to donate valence electrons). This reducing power increases down both groups (as atomic radius increases, meaning that the valence electrons are less tightly bound and more easily donated).

As the names of the groups suggest, the oxides and hydroxides of these metals are basic. Most of the salts are ionic solids and more-or-less colourless (or white, or possessing pale colour) unless the anion is coloured.

**Flame Colours**

When energised into an excited higher energy state, such as upon heating, s-block metals emit brilliant colours of light. These are due to transitions of the valence electron(s) between different electron sub-shells. When energised the electron jumps up to a higher vacant energy orbital in another sub-shell, absorbing energy, and then when the atom de-excites, the electron drops down, releasing the energy it had gained as light in one or more steps. The wavelength/colour of this light depends on the energy of the photons and the photon energy depends upon the energy difference between the sub-shells involved in the jump.
For example, the deep red colour of lithium is due to a $2p \rightarrow 2s$ transition; the yellow of sodium due to a $3d \rightarrow 3p$ transition, and the lilac colour of potassium to a $4d \rightarrow 4p$ transition. These flame colours are utilised in pyrotechnics. Flame tests can be used to help identify inorganic compounds – the colour of the flame indicates any s-block metal (and a few other metals such as Cu) present.

To conduct a flame test:

1. Clean a nichrome wire or wire-loop by dipping in concentrated hydrochloric acid. (The yellow of sodium is particularly intense and will contaminate flame tests if the wire is not cleaned repeatedly).
2. Dip the nichrome wire into the test substance (solution or solid, works best with the chlorides if the wire is cleaned in concentrated hydrochloric acid).
3. Burn off sample in Bunsen flame and observe the colour.

Copper metal is an example of the N+10 relationship: in this relationship, elements behave similar to those ten columns further along the Periodic Table. The Coinage Metal Group (copper (Cu), silver (Ag) and gold (Au), Group 1B or Group 11) is ten groups further along from Group 1 (Group 1A) and these noble (unreactive) metals do have certain behaviours that are similar to Group 1 metals, such as the formation of $M^+$ ions ($Cu^+$, $Ag^+$, $Au^+$ though $Cu^{2+}$ is more stable than $Cu^+$ and $Au^{3+}$ more stable than $Au^+$). Similarly, the zinc group (Zn, Cd, Hg) are ten groups along from Group 2 and these metals tend to form $M^{2+}$ ions ($Zn^{2+}$, $Cd^{2+}$, $Hg^{2+}$). This relationship happens because these d-block groups have filled their d-subshells and so have outermost valence s-subshells and so behave in some ways similar to the s-block metals (though in other ways quite differently, since they can promote additional d-electrons into their valence shell for bonding). Copper compounds give a green flame colour (again due to transitions involving its outer 4s electron).
**Physical properties**

<table>
<thead>
<tr>
<th>Group 1: alkali metals</th>
<th>Melting Temp (°C)</th>
<th>Hardness</th>
<th>Group 2: alkaline earth metals</th>
<th>Melting Temp (°C)</th>
<th>Hardness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lithium (Li)</td>
<td>180</td>
<td>Hard to cut with a steel knife</td>
<td>Beryllium (Be)</td>
<td>1280</td>
<td></td>
</tr>
<tr>
<td>Sodium (Na)</td>
<td>97.8</td>
<td>Cuts with a steel knife</td>
<td>Magnesium (Mg)</td>
<td>650</td>
<td>Thin ribbons can be cut with a steel knife</td>
</tr>
<tr>
<td>Potassium (K)</td>
<td>63.7</td>
<td>Cuts easily with a steel knife</td>
<td>Calcium (Ca)</td>
<td>850</td>
<td></td>
</tr>
<tr>
<td>Rubidium (Rb)</td>
<td>38.9</td>
<td>Putty-like</td>
<td>Strontium (Sr)</td>
<td>768</td>
<td></td>
</tr>
<tr>
<td>Caesium (Cs)</td>
<td>28.7</td>
<td>Putty-like</td>
<td>Barium (Ba)</td>
<td>714</td>
<td></td>
</tr>
<tr>
<td>Francium (Fr)</td>
<td>≈ 27</td>
<td></td>
<td>Radium (Ra)</td>
<td>700</td>
<td></td>
</tr>
</tbody>
</table>

Table 2: physical properties of s-block metals.

The **Group 1 metals** are very soft with low melting and boiling temperatures, since they have only one electron per atom that participates in metallic bonding. The metals become softer as one moves down the group, since the metal atoms become larger down the group and the greater the bond length the weaker the attractive force between the atoms (or between the ion cores and the bonding electrons). Thus, Li is hard to cut with a knife, whereas Cs is soft like putty.

Hardness, strength and melting/boiling points also depend upon the crystal structure. The Group 1 metals all adopt body-centred cubic (bcc) packing, in which the atoms are not close-packed and each is surrounded by fewer neighbours and so bonding between them is weakened.

Group 2 metals are somewhat harder, stronger and have higher melting/boiling points since they have two electrons per atom engaged in metallic bonding. Also, only barium has bcc packing, Be and Mg adopt the hexagonal close-packed structure (hcp) and Ca and Sr adopt the cubic close-packed structures.

Apart from their softness and reactivity, the elements look like typical metals, with metallic lustre. Mg, for example, is a silvery-white metal (and fairly hard) that tarnishes slightly in air and burns with a brilliant white flame (a good lab demonstration!). Ra, for example, is a brilliant white metal which blackens on exposure to air.
The s-block metals are reactive metals (highly reactive in the case of the alkali metals) that tend to lose the s-electron(s) in their outer (incomplete) valence shell to obtain stable noble gas configurations (octets). For example:

Example electron configurations:

Na: 1s\(^2\) 2s\(^2\) 2p\(^6\) 3s\(^1\) → Na\(^+\): 1s\(^2\) 2s\(^2\) 2p\(^6\), i.e. [Ne]

K: 1s\(^2\) 2s\(^2\) 2p\(^6\) 3s\(^2\) 3p\(^6\) 4s\(^1\) → K\(^+\): 1s\(^2\) 2s\(^2\) 2p\(^6\) 3s\(^2\) 3p\(^6\), i.e. [Ar]

Mg: 1s\(^2\) 2s\(^2\) 2p\(^6\) 3s\(^2\) → Mg\(^2+\): 1s\(^2\) 2s\(^2\) 2p\(^6\), i.e. [Ne]

Ca: 1s\(^2\) 2s\(^2\) 2p\(^6\) 3s\(^2\) 3p\(^6\) 4s\(^2\) → Ca\(^2+\): 1s\(^2\) 2s\(^2\) 2p\(^6\) 3s\(^2\) 3p\(^6\), i.e. [Ar]

The radius of an atom/ion are due to the following factors:

1) **Nuclear charge** – increasing the nuclear charge increases the pull on the electrons, shrinking the atom. recall that the charge on the nucleus is positive and due to the protons. The charge on the electrons is negative and opposite charges attract, so the electrons are attracted to the protons. The charge on one proton has the same magnitude as the charge on one electron, but is opposite in sign. The number of protons is the atomic number of the element, e.g. a sodium atom has 11 protons and the atomic number \((Z)\) of sodium is 11.

2) **Number of electron shells.** Electrons in successive shells are further from the nucleus, whilst those within the same shell are more-or-less at the same average distance. Thus, adding electron shells increases the radius of the atom. (The shell nearest the nucleus, the \(n = 1\) or K shell, holds a maximum of 2 electrons, the next shell (L) holds 8 and the next shell (M) holds 18 (but is stable with 8 electrons). Using shell notation (rather than orbital notation) the electron configuration of sodium is: 2.8.1, that of potassium 2.8.8.1. The addition of an extra shell (when moving one step down a Group) which is further from the nucleus, gives K a larger atomic radius than Na.

3) **Screening of the nuclear charge.** Complete electron shells partially screen the nuclear charge, reducing the **effective nuclear charge** seen by electrons further out, which are then less strongly attracted to the nucleus and so move further away from the nucleus. In other words, a complete inner shell partially screens/shields or blocks out the nuclear charge so that a more outer shell of electrons is subject to a weaker nuclear pull and so moves further from the nucleus. An analogy might be to think of electrons as balls on strings, whizzing around a fixed position, lengthen the string and the ball attached to its end moves further out as its tendency is to escape. Similarly with electrons: increase the nuclear pull and they move closer to the nucleus, weaken it and they move further away. In neutral atoms, the net charge is zero since the number of protons equals the number of electrons. Thus, for neutral atoms, the addition of a proton (when moving one step to the right across a Period in the periodic Table, e.g. from sodium, atomic number 11, to magnesium, atomic number 12) is accompanied by an addition of an electron. However, since the electron is added to the same shell, it counters the increase in positive nuclear charge but does very little to increase screening and the increase in nuclear charge outweighs the increase in shielding and the atom contracts as the effective nuclear charge increases.
The radius of the atoms and ions increase down each group, as a new shell of electrons is added which more than off-sets the increase in nuclear charge due to additional shielding of the nucleus by each complete electron shell (a reduction in **effective nuclear charge**). However, the loss of two electrons from the alkaline earths results in a higher proton : electron ratio in these ions and thus a greater increase in the effective nuclear charge than for the Group 1 metals. Thus, during ion formation, the atomic/ionic radius of Group 2 metals shrinks much more than for Group 1 metals. Additionally, the atomic radii of neutral Group 2 metal atoms are smaller than those of Group 1 metals to start with (since on moving to the right across a period the atoms gain one electron and one proton, but the electron adds to the same incomplete valence shell and so has little effect on screening the nuclear charge, whilst the addition of a proton increases the effective nuclear charge).

<table>
<thead>
<tr>
<th>Alkali metals: M / M⁺</th>
<th>Alkaline earth metals: M / M²⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>Be</td>
</tr>
<tr>
<td>Na</td>
<td>Mg</td>
</tr>
<tr>
<td>K</td>
<td>Ca</td>
</tr>
<tr>
<td>Rb</td>
<td>Sr</td>
</tr>
<tr>
<td>Cs</td>
<td>Ba</td>
</tr>
<tr>
<td>Fr</td>
<td>Ra</td>
</tr>
</tbody>
</table>
Periodicity and Atomic Radius

Down a group atomic radius increases as more layers (shells) of electrons are added.

Across a period size decreases as nuclear charge increases.

(Ignoring noble gases)

Noble gases do not form bonds so their (van der Waals) radius is measured to be larger than the metallic/covalent radii of other groups.
The size of the positively-charged metal ions (cations) dramatically affects the chemistry of the metals. Note that Li and Be have particularly small ionic radii. This means that their net +2 charge is concentrated in a very small volume and so these ions have a high charge density. This means that electrons are more strongly attracted towards them and so any ionic bonds containing Be$^{2+}$ or Li$^{2+}$ will be strongly polarised and are often more covalent than ionic. Thus, the chemistry of Be and Mg is very different from the rest of the s-block elements.

<table>
<thead>
<tr>
<th>Group 1: alkali metals</th>
<th>Electron configuration</th>
<th>Group 2: alkaline earth metals</th>
<th>Electron configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lithium (Li)</td>
<td>[He] 2s$^1$</td>
<td>Beryllium (Be)</td>
<td>[He] 2s$^2$</td>
</tr>
<tr>
<td>Sodium (Na)</td>
<td>[Ne] 3s$^1$</td>
<td>Magnesium (Mg)</td>
<td>[Ne] 3s$^2$</td>
</tr>
<tr>
<td>Potassium (K)</td>
<td>[Ar] 4s$^1$</td>
<td>Calcium (Ca)</td>
<td>[Ar] 4s$^2$</td>
</tr>
<tr>
<td>Rubidium (Rb)</td>
<td>[Kr] 5s$^1$</td>
<td>Strontium (Sr)</td>
<td>[Kr] 5s$^2$</td>
</tr>
<tr>
<td>Caesium (Cs)</td>
<td>[Xe] 6s$^1$</td>
<td>Barium (Ba)</td>
<td>[Xe] 6s$^2$</td>
</tr>
<tr>
<td>Francium (Fr)</td>
<td>[Rn] 7s$^1$</td>
<td>Radium (Ra)</td>
<td>[Rn] 7s$^2$</td>
</tr>
</tbody>
</table>

Table 3: electron configurations of s-block metals.
Reactions with other elements

1. Reaction with oxygen

The reactivity increases down each group and Group 1 metals are more reactive than Group 2. Be must be powdered to react, since it is covered by a strong, inert oxide layer. Li requires excess oxygen, but the other s-block metals react well with oxygen when heated. Li, Be, Mg, Ca and Sr react to form ionic oxides, containing the oxide ion $\text{O}^{2-}$, whilst Na, Ba (and possibly Ra) react further to form ionic peroxides, containing the peroxide ion, $\text{O}_2^{2-}$, and the most reactive, K, Rb and Cs form ionic superoxides, containing the superoxide ion, $\text{O}_2^{-}$. Under more favourable conditions, all except Be can be made to form the peroxide, and all except Be, Mg and Li, the superoxide.

The oxides and hydroxides are white crystalline solids. They are basic and their basic nature increases down each group. For example, the oxides react with water to form the hydroxide which is basic (alkali):

$$\text{MgO(s)} + 2\text{H}_2\text{O(l)} \rightarrow \text{H}_2(\text{g}) + \text{Mg(OH)}_2(\text{aq})$$

$$\text{Mg(OH)}_2(\text{aq}) \rightleftharpoons \text{Mg}^{2+}(\text{aq}) + 2\text{OH}^- (\text{aq})$$

BeO is amphoteric (both basic and acidic) for example, it acts as a base in the following (slow) reaction at very low pH:

$$\text{BeO(s)} + \text{H}_2\text{O(l)} + 2\text{H}_3\text{O}^+(\text{aq}) \rightarrow \text{Be(H}_2\text{O)}_4^{2+}$$

in which the beryllium complexes with water, neutralising acid as it does so. BeO is behaving as an acid in the following reaction:

$$\text{BeO(s)} + \text{H}_2\text{O(l)} + 2\text{OH}^-(\text{aq}) \rightarrow \text{Be(OH)}_4^{2-}(\text{aq})$$

in which it neutralises hydroxide ions (alkali) forming the beryllate ion.

The hydroxides are not only basic, but they are alkali, an alkali being a base which directly provides hydroxide, OH$^-$ (aq), ions on dissolving in water.

BeO has the wurtzite structure, which give sit a coordination number of 4 (4:4 so each Be$^{2+}$ ion is surrounded by 4 O$^{2-}$ ions and each O$^{2-}$ ion by 4 Be$^{2+}$). The other Group 2 oxides have the sodium chloride structure (see halides) with a coordination number of 6 (6:6, so each metal ion is surrounded by 6 oxide ions and each oxide ion by 6 metal ions).

All s-block metals except Be and Mg are stored under liquid paraffin to prevent their reaction with oxygen. Be and Mg tarnish in air and this oxide layer prevents further reaction. When cut all the metals rapidly tarnish in air.

Superoxides react vigorously with water to form hydroxide and hydrogen peroxide ($\text{H}_2\text{O}_2$):

$$2\text{O}_2^{-}(\text{s}) + 2\text{H}_2\text{O(l)} \rightarrow 2\text{OH}^-(\text{aq}) + \text{H}_2\text{O}_2(\text{aq}) + \text{O}_2(\text{g})$$

Peroxides also react with water:

$$\text{O}_2^{2-}(\text{s}) + 2\text{H}_2\text{O(l)} \rightarrow \text{H}_2\text{O}_2(\text{aq}) + 2\text{OH}^-(\text{aq})$$

Na$_2$O is a white, deliquescent solid. K$_2$O is a white hygroscopic solid. Rb$_2$O is a pale-yellow solid, whilst Cs$_2$O is an orange solid.
### Reaction of Group 1 Metals with Oxygen and Water

<table>
<thead>
<tr>
<th>Group 1: alkali metals</th>
<th>Reaction with O$_2$(g)</th>
<th>Reaction with H$_2$O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lithium (Li)</td>
<td>2Li(s) + $\frac{1}{2}$O$_2$(g) → Li$_2$O(s) (excess oxygen)</td>
<td>2Li(s) + 2H$_2$O(l) → 2LiOH(aq) + H$_2$(g) (slow)</td>
</tr>
<tr>
<td>Sodium (Na)</td>
<td>2Na(s) + O$_2$(g) → Na$_2$O$_2$(s)</td>
<td>2Na(s) + 2H$_2$O(l) → 2NaOH(aq) + H$_2$(g) (vigorous, fizzes, whizzes about on the surface of the water)</td>
</tr>
<tr>
<td>Potassium (K)</td>
<td>2K(s) + O$_2$(g) → K$_2$O$_2$(s) K(s) + O$_2$(g) → KO$_2$(s)</td>
<td>2K(s) + 2H$_2$O(l) → 2KOH(aq) + H$_2$(g) (hydrogen ignites)</td>
</tr>
<tr>
<td>Rubidium (Rb)</td>
<td>Rb(s) + O$_2$(g) → RbO$_2$(s)</td>
<td>2Rb(s) + 2H$_2$O(l) → 2RbOH(aq) + H$_2$(g) (explosive)</td>
</tr>
<tr>
<td>Caesium (Cs)</td>
<td>Cs(s) + O$_2$(g) → CsO$_2$(s)</td>
<td>2Cs(s) + 2H$_2$O(l) → 2CsOH(aq) + H$_2$(g) (explosive)</td>
</tr>
<tr>
<td>Francium (Fr)</td>
<td>?</td>
<td></td>
</tr>
</tbody>
</table>

Table 4: reaction of Group 1 metals with oxygen and water.

<table>
<thead>
<tr>
<th>Group 2: alkaline earth metals</th>
<th>Reaction with O$_2$(g)</th>
<th>Reaction with H$_2$O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beryllium (Be)</td>
<td>2Be(s) + O$_2$(g) → 2BeO(s) (powdered metal)</td>
<td></td>
</tr>
<tr>
<td>Magnesium (Mg)</td>
<td>2Mg(s) + O$_2$(g) → 2MgO(s) (burns brilliant white)</td>
<td>Mg(s) + H$_2$O(g) → MgO(s) + H$_2$(g) (steam) Mg(s) + 2H$_2$O(s) → Mg(OH)$_2$(aq) + H$_2$(g) (excess steam)</td>
</tr>
<tr>
<td>Calcium (Ca)</td>
<td>2Ca(s) + O$_2$(g) → 2CaO(s)</td>
<td>Ca(s) + H$_2$O(l) → CaO(s) + H$_2$(g) (slow)</td>
</tr>
<tr>
<td>Strontium (Sr)</td>
<td>2Sr(s) + O$_2$(g) → 2SrO(s) (forms SrO$_2$ at high pressure)</td>
<td></td>
</tr>
<tr>
<td>Barium (Ba)</td>
<td>2Ba(s) + O$_2$(g) → 2BaO(s)</td>
<td>Ba(s) + O$_2$(g) → BaO$_2$(s)</td>
</tr>
<tr>
<td>Radium (Ra)</td>
<td>?</td>
<td></td>
</tr>
</tbody>
</table>

Table 5: reaction of Group 1 metals with oxygen and water.
2. Reaction with hydrogen

The s-block metals form ionic hydrides when heated with hydrogen gas, for example magnesium hydride:

\[ \text{Mg(s)} + \text{H}_2(\text{g}) \rightarrow \text{MgH}_2(\text{s}) \]

which is a white crystalline solid which dissociates into magnesium and hydrogen at 327°C. These ionic hydrides contain the hydride ion, \( \text{H}^- \). However, \( \text{BeH} \) and \( \text{MgH}_2 \) are intermediate/covalent, with considerable covalent and ionic character (the bonds are highly polarised). (On the basis of electronegativities we would expect individual M-H bonds to be largely covalent but with significant ionic character).

The Group 1 metal ionic hydrides have the sodium chloride structure:

\[ 2\text{Na(s)} + \text{H}_2(\text{g}) \rightarrow 2\text{NaH(s)} \]

reactivity to hydrogen increases down both groups.

3. Reaction with nitrogen

Of the Group 1 metals, only Li reacts upon heating, forming lithium nitride:

\[ 6\text{Li(s)} + \text{N}_2(\text{g}) \rightarrow 2\text{Li}_3\text{N(s)} \]

Of the Group 2 metals, all except Be react upon heating:

\[ 3\text{Mg(s)} + \text{N}_2(\text{g}) \rightarrow \text{Mg}_3\text{N}_2(\text{s}) \]

The nitrides react with water to produce ammonia:

\[ \text{Mg}_3\text{N}_2(\text{s}) + 6\text{H}_2\text{O(l)} \rightarrow 3\text{Mg(OH)}_2(\text{aq}) + 2\text{NH}_3(\text{g}) \]

Magnesium nitride is a yellow or yellow-green crystalline solid which decomposes to magnesium and nitrogen when heated.

4. Reaction with carbon

Group 1 metals do not react with carbon, but Group 2 metals react at high temperatures to give the metal carbides:

\[ \text{Ca(s)} + 2\text{C(s)} \rightarrow \text{CaC}_2(\text{s}) \]

which are ionic, containing the carbide ion: \( \text{(C≡C)}^2^- \). The carbides react with water to give ethyne (acetylene) gas:

\[ \text{CaC}_2(\text{s}) + 2\text{H}_2\text{O(l)} \rightarrow \text{Ca(OH)}_2(\text{s/aq}) + \text{C}_2\text{H}_2(\text{g}) \]

Ignited Mg metal will also react with carbon dioxide in the absence of air:

\[ \text{Mg(s)} + \text{CO}_2(\text{g}) \rightarrow 2\text{MgO(s)} + \text{C(s)} \]
5. Reaction with halogens

All s-block metals react directly with chlorine, requiring moisture and/or heat to initiate the reaction:

\[ 2\text{Na}(s) + \text{Cl}_2(g) \rightarrow 2\text{NaCl}(s) \]
\[ \text{Ca}(s) + \text{Cl}_2(g) \rightarrow \text{CaCl}_2(s) \]

The reaction of Group 1 metals and chlorine is particularly vigorous as the metals burn vigorously, releasing intense light (this makes a good lab demonstration!). The white crystalline powder of the ionic chloride remains.

BeCl\(_2\) is more-or-less covalent, with a low melting point. MgCl\(_2\) is intermediate between ionic and covalent.

The s-metals are too reactive to be found naturally in their elemental states and NaCl is one of the main minerals of sodium. It occurs as salt deposits, forming the mineral halite, as well as in sea-water. The chlorides are used in industrial preparation of the metals.

Left: the structure of NaCl. The sodium ion and chloride ions each form a face-centred cubic (fcc) lattice. The chloride ions, being negatively charged, are much larger than the Na\(^+\) ions. (When chlorine gains an electron to form Cl\(^-\), repulsion between the additional electron and the other electrons present, expands the outer shell. Additionally, there is no extra proton to counter the addition of the electron and so the proton : electron ratio is reduced and each electron experiences a smaller share of the nuclear pull. In contrast, Na\(^+\) has lost its outer shell, exposing a smaller electron shell beneath, and the proton : electron ratio has increased, increasing the share of the nuclear pull on each electron, pulling them closer to the nucleus.

NaCl, NaBr (sodium bromide) and NaI (sodium iodide) are all white ionic solids, as is kBr, which is used as a sedative and anticonvulsant. NaI is used to treat iodine deficiency and is often added to table salt (NaCl). As a component of sea-water, when animals left the sea they took sodium chloride with them in their tissue fluids, and sodium chloride remains a vital component of blood and tissue fluid. NaI crystals emit a pulse of light when struck by ionising radiation and so are used in scintillation and x-ray detectors. NaI is hygroscopic.

\[ 2\text{NaBr(aq)} + \text{Cl}_2(g) \rightarrow 2\text{NaCl(aq)} + \text{Br}_2(l) \]
\[ \text{NaBr(s)} + \text{H}_2\text{SO}_4(aq) \rightarrow \text{HBr(g)} + \text{NaHSO}_4(aq) \]

In contrast to NaCl, KCl is toxic and one abuse of the substance is in lethal injections. KCl occurs naturally as the mineral sylvite and also as sylvinite, NaCl-KCl.
KBr is transparent to near UV (about 250 nm), visible light, and long IR (about 25 000 nm) and so is useful in UV/IR optics (but is hygroscopic and so must be kept dry!).

**Preparation of KBr:**

$$4\text{K}_2\text{CO}_3(s) + \text{Fe}_3\text{Br}_8 \rightarrow 8\text{KBr}(s) + \text{Fe}_3\text{O}_4(s) + 4\text{CO}_2(g)$$

(The iron bromide is prepared by reacting scrap iron and excess bromine under water)

Potassium iodide, KI, a white solid, turns yellow upon heating in air, or upon standing in moist air as $$2\text{I}^- \rightarrow \text{I}_2$$. Iodine is barely soluble in water, but dissolves in a solution of KI(aq):

$$\text{KI(aq)} + \text{I}_2(s) \rightarrow \text{KI}_3(aq)$$

this ‘iodine water’ solution acts as a source of iodine. KI is prepared as follows:

$$\text{HI} + \text{KHCO}_3 \rightarrow \text{KI} + \text{H}_2\text{O}(l) + \text{CO}_2(g)$$

$$\text{FeI}_2 + \text{K}_2\text{CO}_3 \rightarrow 2\text{KI} + \text{FeCO}_3$$

KI is used in photography (see halogens for details).

**MgCl**$_2$ is a white crystalline solid and very stable. It can be prepared from a solution of the metal in liquid ammonia:

$$\text{Mg(NH}_3\text{)} + \text{NH}_4\text{Cl(s)} \rightarrow 2\text{MgCl}_2(s) + \text{NH}_3(l) + \text{H}_2(g)$$

(The MgCl$_2$ is insoluble in ammonia and precipitates).

MgCl$_2$, although generally considered ionic, is actually comprised of layers of atoms held together by much weaker van der Waals forces between the chloride ions in adjacent layers – a characteristic associated with covalency. Indeed, magnesium has a diagonal relationship with the Group 3 element aluminium (aluminum, Al) which, although a metal, tends towards semi-metal behaviour and forms a covalent chloride, AlCl$_3$(s) which sublimes at moderate temperatures into Al$_2$Cl$_6$(g) molecules.

**6. Reaction with other Group 6 elements**

In addition to forming oxides, the metals form sulphides on heating with sulphur (sulfur), e.g. MgS (a white, red or red-brown solid with the NaCl structure, very stable) selenides, e.g. MgSe (a brown crystalline solid) and tellurides, e.g. MgTe. Magnesium sulphide, MgS, has the 6:6-coordinate structure of NaCl, but much higher melting and boiling points, due to the greater ionic charges producing stronger ionic bonding.

$$\text{Mg(s)} + \text{S(s)} \rightarrow \text{MgS(s)}$$


**Electrolysis of Brine**

The hydroxides of the s-block metals, e.g. NaOH, are colourless/white crystalline compounds and can be prepared by electrolysis of the aqueous chloride solution of the corresponding metal. For example, hydrolysis of dilute NaCl(aq) gives:

Electrolysis of dilute NaCl(aq):

- cathode (negative electrode):
  \[ 2\text{H}_2\text{O}(l) + 2\text{e}^- \rightarrow \text{H}_2(g) + 2\text{OH}^-(aq) \]
- anode (positive anode):
  \[ 2\text{H}_2\text{O}(l) \rightarrow \text{O}_2(g) + 4\text{H}^+(aq) + 4\text{e}^- \]
  \[ 4\text{OH}^-(aq) \rightarrow \text{O}_2(g) + 2\text{H}_2\text{O}(l) + 4\text{e}^- \]

Note that the Na\(^+\) and Cl\(^-\) ions allow electric charge to flow easily through the solution, which results in the decomposition of the water into hydrogen gas (evolved at the cathode) and oxygen gas (evolved at the anode). Any Na\(^+\) ions reacting at the cathode can not deposit sodium metal as this reacts faster with water than it is deposited! However, with a saturated slat solution, chlorine gas will be produced:

Electrolysis of concentrated NaCl(aq):

- cathode: \( \text{H}_2\text{O}^+(aq) + \text{e}^- \rightarrow \frac{1}{2}\text{H}_2(g) + \text{H}_2\text{O}(l) \)
- anode: \( \text{Cl}^-(aq) \rightarrow \frac{1}{2}\text{Cl}_2(g) + \text{e}^- \)

With dilute solutions, some chlorine gas may also be evolved at the anode, but oxygen dominates, however, in saturated solution chlorine evolution dominates (a test-tube of the gas collected will be visibly yellow and will instantly turn an iron nail yellow, as it coats it with iron chloride).

**Industrial Production of Sodium**

Sodium is produced, along with chlorine, by electrolysis of molten NaCl in a Down’s cell (the Down’s Process) in which a molten mixture of 40% NaCl, 60% CaCl\(_2\) is electrolysed at about 580\(^\circ\)C. Na and Ca metals are formed at the cylindrical steel cathode and rise through a cooled pipe, which solidifies the Ca which falls back into the melt.

Electrolysis of molten NaCl will produce sodium metal (in the absence of moisture) and chlorine gas:

Electrolysis of molten (fused) NaCl:

- cathode: \( \text{Na}^+(l) + \text{e}^- \rightarrow \text{Na}(s) \)
- anode: \( \text{Cl}^-(l) \rightarrow \frac{1}{2}\text{Cl}_2(g) + \text{e}^- \)

All the Group 1 metal hydroxides have the NaCl structure and all except LiOH are deliquescent (absorbing moisture from the atmosphere to ...). Aqueous solutions of the hydroxides absorb carbon dioxide gas from the atmosphere. The solubility of the hydroxides increases down the group.
2. Industrial Preparation of Chlorine and Sodium Hydroxide

Chlorine is prepared by the electrolysis of brine. The brine can be obtained by pumping water into underground deposits of rock salt (NaCl(s)).

Things to consider:
1. Cost
4. Siting of the plant.
5. Waste disposal.

Method 1: The mercury cell

http://www.eurochlor.org/animations/mercury-cell.asp

Concentrated aqueous sodium chloride solution with a mercury cathode produces a solution/alloy of sodium metal in mercury ("sodium amalgam") at the cathode and chlorine at the anode. The mercury flows slowly down-slope into another reactor called a decomposer, where the amalgam reacts with water to produce H₂(g), NaOH(aq) as useful products, and Hg(l) which is recycled.

\[
2\text{Cl}^- (aq) \rightarrow \text{Cl}_2 (g) + 2e^- \\
\text{Anode (+)} \quad \text{Anode (+)}
\]

Q.1 Give one disadvantage of the Hg cell.
**Industrial Preparation of Magnesium**

Group 2 metals are prepared by electrolysis of the fused chlorides:

- **Cathode**: \( \text{Mg}^{2+}(l) + 2e^- \rightarrow \text{Mg}(l) \)
- **Anode**: \( 2\text{Cl}^- \rightarrow \text{Cl}_2(g) + 2e^- \)

Magnesium is the lightest metal used in construction, with a density less than two-thirds that of aluminium. Magnesium is also produced by reduction, e.g. reduction of MgO (produced from sea-water) by carbon:

\[
\text{Mg}^{2+}(aq) + \text{Ca(OH)}_2(s) \rightarrow \text{Ca}^{2+}(aq) + \text{Mg(OH)}_2(s/aq)
\]

The Mg(OH)\(_2\) being fairly insoluble largely precipitates out and is thermally decomposed:

\[
\text{Mg(OH)}_2(s) + \text{heat} \rightarrow \text{MgO}(s) + \text{H}_2\text{O}(g)
\]

The MgO is then reduced:

\[
\text{MgO}(s) + \text{C}(s) \rightarrow \text{CO}(g) + \text{Mg}(l)
\]

BaO can be reduced by aluminium:

\[
2\text{Al}(s) + 3\text{BaO}(s) \rightarrow \text{Al}_2\text{O}_3(s) + 3\text{Ba}(g)
\]

Mg is a silvery-white, fairly hard metal, which tarnishes slightly in air. powder, filings and magnesium ribbons ignite when heated in air, burning with a brilliant white flame. It is the second most abundant metal in the sea and also occurs as the mineral carnallite, \( \text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O} \).

Magnesium can also be prepared from the mineral dolomite, \( [\text{MgCa(CO}_3]_2 \). The dolomite is heated (calcined) to form calcined dolomite, \( \text{MgO} \cdot \text{CaO} \), which is reacted with ferrosilicon alloy:

\[
2[\text{MgO} \cdot \text{CaO}] + \text{FeSi} \rightarrow 2\text{Mg} + \text{Ca}_2\text{SiO}_4 + \text{Fe}.
\]

The Mg is then distilled out from the resultant mixture.
**Reactions with common solvents**

1. Reaction with water

Group 1 metals are more reactive than Group 2. In Group 2, magnesium reacts only with steam (it reacts very slowly with liquid water) and calcium reacts only slowly with water. In Group 1, sodium reacts vigorously, fizzing as hydrogen gas is produced and whizzing around on the surface of the water as sodium hydroxide is formed (and which can be visualised as trails behind the metal if universal pH indicator is added to the water). Li reacts slowly with water because the metallic bonds within it are stronger (due to the smaller size of the atom and shorter bond length).

\[ 2K(s) + 2H_2O(l) \rightarrow H_2(g) + 2KOH(aq) \]
\[ Ca(s) + 2H_2O(l) \rightarrow H_2(g) + Ca(OH)_2(aq) \]

2. Reaction with liquid ammonia

All the s-elements dissolve in liquid ammonia to give intensely blue solutions which conduct electricity (contain ions and electrons associated with the ammonia). However, beryllium and magnesium are not very soluble in ammonia and give only dilute solutions by electrolysis (in which an anode of the metal immersed in ammonia slowly dissolves on completing the circuit). In ammonia solution the metals are extremely reactive and powerful reducing agents.

Evaporating off the ammonia gives Li(NH\(_3\))\(_4\) for lithium, and M(NH\(_3\))\(_6\) for the alkaline earths, e.g. Ca(NH\(_3\))\(_6\). The remaining alkali metals, such as Na and K are recovered unchanged. However, if left for prolonged periods of time in ammonia, or in the presence of a catalyst (such as a transition metal oxide) the metals reacts with the ammonia to give amides, such as sodamide:

\[ 2Na(s) + 2NH_3(l) \rightarrow 2NaNH_2 + H_2(g) \]

3. Reaction with organic solvents

Alcohols and phenols react with sodium metal to form (ionic) alkoxides and phenoxides:

\[ 2ROH + 2Na(s) \rightarrow H_2 + 2ROO^-Na^+ \]
\[ e.g. 2CH_3CH_2OH(l) + 2Na(s) \rightarrow H_2(g) + 2CH_3CH_2OO^-Na^+ \]
\[ (ethanol + sodium \rightarrow hydrogen + sodium ethoxide) \]
**Some reactions of the hydroxides**

1. The hydroxides are **basic** (alkali in this case as they provide their own hydroxide ions) and so neutralise common acids (to give salts and water):

   \[ \text{H}^+ (\text{aq}) + \text{OH}^- (\text{aq}) \rightarrow \text{H}_2\text{O}(\text{l}) \]
   
   e.g. \[ \text{HCl(aq)} + \text{NaOH(aq)} \rightarrow \text{NaCl(Aq)} + \text{H}_2\text{O(l)} \]

   general reaction: acid + alkali \(\rightarrow\) salt + water

2. The hydroxides will **displace weak bases** (like ammonia) from their salts:

   \[ \text{NH}_4\text{Cl(aq)} + \text{NaOH(aq)} \rightarrow \text{NaCl(aq)} + \text{NH}_3(\text{g}) + \text{H}_2\text{O(l)} \]

3. Cold, dilute sodium hydroxide reacts with chlorine gas to form bleach (during which the chlorine **disproportionates**, that is it is both oxidised and reduced):

   \[ \text{Cl}_2(\text{g}) + 2\text{OH}^- (\text{aq}) \rightarrow \text{Cl}^- (\text{aq}) + \text{ClO}^- (\text{aq}) + \text{H}_2\text{O(l)} \]

   The \(\text{ClO}^-\) produced is the hypochlorite ion (with Cl in an oxidation state of +1).

4. **Hydrolysis of esters.** When esters are warmed (refluxed) with dilute acid or alkali as catalyst, they are hydrolysed into a carboxylic acid and an alcohol:

   with dilute \(\text{H}_2\text{SO}_4(\text{aq})\) catalyst: \(\text{RCO\cdotOCH}_3 + \text{H}_2\text{O} \rightarrow \text{RCOOH} + \text{CH}_3\text{OH}\)

   with sodium hydroxide catalyst: \(\text{RCO\cdotOCH}_3 + \text{NaOH} \rightarrow \text{RCOO}^-\text{Na}^+ + \text{CH}_3\text{OH}\)

   Note that in ester hydrolysis, the O in the \(-\text{OH}\) group on the carboxylic acid comes from water.

5. **Absorption of carbon dioxide** from the atmosphere

   \[ \text{NaOH(aq)} + \text{CO}_2(\text{g}) \rightarrow \text{NaHCO}_3(\text{aq}) \]

   \[ \text{NaHCO}_3(\text{aq}) + \text{NaOH(aq)} \rightarrow \text{Na}_2\text{CO}_3(\text{aq}) + \text{H}_2\text{O(l)} \]

6. **Effect of heat.** All Group 1 hydroxides, except \(\text{LiOH}\), are stable at Bunsen temperature. Group 2 hydroxides decompose as follows:

   \[ \text{Be(OH)}_2(\text{s}) \rightarrow \text{BeO(s)} + \text{H}_2\text{O}_2(\text{g}) \]

   \[ \text{Ca(OH)}_2(\text{s}) \rightarrow \text{CaO(s)} + \text{H}_2\text{O(g)} \]

   Thermal stability increases down the Group. Instability is caused by the polarising effects of the metal ions, destabilising the hydroxide ion by weakening the O-H bond by drawing charge away from the O atom, which then steals charge from the H atom to compensate. The smaller ions, like \(\text{Be}^{2+}\) and \(\text{Mg}^{2+}\) have higher charge densities and so a greater polarising and destabilising effect:

   (curly arrows show movement of electron pairs)
Solubility of s-block Compounds

Most Group 1 metal salts are ionic. In solution, the metal ions are hydrated, that is each ion surrounded by a shell of water molecules that adhere to the ion. Li⁺ and Be⁺ are very small ions and so have very high charge densities and this makes them attractive to electrons, so that in an ionic bond, these ions draw much of the electron they have lost back towards themselves, polarising the bond and making it more covalent. Thus, lithium and beryllium compounds are typically covalent or intermediate (partly covalent, partly ionic) and only sometimes ionic.

Factors determining solubility:

1. Crystal lattices are hard to break up – it takes a lot of energy to do so (the lattice dissociation enthalpy is highly endothermic - more so for smaller cations) so heat energy is absorbed when the lattice breaks up on dissolving in water.

2. Much energy is released when the ions hydrate (the enthalpy of hydration is highly exothermic) so heat energy is released when the ions hydrate.

The balance of these two processes determines whether or not the overall process of dissolving in water requires heat (is endothermic) or gives out heat (is exothermic). Although it is often true that exothermic reactions occur more readily than endothermic ones, the real determinant of whether or not a reaction proceeds is entropy. In any spontaneous process the overall entropy change of the Universe (the system and its surroundings) must increase (or remain zero for an equilibrium/balanced process).

In a spontaneous process the entropy of the Universe increases

Entropy is a measure of how ‘disordered’ a system is, or more specifically how much information is needed to describe it. In an ionic solid, the positions of the ions are basically fixed, and so we do not need much information to describe the position of each ion. If the salt is vapourised or dissolved, however, the ions are then free to move about at random and it takes much more information to describe the positions and velocities of each ion – the system is more disordered and so has more entropy. Vapourising a solid requires heat energy and in general:

In an exothermic process the system gives out heat to its surroundings and so the entropy of the surroundings increases.

In an endothermic process the system absorbs heat from its surroundings and so the entropy of its surroundings decreases.

E.g. Solid ammonium nitrate, NH₄NO₃, dissolves readily in water despite being an endothermic process, absorbing heat from the surroundings (the beaker of water feels cool when the salt dissolves) because the increase in entropy of the system is greater than the entropy decrease of the surroundings, so total entropy increases. The reaction is endothermic because more
heat energy is required to break-up the lattice than is produced when the ions solvate (because the adhesion between the ions in the solid are stronger than the adhesion between the ions and water molecules).

E.g. In contrast solid sodium hydroxide dissolves easily in an exothermic reaction (the beaker of water heats up).

**Solubility of hydroxides and halides**

Trends in solubility depend upon the size of the anions (the negatively charged ion) and cations (positively charged ions). The size of the metal cations increases down each group.

For example, for the salts of small anions, such as the fluorides and hydroxides, the solubility increases down the groups due to the decrease in lattice dissociation enthalpy - for the larger cations, the bond-length is greater and the bond therefore weaker and so more easily broken. This means that less heat must be borrowed from the environment, reducing the entropy of the surroundings less and increasing the overall entropy of the process.

The larger cation size also means that the enthalpy of hydration is smaller (the charge density is lower and so the water molecules are less strongly attracted).

the Group 1 hydroxides are all very soluble in water. The Group 2 hydroxides are much less soluble. Be(OH)₂ is only sparingly soluble and Mg(OH)₂ dissolves with difficulty. Group 2 salts are generally less soluble because the +2 charge on the cation results in a stronger bond and so the lattice is harder to break apart.

**Carbonates**

The carbonates are white crystalline solids. The carbonates of Group 1 metals are all soluble, Li₂CO₃ only sparingly so, and the solubility increases down the group (Rb₂CO₃ and Cs₂CO₃ are very soluble in water). Group 2 carbonates are all sparingly soluble only. Rain water slowly dissolves limestone due to natural weak acidity imparted by carbon dioxide (and acidic pollutants). the carbonates react with dilute acids:

\[
\text{CaCO}_3(s) + H_2\text{SO}_4(aq) \rightarrow \text{CaSO}_4(aq) + \text{CO}_2(g) + H_2\text{O}(l)
\]

\[
\text{Na}_2\text{CO}_3(s) + 2\text{HCl(aq)} \rightarrow 2\text{NaCl(aq)} + \text{CO}_2(g) + H_2\text{O}(l)
\]

Li₂CO₃ is anhydrous, but generally the other carbonates form with one or more waters of crystallisation in hydrous form, e.g. Na₂CO₃·H₂O, Na₂CO₃·7H₂O, Na₂CO₃·10H₂O. CaCO₃ occurs naturally in two different crustal structures as the minerals calcite and aragonite. SrCO₃ occurs as the mineral strontianite.
Thermal stability of the carbonates. The carbonates, like the hydroxides, also decompose on heating, with Group 2 carbonates again being less stable and the stability increasing down both groups. (Note that the anomalous behaviour of lithium can be attributed to its diagonal relationship with magnesium). Instability of carbonates is again due to the polarising effect of the metal cation destabilising the complex anion:

![Mg$^{2+}$:O$^{2-}$:C$^{2-}$:O$^{2-}$: → Mg$^{2+}$O$^{2-}$(s) + CO$_2$(g)](image)

There is an interesting experimental subtlety here. The decomposition is actually a reversible equilibrium reaction. Consider the following equilibrium reaction in which calcium carbonate decomposes on heating:

$$\text{CaCO}_3(s) \rightleftharpoons \text{CaO}(s) + \text{CO}_2(g)$$

Will increasing the pressure shift the equilibrium left or right? Explain why?

Method A:

Marble chips

Bunsen burner

Method B:

Crucible

Marble chips

Bunsen burner

Limewater (Ca(OH)$_2$)

Consider now the two heating methods, shown above, both using a Bunsen burner.

Q. In order to produce enough carbon dioxide to exceed atmospheric pressure, a temperature of 900°C is required, which is beyond the reach of a Bunsen burner which produces a maximum temperature of about 700°C. Calcium carbonate (as marble chips) is heated to decompose it by two different methods, as shown above. Method A involves heating the marble chips in a sealed tube and trying to get the CO$_2$ produced to bubble through limewater to see if a white precipitate is formed (Ca(OH)$_2$(aq) + CO$_2$(g) → CaCO$_3$(s) + H$_2$O(l)). No bubbles were observed and little decomposition of the CaCO$_3$ results. In method B, the marble chips are heated in an open crucible for ten minutes and then weighed. They lose considerable mass due to the loss of carbon dioxide gas and much of the calcium carbonate has decomposed. Explain why method B is much more successful in getting the calcium carbonate to decompose with reference to Le Chatelier’s Principle.

A. Le Chatelier’s Principle states that a system in equilibrium will adjust itself so as to try and compensate for any external disturbance applied to upset its balance. In this case, if we increase the pressure of the system, by increasing the pressure of CO$_2$(g) by making it harder for the gas to escape, as in method A, then the system compensates so as to reduce the pressure. It achieves this by reducing the rate of CO$_2$ production, in other words it opposes our change by shifting the equilibrium left, so that less carbonate decomposes! In method B, the CO$_2$ escapes as it forms and so is removed from the system. The system compensates by producing more CO$_2$(g) and the equilibrium shifts to the right, with more carbonate decomposing!
Limestone, slaked lime, quicklime and limewater

\[ \text{CaCO}_3(s) + \text{heat} \rightarrow \text{CaO}(s) + \text{CO}_2(g) \]  
\[ \text{slaking of the lime} \]

\[ \text{CaO}(s) + \text{H}_2\text{O}(l) \rightarrow \text{Ca(OH)}_2(s) + \text{heat} \]  
exothermic – water dripped onto CaO(s) hisses

\[ \text{CaCO}_3(s) \text{ is slaked lime} \]

\[ \text{Ca(OH)}_2(aq) + 2\text{HCl}(aq) \rightarrow \text{CaCl}_2(aq) + 2\text{H}_2\text{O}(l) \]
\[ \text{Ca(OH)}_2(aq) \text{ is basic} \]

\[ \text{CaO}(s) + \text{H}_2\text{O}(l) \rightarrow \text{Ca(OH)}_2(aq) \]
\[ \text{Ca(OH)}_2(aq) \text{ is limewater which can be used to test for CO}_2(g) \]

\[ \text{test for CO}_2(g) \]

\[ \text{Ca(OH)}_2(aq) + \text{CO}_2(g) \rightarrow \text{CaCO}_3(s) + \text{H}_2\text{O}(l) \]
\[ \text{The limewater turns cloudy as CaCO}_3(s) \text{ precipitates} \]

\[ \text{excess CO}_2(g) \]

\[ \text{CaCO}_3(s) + \text{H}_2\text{O}(l) + \text{CO}_2(g) \rightarrow \text{Ca(HCO}_3)_2(aq) \]
\[ \text{The limewater clears again as soluble calcium hydrogen carbonate (calcium bicarbonate) forms} \]

\[ \text{Limestone, slaked lime, quicklime and limewater} \]

Limestone, slaked lime, quicklime and limewater

\[ \text{CaCO}_3(s) + \text{heat} \rightarrow \text{CaO}(s) + \text{CO}_2(g) \]  
\[ \text{(quicklime)} \]

\[ \text{slaking of the lime} \]

\[ \text{CaO}(s) + \text{H}_2\text{O}(l) \rightarrow \text{Ca(OH)}_2(s) + \text{heat} \]  
exothermic – water dripped onto CaO(s) hisses

\[ \text{CaCO}_3(s) \text{ is slaked lime} \]

\[ \text{Ca(OH)}_2(aq) + 2\text{HCl}(aq) \rightarrow \text{CaCl}_2(aq) + 2\text{H}_2\text{O}(l) \]
\[ \text{Ca(OH)}_2(aq) \text{ is basic} \]

\[ \text{CaO}(s) + \text{H}_2\text{O}(l) \rightarrow \text{Ca(OH)}_2(aq) \]
\[ \text{Ca(OH)}_2(aq) \text{ is limewater which can be used to test for CO}_2(g) \]

\[ \text{test for CO}_2(g) \]

\[ \text{Ca(OH)}_2(aq) + \text{CO}_2(g) \rightarrow \text{CaCO}_3(s) + \text{H}_2\text{O}(l) \]
\[ \text{The limewater turns cloudy as CaCO}_3(s) \text{ precipitates} \]

\[ \text{excess CO}_2(g) \]

\[ \text{CaCO}_3(s) + \text{H}_2\text{O}(l) + \text{CO}_2(g) \rightarrow \text{Ca(HCO}_3)_2(aq) \]
\[ \text{The limewater clears again as soluble calcium hydrogen carbonate (calcium bicarbonate) forms} \]

\[ \text{Limestone is very slightly soluble in acidic water, leading to the gradual formation of} \]
\[ \text{caves and speleothems (rock formations such as stalagmites, which grow upwards, and} \]
\[ \text{stalagtites, which grow downwards) and other features of karst landscapes. limestone is} \]
\[ \text{strong enough to be used as building stone.} \]
**Bicarbonates (Hydrogen carbonates)**

**Hard water** is water that does not foam well with soap and typically contains calcium bicarbonate and/or magnesium bicarbonate, which are water soluble. On boiling, these form insoluble precipitates of calcium carbonate (white) and magnesium carbonate (yellowish-white) - collectively called **limescale**:

\[
\text{Ca(HCO}_3\text{)}_2(aq) \rightarrow \text{CO}_2(g) + \text{H}_2\text{O(l)} + \text{CaCO}_3(s)
\]

\[
\text{Mg(HCO}_3\text{)}_2 \rightarrow \text{CO}_2(g) + \text{H}_2\text{O(l)} + \text{MgCO}_3(s)
\]

Thus boiling and filtering results in soft water in which the hardness, called temporary hardness, has been removed. CaCl$_2$, CaSO$_4$, MgCl$_2$, MgSO$_4$, are not removed by boiling and give water permanent hardness (though it can be removed by other methods, such as ion-exchange). Hard water, apart from forming limescale which can damage appliances, also adversely effects the flavour of a cup of tea!

The mineral dolomite is a mixed carbonate of calcium and magnesium: [MgCa(CO$_3$)$_2$] and its structures consists of alternating layers of CaCO$_3$ (calcite) and MgCO$_3$ (magnesite). Mixed carbonates / bicarbonates also occur, e.g. Na$_2$CO$_3$·NaHCO$_3$·2H$_2$O.

**Beryl**

Beryl occurs in about 30 mineral species, including beryls, Be$_3$Al$_2$Si$_6$O$_{18}$. The structure of beryl is remarkable. Beryl is made up of hexagonal rings of Si and O atoms joined together by the metal ions. These hexagonal structures are joined together in hollow columns, forming open tubes that can trap small quantities of other elements. These trapped trace elements determine the colour. Colourless beryl is goshenite, blue beryl is aquamarine, yellow beryl is heliodor, pink beryl is morganite, red beryl is bixbite. The green variety of beryl is the best known, as emerald, and the green colour is due to Cr, V and Fe impurities.
**Other Oxoacid Salts of s-block Metals**

**Nitrates**

These can be formed, for example, by the following reactions:

- sodium carbonate and nitric acid:
  \[ \text{Na}_2\text{CO}_3(\text{s}) + 2\text{HNO}_3(\text{aq}) \rightarrow 2\text{NaNO}_3(\text{aq}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \]
  (the solid salt can then be extracted by evaporation and crystallisation)

- sodium hydroxide and nitric acid
  \[ \text{NaOH}(\text{aq}) + \text{HNO}_3(\text{aq}) \rightarrow \text{NaNO}_3(\text{aq}) + \text{H}_2\text{O}(\text{l}) \]

- sodium chloride and nitric acid
  \[ \text{NaCl}(\text{s}) + \text{HNO}_3(\text{g}) \rightarrow \text{NaNO}_3(\text{s}) + \text{HCl}(\text{g}) \]
  or
  \[ \text{NaCl}(\text{aq}) + \text{HNO}_3(\text{aq}) \rightarrow \text{NaNO}_3(\text{aq}) + \text{HCl}(\text{aq}) \]

- sodium nitrate and potassium chloride
  \[ \text{NaNO}_3(\text{aq}) + \text{KCl}(\text{aq}) \rightarrow \text{KNO}_3(\text{aq}) + \text{NaCl}(\text{aq}) \]
  This is a metathesis (double displacement) reaction

The s-block nitrates are all soluble in water. LiNO\(_3\) is anhydrous and hygroscopic and is used in scarlet flares and pyrotechnics. Solid sodium nitrate, NaNO\(_3\), or saltpetre is found in large deposits in Chile (possibly as the result of bacterial decomposition of marine detritus).

The nitrates decompose on heating:

- at 500°C: \( 2\text{NaNO}_3(\text{s}) \rightleftharpoons 2\text{NaNO}_2(\text{s}) + \text{CO}_2(\text{g}) \)
- at 800°C: \( 2\text{NaNO}_3(\text{s}) \rightleftharpoons \text{Na}_2\text{O}(\text{s}) + \text{N}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \)

Thermal stability increases down the groups.

Potassium nitrate is used in black **gunpowder**, the combustion of which is complex and depends on the mixture of KNO\(_3\), S and C, but can be approximated by:

- \( 2\text{KNO}_3(\text{s}) + \text{S}(\text{s}) + 3\text{C}(\text{s}) \rightarrow \text{K}_2\text{S}(\text{s}) + \text{N}_2(\text{g}) + 3\text{CO}_2(\text{g}) \)
  or
- \( 10\text{KNO}_3(\text{s}) + 3\text{S}(\text{s}) + 8\text{C}(\text{s}) \rightarrow 2\text{K}_2\text{CO}_3(\text{s}) + 3\text{K}_2\text{SO}_4 + 6\text{CO}_2(\text{g}) + 5\text{N}_2(\text{g}) \)

A typical mixture might be: 75% KNO\(_3\) powder, 15% C powder and 10% S powder by weight.
Nitrites
The s-block metal nitrites are white crystalline hygroscopic salts and very soluble in water.

_Preparation:_

\[
\begin{align*}
4\text{NO(g)} + 2\text{KOH(aq)} & \rightarrow 2\text{KNO}_2\text{(aq)} + \text{N}_2\text{O(g)} + \text{H}_2\text{O(l)} \\
6\text{NO(g)} + 4\text{KOH(aq)} & \rightarrow 4\text{MNO}_2\text{(aq)} + \text{N}_2\text{(g)} + 2\text{H}_2\text{O(l)}
\end{align*}
\]

From thermal decomposition of nitrates:

\[
\begin{align*}
\text{KNO}_3\text{(s)} + \text{Pb(s)} & \rightarrow \text{KNO}_2\text{(s)} + \text{PbO(s)} \\
2\text{RbNO}_3\text{(s)} + \text{C(s)} & \rightarrow 2\text{RbNO}_2\text{(s)} + \text{CO}_2\text{(g)}
\end{align*}
\]

_Commercial production of sodium nitrite:_

\[
\text{Na}_2\text{CO}_3\text{(aq)} + \text{NO(g)} + \text{NO}_2\text{(g)} \rightarrow 2\text{NaNO}_3\text{(s)} + \text{CO}_2\text{(g)}
\]

The nitrites disproportionate (some of the N is reduced, some oxidised) when heated in the absence of air:

\[
5\text{NaNO}_2\text{(s)} \rightarrow 3\text{NaNO}_3\text{(s)} + \text{Na}_2\text{O(s)} + \text{N}_2\text{(g)}
\]

Sulphates
The s-block sulphates are white crystalline ionic solids. Anhydrous sodium sulphate, \(\text{Na}_2\text{SO}_4\), occurs naturally as the mineral thenardite, in arid conditions (it is found, for example, in volcanic caves and Mt. Etna). The mineral mirabilite is \(\text{Na}_2\text{SO}_4\cdot10\text{H}_2\text{O}\), which is Glauber’s salt (sal mirabilis). In moist air, thenardite converts to mirabilite. Sodium sulphate is stable and unreactive at room temperature, but can be reduced at high temperatures to sodium sulphide, \(\text{Na}_2\text{S}\). Solutions of the salt are neutral (pH 7). Some reactions of sodium sulphate are:

\[
\begin{align*}
\text{Na}_2\text{SO}_4\text{(aq)} + \text{H}_2\text{SO}_4\text{(aq)} & \rightleftharpoons 2\text{NaHSO}_4\text{(aq)} \\
(\text{sodium hydrogen sulphate or sodium bisulphate})
\end{align*}
\]

_Precipitation of insoluble sulphates:_

\[
\begin{align*}
\text{Na}_2\text{SO}_4\text{(aq)} + \text{BaCl}_2\text{(aq)} & \rightarrow 2\text{NaCl(aq)} + \text{BaSO}_4\text{(s)} \\
\text{SO}_4^{2-}\text{(aq)} + \text{Pb}^{2+}\text{(aq)} & \rightarrow \text{PbSO}_4\text{(s)}
\end{align*}
\]

The s-block sulphate are soluble in water, and though \(\text{BaSO}_4\) is barely soluble and solubility of \(\text{SrSO}_4\) and \(\text{CaSO}_4\) is low. Anhydrous \(\text{CaSO}_4\) occurs as the mineral anhydrite and \(\text{CaSO}_4\cdot2\text{H}_2\text{O}\) is gypsum, with a variety of forms such as the transparent, colourless selenite (‘Moon rock’), the fibrous satin spar and the fine-grained alabaster. Gypsum forms rosettes, needle and fibres. Gypsum is used to make Plaster of Paris (\(\text{CaSO}_4\cdot½\text{H}_2\text{O}\)). \(\text{MgSO}_4\cdot7\text{H}_2\text{O}\) is sold in pharmacies as ‘epsom salts’ for health and medicinal uses.
Potassium sulphate, K₂SO₄, also called potash of sulphur, is a white, ionic and crystalline solid, soluble in water. It is used in the manufacture of fertilisers. Anhydrous K₂SO₄ forms beautiful 6-sided pyramidal (rhombic) crystals, which are hard, resistant to corrosion and has a bitter-salty taste.

Some more s-block sulphate minerals are:
- kainite MgSO₄·KCl·H₂O
- schonite K₂SO₄·MgSO₄·6H₂O
- leonite K₂SO₄·MgSO₄·4H₂O
- langbeinite K₂SO₄·2MgSO₄
- glaserite K₃Na(SO₄)₂
- polyhalite K₂SO₄·MgSO₄·2CaSO₄·2H₂O

Potassium bisulphate, or potassium hydrogen sulphate, KHSO₄ can be formed from potassium sulphate and sulphuric acid:

\[ \text{K}_2\text{SO}_4 + \text{H}_2\text{SO}_4 \rightleftharpoons 2\text{KHSO}_4(aq) \]

(addition of excess ethanol precipitates ethanol)

The resulting solution behaves like a mixture of the reagents, however, dry molten KHSO₄(l) behaves like concentrated sulphuric acid heated beyond its normal boiling point and is a disintegrating agent.

Bologna stones are stones made from impure BaSO₄ and they will glow in the dark for up to six years if heated with charcoal! BaSO₄ is used as a white paint pigment.

SrSO₄ occurs as the mineral celestite.

Calcium hydrogen sulphite (calcium bisulphite) Ca(HSO₃)₂ has been used in the paper industry to remove lignin from wood to leave the cellulose which is used to make paper.

**Phosphates**

Sodium phosphate, Na₃PO₄, is a white powder (Na₃PO₄·12H₂O) and is used as a cleaning agent and degreaser. It is very water soluble, ionic, and dissolves to give solutions of alkaline pH. It is the food additive E339 (used as a buffer, emulsifier, thickening agent and metal-chelator). The hydrogen phosphates are also white powders: NaH₂PO₄·2H₂O (sodium biphosphate or sodium dihydrogen phosphate), Na₂HPO₄ and its hydrated form, Na₂HPO₄·7H₂O.
Complexes

In solution, positive metal ions attract electrons. If a chemical that is able to donate a pair of electrons is present, then it can donate both electrons, forming a covalent bond with the metal. Such a covalent bond, in which both electrons come from one reactant is called a dative or coordinate bond, but is otherwise simply a covalent bond. (However, measurements suggest that these dative bonds may be more ionic than covalent). Transition (d-block) metals form these complexes readily, since they can accommodate additional electrons in their d-orbitals, and the complexes formed are often highly coloured. The metal ion sits at the centre of the complex and one or molecules, called ligands, dative bond to it. The remaining net charge, however, is usually depicted distributed around the molecule (is this what happens if the bonds are largely ionic?).

The s-block metals do not form complexes as readily as d-block metals. In Group 1 metals, the ability to form complexes decreases down the group. Li forms complexes most easily, since it is small and has a very high charge density to attract electrons for dative bond formation. Molecules containing oxygen atoms with one or lone-pair of electrons make good ligands (O-ligands). For example:

\[
\text{OH} + \text{Li} + \text{acetone (propanone)} \rightarrow \text{Li acetone acetone}
\]

Group 2 metals form more complexes than Group 1 metals, especially with O and N-ligands, since they have a higher charge density. Be has the greater tendency to form covalent bonds and so forms the most stable complexes. These complexes are mostly confined to rings molecules, such as ion-chelators like EDTA (ethylene diamine tetra-acetic acid).

\[
\text{EDTA complex of calcium}
\]

EDTA: \((\text{HOOCCCH}_2)_2\text{NCH}_2\text{CH}_2\text{N(CH}_2\text{COO}^-\text{H}^+)\)
The anomalous behaviour of lithium

Lithium (Li) has a diagonal relationship to magnesium (Mg) with both metals exhibiting some behaviours traditionally considered non-metallic. The reason for lithium’s anomalous behaviour is the very small size of the Li\(^+\) ion which is therefore highly polarising and quite electronegative for a metal – polarising ionic bonds to make them partially or mostly covalent. These anomalies are:

1. **Thermal stability.** Li\(^+\) ionic salts of large polarisable anions, such as carbonate (CO\(_3\)^{2−}\) and nitrate (NO\(_3\)^{−}\) are less thermally stable, suggestive of covalent character and decompose at lower temperatures than the corresponding sodium salts:

   \[
   \text{Li}_2\text{CO}_3(s) \rightarrow \text{Li}_2\text{O}(s) + \text{CO}_2(g) \\
   (\text{Li}_2\text{CO}_3 \text{ decomposes at about } 700^\circ\text{C, Na}_2\text{CO}_3 \text{ at } 800^\circ\text{C}) \\
   \text{LiNO}_3(s) \rightarrow \text{Li}_2\text{O}(s) + \text{NO}_2(g) \\
   \text{NaNO}_3(s) \rightarrow \text{NaNO}_2(s) + \frac{1}{2}\text{O}_2(g)
   \]

   LiOH is thermally unstable, the other Group 1 metal hydroxides are stable:

   \[
   2\text{LiOH}(s) \rightarrow \text{Li}_2\text{O}(s) + \text{H}_2\text{O}(l)
   \]

   Additionally, Li forms no solid bicarbonate, hydrosulphide, triiodide or superoxide, as these are too unstable at room temperature.

   Note: in no way are we implying that covalent bonds are weaker than ionic bonds, since they are of comparable strength, but often in covalently bound molecules, individual molecules in a solid are held together by weaker van der Waals forces and so the solids are thermally unstable and volatile, often subliming, although individual molecules are very stable. Exceptions to this occur when covalent solids form macromolecular crystals, as in diamond and quartz, for example, in each atom/molecule is held by covalent bonds – these are thermally very stable structures.

2. **Solubility.** Li\(^+\) salts of anions of high charge density (such as fluoride, F\(^−\)) are less soluble than for other Group 1 metals, e.g. LiOH, LiF, Li\(_3\)PO\(_4\), Li\(_2\)CO\(_3\). Lithium halides are more covalent and so are more soluble in organic solvents, and less soluble in water. (The tendency towards a reduction of charge on the Li means that less heat is released when the ‘ions’ solvate and so there is tendency toward lower entropy in the end-products).

3. **Complex formation.** Li forms more stable covalent bonds than other alkali metals and forms more complexes, especially with O and N-donors.

4. **Li Reacts very slowly with water.**

5. **Li forms stable salts with anions of high charge density due to high lattice energy.** E.g., Li forms only the normal oxide in air (not the peroxide or superoxide) and reacts with nitrogen to form lithium nitride, Li\(_3\)N, whilst the other Group 1 metals do not react with nitrogen.

6. **Li compounds are more covalent.** The tendency of Li to form covalent bonds with carbon makes lithium alkyls and lithium aryls more stable than those of the other Group 1 metals.

7. **Li forms shorter and stronger metallic bonds and so has a higher melting/boiling point, higher density and greater hardness than other Group 1 metals.** Its small atomic radius also gives it a high first ionisation energy (the outermost electrons are closer to the nucleus and so more tightly bound to it).
The anomalous behaviour of beryllium

Be differs more from Mg than Li does from Na. Be has a diagonal relationship to aluminium and both elements have some behaviours in common. Be is a steel-grey metal.

1. Be has a higher melting/boiling point, higher density and much greater hardness than Mg.

2. Like Li, Be has a small atomic radius and there is a higher attraction between the nucleus and the outer electrons, resulting in a higher electronegativity and electron affinity and a higher ionisation energy.

3. The small Be$^{2+}$ ion has a higher polarising power and so all or most of its compounds are largely covalent (and so often have lower melting/boiling points due to weak intermolecular forces). Its compounds are also more soluble in organic solvents.

4. Be does not react with water and is resistant to acid (presumably due to a protective oxide film). The metal is rendered passive by concentrated nitric acid.

5. Beryllium halides, BeX$_2$, are hygroscopic solids that fume in air.

6. Beryllium is amphoteric:

$$2[\text{Be(H}_2\text{O)}_4]^{2+} \rightleftharpoons 2\text{H}_3\text{O}^+ + [(\text{H}_2\text{O})_3\text{BeOBe(H}_2\text{O)}_3]^2+$$

$$\text{OH}^-$$

$$[\text{Be(OH)}_4]^{2-}(\text{aq}) \rightleftharpoons \text{Be(OH)}_2(\text{s})$$

7. Be is a poor reducing agent (due to its reluctance to lose its valence electrons) and does not normally dissolve in ammonia to give a blue reducing solution (though it can be made to dissolve in ammonia by electrolysis).

8. Salts of large anions are very unstable and those that are stable are hydrated, e.g. BeCO$_3$·4H$_2$O, BeSO$_4$·4H$_2$O, both of which decompose on heating to give BeO.

9. Be compounds tend to have coordination numbers of 4. The ion is too small to have higher coordination numbers. E.g. [Be(H$_2$O)$_4$]$^{2+}$ occurs in hydrated beryllium salts (see point 8). BeO has 4:4 coordination (and is a high melting point solid, hard and amphoteric). Also: BeF$_4^{2-}$, Be(acac)$_2$ (where acac is acetylacetone). In the vapour phase, the chloride contains (BeCl$_2$)$_2$ molecules, with chlorines bridging between the two Be atoms.

9. BeCl$_2$ is a covalent chain polymer, existing as dimers, Be$_2$Cl$_4$, in the vapour phase, which break-up into monomers, BeCl$_2$, at higher temperatures (AlCl$_3$ is similar).

10. No peroxide or superoxide is formed.

11. Be is poisonous since it has strong complexing power with O and N-ligands.

12. When treated with acetylene, Mg forms the acetylide, MgC$_2$, whereas Be forms the carbide, Be$_2$C.
Note the halide bridge structure with the halogens arranged tetrahedrally around each Be.

\[
\text{BeCl}_2
\]

AlCl\(_3\) has a similar structure, but existing as shorter Al\(_2\)Cl\(_6\) molecules held together by weak intermolecular van der Waal’s forces. In the gas phase it forms Al\(_2\)Cl\(_6\) dimers which break-up into AlCl\(_3\) monomers at higher temperatures. AlBr\(_3\) and AlI\(_3\) are similar.

**Organometallic compounds**

**Beryllium alkyls**

These are solids or liquids of high reactivity – they are spontaneously flammable in air and violently hydrolysed by water. They contain a metal atom covalently bonded to a carbon atom, the latter being part of a hydrocarbon chain (alkyl) or aromatic ring (aryl). For example, dimethylberyllium can be prepared by heating Be metals and dimethylmercury at 110\(^\circ\)C:

\[
\text{Hg(CH}_3\text{)}_2 + \text{Be} \rightarrow \text{Be(CH}_3\text{)}_2 + \text{Hg}
\]

which can be written: HgMe\(_2\) + Be \rightarrow BeMe\(_2\) + Hg, where Me = CH\(_3\) (methyl group)

beryllium aryls can be formed by reacting the lithium aryl (in hydrocarbon solution) with beryllium chloride:

\[
2\text{LiC}_6\text{H}_5 + \text{BeCl}_2 \rightarrow 2\text{LiCl(s)} + \text{Be(C}_6\text{H}_5)_2
\]

Dimethylberyllium is a chain polymer like BeCl\(_2\), with bridging methyl (CH\(_3\)) groups, and is monomeric, BeMe\(_2\), in the vapour phase. Higher alkyls are progressively less polymerised, for example, diethylberyllium, Be(CH\(_3\)CH\(_3\))\(_2\) is dimeric in benzene and t-butyl-beryllium is monomeric.
Organomagnesium Compounds

These are probably the most widely used organometallic compounds, for example the Grignard reagents, RMgX where \( X \) is a halogen and \( r \) a hydrocarbon group, used in the synthesis of alkyl and aryl compounds of other elements and in organic synthesis. Sometimes a Grignard reagent is written as R-MgX, to emphasise the covalent bond between carbon and Mg.

Formation of a Grignard reagent from organic halide, RX:

\[
RX + Mg \rightarrow RMgX
\]

(usually most rapid when \( X = I \), iodine).

The hydrolysis of Grignard reagents by dilute acids is one method of preparing alkanes:

\[
RMgCl + HCl \rightarrow RH + MgCl_2
\]

Reaction of a Grignard reagent (in ether) with carbon dioxide, followed by hydrolysis of the resultant salt with dilute acid, gives a carboxylic acid:

\[
RMgBr + CO_2 \rightarrow RCOOMgBr + HBr \rightarrow RCOOH + MgBr_2
\]

Grignard reagents react with esters, and hydrolysis of the end-product results in a tertiary alcohol (an alcohol in which the c atom joins the –OH group has three other C atoms bonded to it). E.g reaction of an ester with \( C_2H_5MgBr \), followed by hydrolysis in dilute hydrobromic acid, HBr(aq):

Another example are the magnesium alkyls, e.g. dialkylmagnesium:

\[
HgR_2(s) + Mg(s) \rightarrow Hg(l) + MgR_2(s)
\]

(the Mg is in excess and the product is extracted in an organic solvent)

Lithium alkyls also occur and are synthesised by reaction with alkyl halides in organic solvent:

\[
2Li(s) + C_2H_5Cl(in ether) \rightarrow C_2H_5Li + LiCl
\]

Organic Salts

Organic salts of s-block metals differ from organometallic compounds in that the bond between the metal and the organic ion is ionic.

Alcohols and phenols react with sodium metal to form alkoxides and phenoxides:

\[
2ROH + 2Na(s) \rightarrow H_2 + 2ROO^-Na^+
\]

e.g. \( 2CH_3CH_2OH(l) + 2Na(s) \rightarrow H_2(g) + 2CH_3CH_2O^-Na^+ \)

(ethanol + sodium \( \rightarrow \) hydrogen + sodium ethoxide)
Phenols, being more acidic than alcohols, will also neutralise NaOH:

\[ C_6H_5OH + NaOH \rightarrow C_6H_5^+Na^- + H_2O \]

(phenol + sodium hydroxide → sodium phenoxide + water)

In these equations, the charges have been added to illustrate the ionic nature of the bonding with the sodium.

Sodium and sodium hydroxide will also react with carboxylic acids:

\[ CH_3COOH + NaOH \rightarrow CH_3COO^-Na^+ + H_2O \]

**Uses of the Metals**

The s-block metals and their compounds have so many applications, that only a selected view will be mentioned here.

**Concrete and Cement**

Cement is manufactured from limestone (CaCO_3), clay/sand as follows:

1. Calcining (heating) of limestone

\[ CaCO_3(s) \rightarrow CaO(s) + CO_2(g) \]

This occurs in the lower temperature region of a kiln (cooler than about 900°C). In this process, the limestone and silica (clay/sand) and small amounts of bauxite and iron ore, ground to a fine powder and mixed, are fed into a rotary cement kiln (the largest piece of moving industrial equipment in the World?). This kiln is a long sloping cylinder with a temperature gradient up to 1480°C and rotates slowly to mix the contents.

2. Bonding of CaO and silicates to give di- and tricalcium silicates (and small amounts of tricalcium aluminate and tetracalcium aluminoferrite, the levels of which produce different types of cement). This bonding occurs at high temperatures, in the molten state. The products cool to form solid pellets (clinker) and are ground to a fine powder and then a small amount of gypsum (CaSO_4·2H_2O) is added.

Concrete is produced from cement and a fine aggregate (sand) and a coarse aggregate (gravel or crushed stone) and water (and various small quantities of other chemicals to alter the properties).

When water is added to cement, it forms a hydrated gel or slurry that fills spaces between aggregates in concrete. Mortar, for binding bricks, is a mixture of slaked lime, sand and water.

**Alloys**

Be alloys are light, but strong and hard, and used as structural alloys in aircraft, missiles, spacecraft and satellites. Mg alloys have similar uses. Duralumin (>90% Al, about 4% Cu, 0.5-1% Mg and <1% Mn) has been used in aircraft manufacture (the alloy is initially too soft, but hardens on heating). Magnalium (Al + 5% Mg) is used in metal mirrors for scientific instruments. Be alloys are also used to make golf clubs, gyroscopes and inertial guidance systems, rocket engine liners and laser tubes. Be is also used as a reflector/moderator in nuclear reactors.
BeO has a very high melting point, making it useful for nuclear work and in ceramics. SrO screens out X-rays (as does BaO) and is used in TV screen glass for old cathode-ray tube sets. $^{90}\text{Sr}$ is a radioisotope of strontium produced in nuclear explosions. It is incorporated into bone, in place of calcium, and can be used to distinguish archaeological finds from recent human remains in forensics.

Ba is radioactive and has been used in radiotherapy, as a source of neutron radiation, and in self-luminous paints in clock faces.

**Pyrotechnics**

With their brilliant flame colours, s-block metal compounds find uses in fireworks, Sr is used in red fireworks and flares as SrCO$_3$ and Sr(NO$_3$)$_2$. Ba(NO$_3$)$_2$ and Ba(ClO$_3$)$_2$ give green flames, whilst Mg gives brilliant white sparks. LiNO$_3$ is used in scarlet flares. Ca salts deepens firework colours and produce orange colours.