# Oxidation numbers

## Introduction

- Oxidation numbers (also called oxidation states) express the combining power of elements.
- The concept of oxidation numbers was developed to overcome the uncertainties associated with the use of valency to describe the combining power of atoms of elements.
  For example, in $Ni(CO)_4$, the valency concept gives the valency of nickel as 4 yet it is 0. This is because no electrons from nickel atom have involved in bond formation.
- Oxidation number refers to the net charge that would remain on an atom of an element in a compound if all the other atoms bonded to it were to be removed.

## Useful concepts in determining the oxidation numbers

1. The oxidation state of an element can be zero, positive or negative, whole number or fraction.
2. The signs on oxidation states are put before the number. This helps to distinguish them from valencies/charges.
   For example; $+2$ $\mathbf{not}$ $2$ $or$ $2^+$$or$ $^+2$, $-3$ $\mathbf{not}$ $3$ $or$ $3^-$$or$ $^-3$ etc.
3. The oxidation state (s) of:
   (a) uncombined elements (such as $Cl, Na, Al, S$, etc.) is **zero**.
   Similarly the oxidation number of iodine in $I_2$, oxygen in $O_2$, sulphur in $S_8$, etc. is **zero**.
   (b) one-atom ions (monoatomic ions) is equal to the charge on the ions.
   For example:

| Ion | $Na^+$ | $Cu^{2+}$ | $O^{2-}$ | $Cl^-$ |
|---|---|---|---|---|
| Oxidation state | $+1$ | $+2$ | $-2$ | $-1$ |

   (c) each fluorine atom is always $-1$.
   (d) elements in group I and group II in compounds are fixed as $+1$ and $+2$ respectively.
   (e) each hydrogen atom is always $+1$ in most compounds except in ionic/metal hydrides such as $NaH$ and $MgH_2$, where it assumes an oxidation state of $-1$.
   (f) oxygen in most compounds is $-2$ except in:
   (i) peroxides where it occurs as $O_2^{2-}$ ion with each atom having an oxidation state of $-1$.
   (ii) superoxides where it occurs as $O_2^-$ ion with each atom having an oxidation state of $-\frac{1}{2}$.

(iii) oxygen difluoride, $F_2O$ where it has an oxidation state of $+2$. This is because fluorine atom is more electronegative than the oxygen atom.

(g) neutral molecules (such as $H_2O$, $CO$, $NH_3$ etc.) in complexes is **zero**.

4. When two or more atoms of the same element occur in the compound, the oxidation state of the element is the average of the oxidation state of the group.
   For example, the oxidation state of chromium in $K_2Cr_2O_7$ should be divided by 2 since there are two atoms of chromium in the compound.
5. The **sum** of the oxidation numbers of the atoms or ions in a compound is **zero**.
   For example:
   (a) In NaCl; $(oxidation\ number\ of\ Na) + (oxidation\ number\ of\ Cl) = 0$
   (b) In $CaBr_2$; $(oxidation\ number\ of\ Ca) + 2(oxidation\ number\ of\ Br) = 0$
6. The **sum** of the oxidation numbers of the atoms in an ion is equal to the charge on the ion.
   For example:
   (a) In $SO_4^{2-}$; $(oxidation\ number\ of\ S) + 4(oxidation\ number\ of\ O) = -2$
   (b) In $Cr_2O_7^{2-}$; $2(oxidation\ number\ of\ Cr) + 7(oxidation\ number\ of\ O) = -2$
7. Some elements have variable oxidation states. For example, iron exhibits oxidation states of $+2$ and $+3$ in its ions/compounds.
8. In either a compound or an ion, the more electronegative element is given the negative oxidation number.

## Some worked out examples

Work out the oxidation state of each of the following elements.

| | | |
|---|---|---|
| (a) carbon in $CO_2$<br>Let the o.s be $x$<br>$x + 2(-2) = 0$<br>$\Rightarrow x = +4$ | (b) nitrogen in $HNO_2$<br>Let the o.s be $x$<br>$(+1) + x + 2(-2) = 0$<br>$\Rightarrow x = +3$ | (c) nitrogen in $HNO_3$<br>Let the o.s be $x$<br>$(+1) + x + 3(-2) = 0$<br>$\Rightarrow x = +5$ |
| (d) chromium in $K_2Cr_2O_7$<br>Let the o.s be $x$<br>$2(+1) + 2x + 7(-2) = 0$<br>$\Rightarrow x = +6$ | (e) chromium in $Cr_2O_7^{2-}$<br>Let the o.s be $x$<br>$2x + 7(-2) = -2$<br>$\Rightarrow x = +6$ | (f) sulphur in $SO_4^{2-}$<br>Let the o.s be $x$<br>$x + 4(-2) = -2$<br>$\Rightarrow x = +6$ |
| (g) Cr in $[Cr(H_2O)_4Cl_2]^+$<br>Let the o.s be $x$<br>$x + 4(0) + 2(-1) = +1$<br>$\Rightarrow x = +3$ | (h) silver in $[Ag(NH_3)_2]^+$<br>Let the o.s be $x$<br>$x + 2(0) = +1$<br>$\Rightarrow x = +1$ | (i) Al in $Al(OH)_6^{3-}$<br>Let the o.s be $x$<br>$x + 6(-1) = -3$<br>$\Rightarrow x = +3$ |

**Question**:
Work out the oxidation state of each of the following elements.
(a) Sulphur in (i) $H_2S$ (ii) $SO_4^{2-}$ (iii) $S_2O_8^{2-}$ (iv) $S_2O_3^{2-}$ (v) $S_4O_6^{2-}$
(b) Iodine in $IO_3^-$.

(c) Chlorine in (i) $HClO$ (ii) $HClO_3$ (iii) $HClO_4$ (iv) $ClO^-$(v) $ClO_4^-$
(d) Iron in (i) $Fe(CO)_5$ (ii) $[Fe(SCN)(H_2O)_5]^{2+}$ (iii) $Fe(CN)_6^{3-}$
(e) Chromium in (i) $[Cr(H_2O)_6]^{3+}(Cl^-)_3$ (ii) $[CrCl(H_2O)_5]^{2+}$
(f) Platinum in $[Pt(NH_3)_4]^{2+}$

## Oxidation numbers and nomenclature

- The knowledge of oxidation numbers is useful in naming of compounds/ions.

**Case 1: Cations**

- These are positive ions.
- They are given the name of the element together with the oxidation number, if oxidation state is variable.

For example:

| Cation | Name | Cation | Name |
|---|---|---|---|
| $Na^+$ | Sodium ion **not** sodium(I) ion | $Fe^{3+}$ | Iron(III) ion **not** iron ion |
| $Al^{3+}$ | Aluminium ion **not** aluminium(III) ion | $Cr^{2+}$ | Chromium(II) ion |
| $Fe^{2+}$ | Iron(II) ion **not** iron ion | $Cr^{6+}$ | Chromium(VI) ion |

**Case 2: Anions**

- These are negative ions.
- Elemental anions are named after the element, with the ending $-ide$.

For example:

| Anion | Name | Cation | Name |
|---|---|---|---|
| $H^-$ | Hydride | $Cl^-$ | Chloride |
| $S^-$ | Sulphide | $N^{3-}$ | Nitride |

- Polyatomic/compound anions have names with the ending $-ide$, $-ite$ or $-ate$.

The names of oxoanions/oxyanions in which the oxidation state of the element bonded to oxygen differs are derived from the name of the element with the ending $-ate$. The oxidation state of the element is added to help distinguish the oxyanions.

Example of some common oxyanions are:

| Anion | Name | Anion | Name |
|---|---|---|---|
| $CO_3^{2-}$ | Carbonate ion | $ClO^-$ | Chlorate(I) ion |
| $HCO_3^-$ | Hydrogencarbonate ion | $ClO_3^-$ | Chlorate(V) ion |
| $SO_3^{2-}$ | Sulphate(IV) ion or sulphite ion | $CrO_4^{2-}$ | Chromate(VI) ion |
| $SO_4^{2-}$ | Sulphate(VI) ion or sulphate ion | $Cr_2O_7^{2-}$ | Dichromate(VI) ion |
| $NO_2^-$ | Nitrate(III) ion or nitrite ion | $MnO_4^{2-}$ | Manganate(VI) ion |
| $NO_3^-$ | Nitrate(V) ion or nitrate ion | $MnO_4^-$ | Manganate(VII) ion |

**Case 3: Acids**

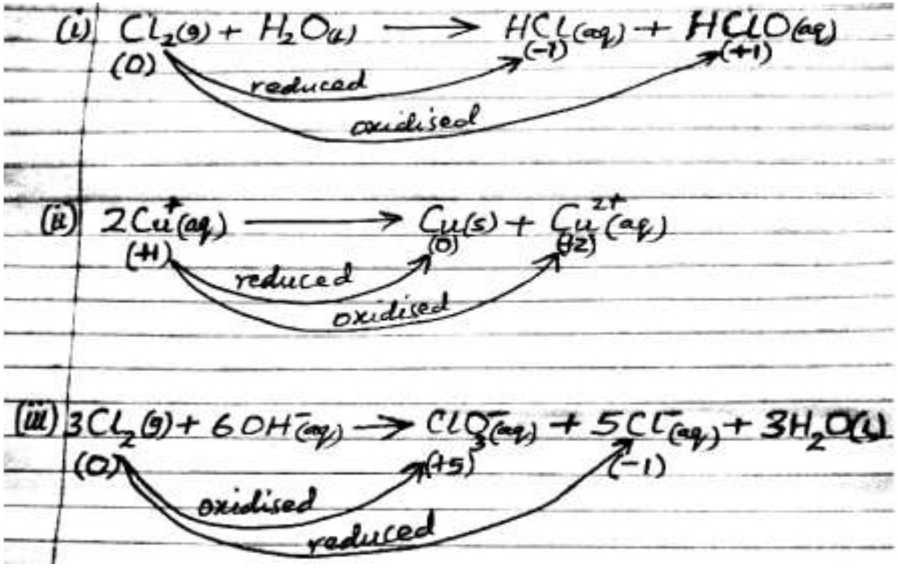
- They are named after their anions.

  Examples of some common oxyanions are:

| **Anion** | **Name** | **Anion** | **Name** |
|---|---|---|---|
| $HClO$ | Chloric(I) acid | $HNO_2$ | Nitric(III) acid/nitrous acid |
| $HClO_2$ | Chloric(III) acid | $HNO_3$ | Nitric(V) acid/nitric acid |
| $HClO_3$ | Chloric(V) acid | $H_2SO_3$ | Sulphuric(IV) acid/sulphurous acid |
| $HClO_4$ | Chloric(VII) acid/ perchloric acid | $H_2SO_4$ | Sulphuric(VI) acid/sulphuric acid |
| $H_3PO_3$ | Phosphoric(III) acid/ phosphonic acid | $H_3PO_4$ | Phosphoric(V) acid/ orthophosphoric acid |

## Disproportionation reactions

- A reaction in which a single chemical species undergoes simultaneous oxidation and reduction is a called a **disproportionation reaction**.
- Examples of some common disproportionation reactions.



# The s block elements

## Introduction

- These include the elements in group I and group II of the Periodic Table.
- They are called s block elements because their outermost electrons are being filled in s sub energy level.

## The chemistry of group I elements

- The members of Group I include:

| | | |
|---|---|---|
| Lithium; Li | Potassium; K | Caesium; Cs |
| Sodium; Na | Rubidium; Rb | Francium; Fr |

- The some of the physical properties of the elements are:

| Element | Outermost E.C | 1st I.E (kJ mol$^{-1}$) | 2nd I.E (kJ mol$^{-1}$) | Atomic radius (nm) | M.pt (℃) | B.pt (℃) | Density $(gcm^{-3})$ | S.E.P $E^{\theta}$ (Volts) |
|---|---|---|---|---|---|---|---|---|
| Li | $2s^2$ | 520 | 7300 | 0.155 | 180 | 134 | 0.53 | $-3.04$ |
| Na | $3s^2$ | 496 | 4600 | 0.190 | 98 | 883 | 0.97 | $-2.71$ |
| K | $4s^2$ | 418 | 3100 | 0.235 | 64 | 774 | 0.86 | $-2.92$ |
| Rb | $5s^2$ | 403 | 2700 | 0.248 | 39 | 688 | 1.53 | $-2.92$ |
| Cs | $6s^2$ | 374 | 2400 | 0.267 | 28 | 678 | 1.87 | $-3.02$ |
| Fr | $7s^2$ | | | | | | | |

## Some general remarks about the elements

- They are called alkali metals since:
  (i) their hydroxides dissolve in water to form alkalis.
  (ii) elements react with water to form alkalis.
- Their general outermost electronic structure is $ns^1$; where $n$ is the principal quantum number denoting the outermost energy level.

- All show a fixed oxidation state of $+1$. This is because loss of the one outermost $s-$electron leaves a fully filled and stable outermost sub energy level (i.e. an inert gas electronic structure is formed).
- As the atomic number increases (i.e. down the group, from lithium to caesium);
  (i) the atomic radius increases and the outermost $s -$ electrons (valence electrons) become more distant from the nucleus.
  (ii) both first ionization energy and electropositvity decrease.
  (iii)reactivity of the elements increases.
- The elements are strongly electropositive due to low first ionization energy as a result of their large atomic radii. The inner fully filled energy levels effectively shield the valency electron. As a result, the valency electron is weakly attracted by the nucleus and is easily lost with formation of positive ions.
- The second ionization energies are much greater than the first ionization energies.
  **Explanation**:
  This is because the second electron is being removed from a fully filled and stable p sub energy level. Also, after the removal of the first electron, the number of protons are more than the number of electrons. Effective nuclear charge increases. The remaining fewer electrons are strongly attracted by the same number of protons, thus, a relatively high amount of energy is required to remove an electron
- The melting points and boiling points are generally low.
  **Explanation**
  This is because each atom contributes one electron for metallic bonding and their atomic radii are large. Thus, the elements form weak metallic bonds.
  The strength of metallic bond formed decreases from lithium to caesium due to increase in atomic radii. Thus, the force of attraction between the bonding/delocalized electrons and the large cations reduces.
- The weak melting bonds in the elements explains why they are soft and can be cut by a knife.

| | |
|---|---|
| <br>**Sodium metal being cut by a knife** | The other physical properties are:<br>The elements are:<br>• shiny (lustrous) when freshly cut.<br>• good electrical and thermal conductors. This is due to the presence of delocalised electrons.<br>• less dense than water and thus, float on water. |

- The elements are good reducing agents as a result of being highly electropositive.

The standard electrode potential (S.E.P), $E^{\theta}$, measures the tendency for the reduction process to occur.

A high negative value for S.E.P indicates that the process, $M(s) \longrightarrow M^{+}(aq) + e^{-}$, takes place easily/readily (i.e. indicates that the metal is a good reducing agent/good electron donor).
Generally, the S.E.P values become more negative down the group, with lithium having the most negative value of S.E.P.
Lithium forms lithium ion with a very small ionic radius and hence, high charge density/polarizing power. In aqueous solution, the cation is heavily hydrated and releases a lot of heat energy. The hydration energy more than offsets its relatively high enthalpy of atomization and first ionization energy resulting from its very small atomic radius. Therefore lithium is a better reducing agent than the other group metals in aqueous solution but a poorer reducing agent when solvation cannot take place.
Down the group, the magnitude of atomization energy, first ionization energy and hydration energy decrease. This is due to increase in atomic radius in the same order. However, the magnitude of atomization energy and first ionization energy decrease more rapidly than the magnitude of hydration energy, and this makes the S.E.P values become more negative as the group is descended.

- Lithium, the first member in the Group, behaves differently from the rest of the other group members and in some respects it closely resembles Group II elements of the Periodic Table. It is said to have a **diagonal relationship** with magnesium.
  **Reason/explanation:**
  Lithium atom has the smallest atomic radius. The atom forms a cation with a very small ionic radius and hence, highest charge density/polarizing power. The S.E.P value for lithium is the most negative.
- Due to their high reactivity, the elements are found in combination with other elements or radicals. For example, sodium occurs as sodium carbonate, sodium chloride etc.
- Francium is a radioactive element which occurs in uranium and thorium ores.

## Reactions of group I elements

- Because of their large atomic radii, the elements have:
  (i) low first ionization energy
  (ii) low enthalpy of atomization
  The two factors make the elements form stable ions more readily than any other element and consequently, they are the most reactive metals in the Periodic Table.
  Reactivity of the metals increases as the group is descended. This is due to increase in atomic radius which increases the ease of electron loss in the same order.

## 1. Reaction with air

- In damp air, all tarnish (i.e. become dull in appearance) due to formation of oxide layer on their surfaces.
- Prolong exposure of the elements results into a series of reactions and a carbonate is formed. K, Rb and Cs readily catch fire on exposure.
- The elements readily burn in air with different flames forming different oxides.
  - ✓ All form monoxides in limited supply of oxygen.
    $4M(s) + O_2(g) \rightarrow 2M_2O(s)$,
  - ✓ In excess supply of air;
    (i) sodium forms sodium peroxide: $2Na(s) + O_2(g) \rightarrow Na_2O_2(s)$.
    (ii) potassium, caesium and rubidium form superoxides (or hyperoxides) in addition to the peroxides.
    For example:
    $2K(s) + O_2(g) \rightarrow K_2O_2(s)$ (peroxide)
    $K(s) + O_2(g) \rightarrow KO_2(s)$ (superoxide)

**A violent reaction of potassium with air gives a lilac flame**

*Note*
Lithium forms only a normal oxide (monoxide) because its cation has a small ionic radius. Thus, the cation cannot surround itself with sufficient peroxide or superoxide ions to give stable crystal lattices. As a result only the monoxide exists. The other metals form cations with larger ionic radii and thus, are able to form stable crystal lattices with either the peroxide ions or superoxide ions.

## 2. Reaction with Water

- All liberate hydrogen from **cold** water and a metal hydroxide is formed in solution.
  $2M(s) + 2H_2O(l) \rightarrow 2MOH(aq) + H_2(g)$

**Potassium reacting with water**

The vigour of reactivity with water increases down the group. This is due to electropositivity which increases in the same order. The resultant solutions formed are alkaline to litmus.

- Lithium reacts slowly with cold water but vigorously with steam to form an oxide and hydrogen.
  $2Li(s) + H_2O(g) \rightarrow Li_2O(s) + H_2(g)$

## 3. Reaction with non-metals

- All the metals react with dry halogens, sulphur, hydrogen and nitrogen when strongly heated to form corresponding ionic compounds; halides, sulphides, hydrides and nitrides respectively.
  For example: $2Na(s) + Cl_2(g) \longrightarrow 2NaCl(s)$
- Lithium is the only metal that reacts directly with dry nitrogen on strong heating.
  $6Li + N_2\ (s) \rightarrow 2Li_3N(s)$; lithium nitride (white solid)

## 4. Reaction with hydrogen chloride and ammonia

- All burn in a stream of dry hydrogen chloride and dry ammonia when heated to form the corresponding ionic compounds; the chlorides and amides.
  For example:
  $2Na(s) + 2HCl(g) \rightarrow 2NaCl(s) + H_2(g)$
  $2Na(s) + 2NH_3(g) \rightarrow 2NaNH_2(s) + H_2(g)$

## Compounds of group I elements

- The compounds are generally ionic in character, crystalline solids, stable in air and soluble in water.
- Compounds of lithium have some covalent character. This is due to the small ionic radius of lithium ion which gives it high charge density/polarizing power. Hence, the

cation greatly polarise the accompanying anions. The other form cations with large ionic radii and thus, low charge density. This makes the cations not to polarize the neighbouring anions appreciably.

## A. Oxides

- All the oxides are basic and dissolve in cold water to form strongly alkaline solution.
  For example:
  $K_2O(s) + H_2O(l) \rightarrow 2KOH(aq)$
  $2K_2O_2(s) + 2H_2O(l) \rightarrow 4KOH(aq) + O_2(g)$
  $2KO_2(s) + 2H_2O(l) \rightarrow 2KOH(aq) + H_2O_2(aq) + O_2(g)$
- The peroxides and superoxides are powerful oxidizing agents.
  For example, chromium(III) hydroxide can be oxidized to sodium chromate by fusing it with sodium peroxide.
  For example: $2Cr(OH)_3(s) + 3Na_2O_2(s) \rightarrow 2Na_2CrO_4(aq) + 2NaOH(aq) + H_2O(l)$

## B. Hydroxides

- All readily dissolve and completely dissociate in water to form strongly alkaline solutions. A lot of heat is produced during the process.

| | |
|---|---|
|  | Heat of solution is negative (i.e. the process is exothermic).<br>$\Delta H_{soln} = Lattice\ energy + hydration\ energy$ |

- The solubility of the hydroxides in water increases from lithium hydroxide to caesium hydroxide and so does the basic strength of the aqueous solution they form. This is because of the increase in the ionic character of the hydroxides resulting from the decrease in the charge density of the cations.
- The hydroxides are deliquescent except, lithium hydroxide. Lithium hydroxide is slightly soluble in water.
- Aqueous solutions of sodium hydroxide and potassium hydroxide neutralise acids, evolve ammonia from ammonium salts on warming, precipitate insoluble metal hydroxides from their salts in aqueous solution and, readily absorb carbon dioxide from air and react with it to form carbonates (or hydrogencarbonates) and water.

For example:
$2NaOH(aq) + CO_2(g) \rightarrow Na_2CO_3(aq) + H_2O(l)$
The reaction of sodium hydroxide and potassium hydroxide with carbon dioxide from air makes:

(i) the alkalis not regarded as primary standards.
(ii) the aqueous solutions of the alkalis for use in volumetric analysis be prepared using freshly boiled distilled water; which is carbon dioxide free.

**Trial Questions**

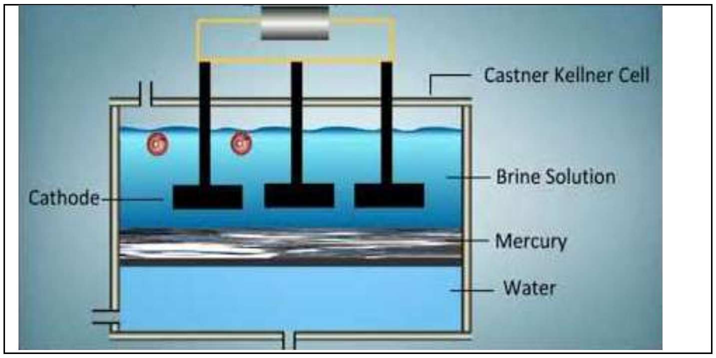
1. Give reasons for the following procedures as used in volumetric analysis/analytical chemistry. Illustrate your answers with equations where possible.
   (a) Sodium hydroxide is not suitable as a primary standard in volumetric analysis.
   (b) Aqueous solutions of sodium hydroxide for use in volumetric analysis should be prepared using freshly boiled distilled water.
2. State **two** large uses of the hydroxides of group I elements of the Periodic Table.

## Manufacture of sodium hydroxide

Sodium hydroxide is obtained by electrolysis of brine (concentrated sodium chloride solution) in either Castner-Kellner cell or a diaphragm cell. Chlorine and hydrogen are important bi-products of both methods.

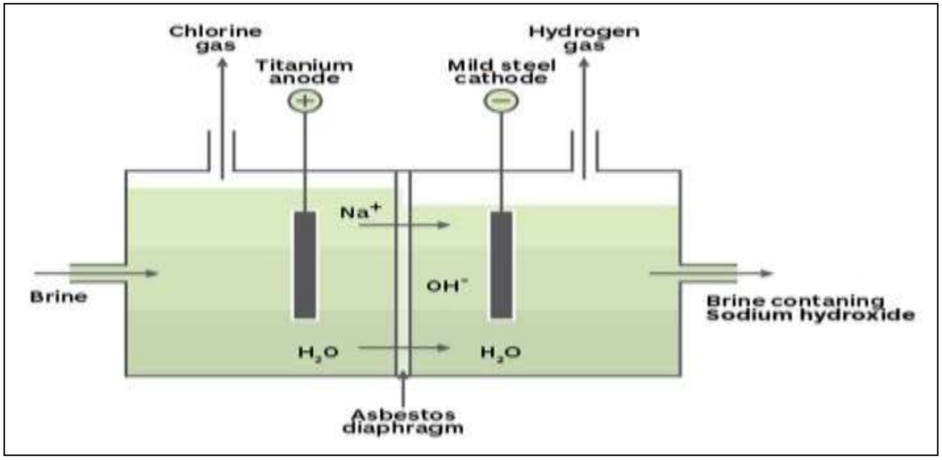
(a) The Castner-Kellner cell

- ✓ Brine is electrolyzed in a cell made up of mercury cathode and titanium/graphite as the anode.
- ✓ At the cathode, sodium ions are discharged in preference to hydrogen ions. Thus, solid sodium is formed.
  $Na^+(aq) + e^- \longrightarrow Na(s)$
- ✓ The sodium formed dissolves in the mercury to form am alloy, sodium amalgam which is reacted with water to form sodium hydroxide with evolution of hydrogen. Liquid mercury is regenerated for re-use in the cell. Thus, hydrogen is also a product at the cathode.
  $Na(s) + Hg(l) \longrightarrow Na/Hg(l)$
  $2Na/Hg(l) + 2H_2O(l) \longrightarrow 2NaOH(aq) + H_2(g) + 2Hg(l)$
- ✓ Solid sodium hydroxide is obtained by careful evaporation to dryness of the resultant solution.
- ✓ At the anode, chloride ions are discharged in preference to the hydroxide ions. Thus, chlorine is formed at the anode.
  $2Cl^-(aq) \longrightarrow Cl_2(g) + e^-$
- ✓ The setup of the cell is as follows:



(b) The Diaphragm cell

- ✓ Brine is electrolyzed in a cell made up of iron/steel cathode and titanium/graphite as the anode separated by an asbestos diaphragm.
- ✓ At the anode compartment, chloride ions are discharged in preference to the hydroxide ions. Chlorine gas is formed.
  $2Cl^{-}(aq) \longrightarrow Cl_2(g) + e^{-}$
- ✓ The remaining solution seeps/passes through the asbestos diaphragm into the cathode compartment.
- ✓ At the cathode compartment, hydrogen ions are discharged to form hydrogen gas.
  $2H^{+}(aq) + 2e^{-} \longrightarrow H_2(g)$
- ✓ The solution in the cathode compartment contains sodium hydroxide mixed with sodium chloride as an impurity.
- ✓ The resultant solution from the cathode compartment is concentrated by evaporation so that sodium chloride crystallizes out leaving a concentrated solution of sodium hydroxide.
- ✓ The setup of the cell is as follows:



**Note:**

- Potassium hydroxide can be made by both cells using concentrated potassium chloride solution in place of brine.
- The diaphragm in the diaphragm cell mechanically separates the anode and the cathode products since they react as below:
  $Cl_2(g) + 2NaOH(aq) \longrightarrow NaOCl(aq) + NaCl(aq) + H_2O(l)$

## C. Carbonates

- All the carbonates are ionic except lithium carbonate which is mainly covalent.
  Thus, lithium carbonate decomposes when heated to form lithium oxide and carbon dioxide. The rest are unaffected by heat.
  $Li_2CO_3(s) \longrightarrow Li_2O(s) + CO_2(g)$
- The most important of the carbonates are sodium carbonate and potassium carbonate.
- Sodium carbonate has the following applications:
  (i) Anhydrous sodium carbonate is used as a primary standard in volumetric analysis. Anhydrous potassium carbonate is deliquescent and cannot be used for this purpose.
  (ii) Hydrated sodium carbonate (washing soda) is used in water treatment. It precipitates out dissolved calcium and magnesium ions in hard water. Washing soda also neutralises the pH of water during water treatment.
  (iii) It is used in the manufacture of glass, paper, soaps and detergents. Potassium carbonate can also be used for this purpose.
- On a large scale, sodium carbonate is made by **Solvay (ammonia-soda) process**. During the process, insoluble sodium hydrogencarbonate formed is strongly heated to form anhydrous sodium carbonate.
  $2NaHCO_3(s) \xrightarrow{heat} Na_2CO_3(s) + CO_2(g) + H_2O(l)$
- Potassium carbonate cannot be obtained by Solvay process because potassium hydrogencarbonate is too soluble in water to be precipitated.
- The carbonates dissolve in water to form an aqueous solution whose $pH > 7$.
  **Explanation**:
  Consider sodium carbonate which is a salt formed from a strong base (sodium hydroxide) and a weak acid (carbonic acid).
  When dissolved in water, the salt dissociates into sodium and carbonate ions. The carbonate ions **hydrolyze** in water forming a weak carbonic acid and hydroxide ions.
  $CO_3^{2-}(aq) + 2H_2O(l) \rightleftharpoons \mathrm{H_2CO_3(aq)} + 2OH^-\mathrm{(aq)}$
  The hydrolysis reaction disturbs the equilibrium, $H_2O(l) \rightleftharpoons \mathrm{H^+(aq)} + OH^-\mathrm{(aq)}$ due to the removal of hydrogen ions. Thus, more water molecules ionize in order to restore the equilibrium. The ionization reaction produces an **excess** of hydroxide ions which make the resultant solution react alkaline and have a pH above 7.

- The above hydrolysis reaction explains why:
  - (i) An aqueous solution of sodium (potassium) carbonate behaves like as alkali in acid-base titrations.
  - (ii) Use of aqueous sodium (potassium) carbonate solution to precipitate some insoluble carbonates gives a basic carbonates instead.

    For example:

$$2Cu^{2+}(aq) + \underbrace{CO_3^{2-}(aq) + 2OH^-(\mathrm{aq})}_{sodium\ carbonate\ solution} \longrightarrow \underbrace{\mathrm{Cu}CO_3.Cu(OH)_2(s)\ or\ \mathrm{Cu_2(OH)_2CO_3(s)}}_{\substack{basic\ copper(II)\ carbonate \\ (green\ precipitate)}}$$

## D. Hydrogencarbonates

- Lithium hydrogencarbonate only exists in aqueous state while sodium hydrogencarbonate and potassium hydrogencarbonate exist in solid state.
- The hydrogencarbonates of sodium and potassium are:
  - (i) thermally unstable and decompose into the metal carbonate, carbon dioxide and water on strong heating.
  - (ii) slightly soluble in water.
- Aqueous solutions of the hydrogencarbonates are alkaline due to hydrolysis.

  $HCO_3^-(aq) + H_2O(l) \rightleftharpoons \mathrm{H_2CO_3(aq)} + OH^-(\mathrm{aq})$
- However, they are less alkaline than corresponding carbonates. Because of this, normal carbonates are precipitated by use of sodium (potassium) hydrogencarbonate solution but not sodium (potassium) carbonate solution, which would form basic carbonates.

  $Cu^{2+}(aq) + 2HCO_3^-(aq) \longrightarrow \mathrm{Cu}CO_3 + \mathrm{H_2}O(l) + \mathrm{CO_2}(g)$
- Sodium hydrogencarbonate is used as primary standard in volumetric analysis, since it is stable during storage. It is also used in baking powder.

## E. Nitrates

- The nitrates of all the group members exist and are thermally stable.
- However, at very high temperatures, the nitrates melt and decompose to give a nitrite and oxygen except, lithium nitrate forms lithium monoxide, nitrogen dioxide and oxygen on strong heating.

  For example:

  $2NaNO_3(s) \rightarrow 2NaNO_2(s) + O_2(g)$

  $4LiNO_3(s) \rightarrow 2Li_2O(s) + 4NO_2(g) + O_2(g)$
- The nitrates of potassium and sodium occur naturally as Chile saltpetre and saltpetre (nitre) respectively and are purified by **fractional crystallization**; where the salt with the least solubility at lower temperatures crystallizes out first as the hot saturated solution of the salt mixture is cooled slowly.
- Both potassium and sodium nitrates are used as nitrogenous fertilisers and to prepare nitric acid in the laboratory.

## F. Halides

- All form halides which are ionic except, lithium halides which are covalent.
- Lithium chloride dissolves in organic solvents (such as ethanol or methylbenzene) more than in pure water. This is due the covalent nature of the chloride.
- The halides have a number of applications which include:
  - (i) Fused sodium chloride is used to produce sodium, sodium hydroxide, chlorine, sodium chlorate(I) and chlorate(V) by electrolysis.
  - (ii) Potassium chloride is used as a fertiliser and a source potassium hydroxide.
  - (iii) Sodium chloride used in making soap and sodium carbonate.
  - (iv) Potassium iodide used is in the laboratory to confirm the presence of lead(II) ions and copper(II) ions. Formation of a bright yellow precipitate confirms lead(II) ions in solution while formation of a white precipitate in a brown solution confirms copper(II) ions.

    $$Pb^{2+}(aq) + 2I^-(aq) \longrightarrow \underbrace{PbI_2(s)}_{yellow\ precipitate}$$

    $$2Cu^{2+}(aq) + 4I^-(aq) \longrightarrow \underbrace{Cu_2I_2(s)}_{white\ precipitate} + \underbrace{I_2(aq)}_{brown\ solution}$$
  - (v) Potassium iodide is also used to increase the solubility of iodine in pure water during volumetric analysis.

    The increased solubility of iodine in aqueous potassium iodide is due to the reaction between iodide ions (from potassium iodide) and iodine molecules to form triiodide ions; which are **soluble** in water.

    $I^-(aq) + I_2(s) \rightleftharpoons I_3^-(aq)$

    The low solubility of iodine in pure water is because iodine molecules do not react with water molecules. Also, iodine molecules are non-polar with weak van der Waals forces and thus, do not form bonds with water molecules which are polar and having strong hydrogen bonds.
  - (vi) Potassium bromide is used as anticonvulsant and a sedative.

## The chemistry of group II elements

### Introduction

- The groups II elements include beryllium (Be), magnesium (Mg), calcium (Ca), strontium (Sr), barium (Ba) and radium (Ra).

| | | |
|---|---|---|
| <br>Beryllium | <br>Magnesium | <br>Calcium |
| <br>Strontium | <br>Barium | |

- Radium is rare because it is radioactive.
- They are metals and are referred to as **alkaline-earth metals** because their oxides are alkaline (that is, dissolve in water to form alkaline solutions) and their salts (sulphates, chlorides and carbonates) are wide spread on the Earth's crust.

### Some of the physical properties of Group II elements

| Element | Outermost EC | Atomic radius (nm) | M.pt(℃) | B.pt (℃) | S.E.P (Volts) | Ionisation energy | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | 1st | 2nd | 3rd |
| Be | $2s^2$ | 0.112 | 1280 | 2770 | $-1.85$ | 900 | 1800 | 14800 |
| Mg | $3s^2$ | 0.160 | 650 | 1110 | $-2.37$ | 740 | 1450 | 7730 |
| Ca | $4s^2$ | 0.197 | 840 | 1440 | $-2.87$ | 590 | 1150 | 4910 |
| Sr | $5s^2$ | 0.215 | 768 | 1380 | $-2.89$ | 550 | 1060 | 4300 |
| Ba | $6s^2$ | 0.221 | 714 | 1640 | $-2.91$ | 500 | 970 | |
| Ra | $7s^2$ | | | | $-2.92$ | | | |

### Some general remarks about the elements

- Their general outermost electronic structure is $ns^2$.
- All show a fixed oxidation state of $+2$. This is because the loss of the two outermost s–electrons leaves an outermost sub energy level which is fully filled and stable (i.e. an inert gas electronic structure is formed).

- The elements never form $M^{3+}$ ions because the third ionization is very high, since the third electron is being removed from a fully filled and energetically stable sub energy level. Also, the increased effective nuclear charge strongly attracts and holds the remaining few electrons.
- The formation of $M^{2+}$ ions by the elements is energetically favourable. This is because the inner fully filled energy levels of electrons effectively shield the outermost $ns^2$ electrons from the nuclear attraction. Thus, outermost $ns^2$ electrons are weakly attracted by the nucleus and are easily lost.
- As the atomic number increases (i.e. down the group);
  (iv) The atomic radius increases and the outermost $s-$ electrons (valence electrons) become more distant from the nucleus.
  (v) Both first and second ionization energies decrease. The second ionisation energy is much higher than the first ionisation energy because after the removal of the first electron, the number of protons become more than the number of electrons. Effective nuclear charge increases. The remaining fewer electrons are strongly attracted by the same number of protons, thus, a relatively high amount of energy is required to remove an electron.
  As compared to group I metals, the first ionisation energies of group II metals are much higher. This is because group II metals have relatively smaller atomic radii than the corresponding alkali metals.
  (vi) Electrode potential becomes more negative.
  (vii) Reactivity of the elements increases.
- The elements reactive by reducing. They less reactive (reductive) than group I elements. This is because of their much smaller atomic radii which makes both ionization and atomization energies so high.
- The group II elements are metals with giant metallic structures. Their atoms are held by strong metallic bonds. A lot of heat energy is required to break the strong bonds. This makes their melting and boiling points high.
- Their densities, melting point and boiling point are much higher than those of the corresponding group I elements. This is because:
  (i) Alkaline-Earth metals use two electrons per atom in forming metallic bonds while group I elements use only one electron per atom for metallic bond formation.
  (ii) Alkaline-Earth metals have much smaller atomic radii than their corresponding elements in group I, as a result their atoms are closely packed together in the lattices.

  The above two factors make the metallic bonds in group II elements much stronger than those in group I elements.
- On descending the group, the melting point, boiling point and hardness of alkaline-earth metals decrease.

This is because as the atomic radius down the group, the bonding electrons get further from the attracting nucleus. Therefore the atoms will be less strongly held together as the group is descended (i.e. metallic bond strength decreases down the group). The melting point of magnesium is lower than that of calcium. This is because the two elements adopt different structures/ different crystal structures. Magnesium has hexagonal close packed arrangement while calcium has a body centred cubic arrangement

**Alternatively:**

As the group is descended, the cation radius increases. The charge density of the cations decreases in the same order and hence, the bonding/valence electrons become less strongly attracted. Strength of the metallic bonds formed decreases and hence, melting point decreases down the group. The melting point of magnesium is lower than that of calcium. This is because the two elements adopt different structures.

- All the elements are soft and can be cut by a knife. This is because of weak metallic bonds in their structures.
- The metals are good conductors of heat and electricity. This is due to the presence of delocalized electrons. Conductivity increases as the group is descended from beryllium to barium. This is due to increase in atomic radii in the same order which makes the outermost electrons to be weakly attracted by the nucleus and hence, easily delocalized.
- Beryllium differs considerably in its chemistry from the rest of the other elements and resembles aluminium.

  **Reason/explanation:**

  Beryllium atom has a small atomic radius. The atom forms a cation with a very small ionic radius and high charge density and hence high polarizing power.

- The standard electrode potential values ($E^\theta$ ) become more negative as the group is descended. (Refer to the previous notes on alkali metals for explanation).
- All are highly reactive and are thus, never found in a free state in nature. On a large scale, the metals are obtained by electrolysis of the molten chlorides.

## Chemical properties of Group II Elements

### 1. Reaction with air

All metals:

(a) tarnish in air forming a film of oxide, which later forms hydroxide and carbonate on prolonged exposure. This makes them lose the shiny appearance.

(b) burn brilliantly when heated in air to from an oxide along with some nitride.

$M(s) + O_2(g) \rightarrow 2MO(s)$; $3M(s) + N_2(g) \rightarrow M_3N_2(s)$

For example;

$Ca(s) + O_2(g) \rightarrow 2CaO(s)$; $3Ca(s) + N_2(g) \rightarrow Ca_3N_2(s)$

If the product is made damp and warmed, ammonia is evolved.

For example: $Ca_3N_2(s) + 6H_2O(l) \rightarrow 3Ca(OH)_2(aq) + 2NH_3(g)$

The oxides sparingly dissolve in water to give alkaline solutions.

For example: $CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(aq)$

***Question**:*
*Reactivity of the elements increases down the group from beryllium to barium. Explain this observation.*

### 2. Reaction with water

The reactivity with water is not as vigorous as it is with alkali metals. It occurs at different rates depending on the conditions.

Beryllium is unaffected by water at all conditions.

Clean magnesium reacts with cold water slowly forming magnesium hydroxide and hydrogen.

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

However, strongly heated magnesium burns brilliantly in steam to give its oxide and hydrogen gas.

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

Calcium, strontium and barium react with cold water to form a metal hydroxide in solution and hydrogen gas is evolved.

$M(s) + 2H_2O(l) \rightarrow M(OH)_2(aq) + H_2(g)$; $M = Ca; Sr \text{ or } Ba$

Reactivity increases down the group.

This is because the solubility of hydroxide formed increases in the same order and the metals became more reducing down the group (atomic radius increases down the group).

### 3. Reaction with Acids

#### (a) With dilute hydrochloric acid and dilute sulphuric acid

All the metals liberate hydrogen from dilute hydrochloric and dilute sulphuric acids forming the corresponding salts in solution.

$M(s) + 2H^+(aq) \longrightarrow M^{2+}(aq) + H_2(g)$;

With beryllium the reaction takes place on **warming** while others react vigorously in the cold/at room temperature.

The reaction of calcium, strontium and barium with dilute sulphuric acid occurs for a **short time and stops**. This is because the sulphate formed in each case is **insoluble** and forms a coating on the metal. This prevents further contact between the metal and the acid for the reaction to progress.

$M(s) + H_2SO_4(aq) \rightarrow MSO_4(s) + H_2(g)$; $M = Ca; Sr \text{ or } Ba$

**(b) With concentrated sulphuric acid**

All are oxidized by hot concentrated sulphuric acid to their respective metal sulphates in solution. The acid is reduced to sulphur dioxide gas and water.

$M(s) + 2H_2SO_4(l) \rightarrow MSO_4(aq) + 2H_2O(l) + SO_2(g)$

The rate of the reaction decreases down the group due decrease in the solubility of the sulphates being formed.

**(c) With nitric acid**

(i) Very dilute nitric acid has no effect on beryllium, strontium, and barium but reacts with magnesium and calcium slowly at room temperature to give some hydrogen.
For example: $Mg(s) + 2H^+(aq) \rightarrow Mg^{2+}(aq) + H_2(g)$

(ii) Concentrated nitric acid renders beryllium passive.
The rest of the elements are oxidized by hot concentrated nitric acid to their respective nitrates in solution. The acid is reduced to oxides of nitrogen and water.
For example:
$3Mg(s) + 8HNO_3(aq) \rightarrow 3Mg(NO_3)_2 + 4H_2O(l) + 2NO(g)$
$Mg(s) + 4HNO_3(aq) \rightarrow Mg(NO_3)_2 + 2H_2O(l) + 2NO_2(g)$

**4. Reaction with aqueous alkalis**

Beryllium being amphoteric, reacts with hot concentrated sodium (potassium) hydroxide solution to evolved hydrogen gas and beryllate ions are left in solution

$Be(s) + 2OH^-(aq) + 2H_2O(l) \rightarrow Be(OH)_4^{2-}(aq) + H_2(g)$

The rest do not react with alkalis at all conditions.

**5. Reaction with non-metals**

All the metals react when heated with dry halogen (chlorine or bromine), sulphur, phosphorus and carbon to form the corresponding compounds. Except beryllium, the rest react directly when strongly with dry hydrogen under pressure to form ionic hydrides.

| | |
|---|---|
| $M(s) + X_2(g) \rightarrow MX_2(s)$; (X= Cl or Br) | $M(s) + S(g) \rightarrow MS(s)$ |
| $3M(s) + 2P(s) \rightarrow M_3P_2(s)$ | $M(s) + 2C(s) \rightarrow MC_2(s)$; M= Mg, Ca, Sr or Ba<br>$2Be(s) + C(s) \rightarrow Be_2C(s)$ |

Calcium carbide yields ethyne on hydrolysis with water while beryllium carbide gives methane on the same treatment.

> ***Note***
> - The calcium carbide can also be obtained by heating the oxide with carbon (coke) at very high temperatures. $CaO(s) + 3C(s) \xrightarrow{2000^0C} CaC_2(s) + CO(g)$
> - Hydrolysis of beryllium carbide proceeds faster in dilute acids and is more rapid in hot concentrated solutions of alkalis.
>   $Be_2C(s) + 4H^+(aq) \rightarrow 2Be^{2+}(aq) + CH_4(g)$
>   $Be_2C(s) + 4OH^-(aq) + 4H_2O(l) \rightarrow 2Be(OH)_4^{2-}(aq) + CH_4(g)$

## Uses of group II elements

Group II elements of the Periodic Table have a wide range of applications which include:

| **Element** | **Use(s)** |
|---|---|
| Beryllium | • Making containers for uranium-238 since it does not absorb neutrons and therefore, does not become radioactive<br>• As an alloying agent when low density is a primary requirement<br>• Making windows for X-ray tubes since they can easily be penetrated by X-rays |
| Magnesium | • Make alloys e.g. duralumin and magnalium<br>• Sacrificial anode to prevent iron from rusting<br>• In flares and distress signals due to its intense white light it forms when burning<br>• Source of light in photography<br>• Extraction of titanium, chromium |
| Calcium | • In extraction of certain elements from their stable compounds for example chromium from chromium(III) oxide. |
| Strontium | • In fire works<br>• Used in producing ferrite magnets and refining zinc |
| Barium | • Often used for spark-plug electrodes and in vacuum tubes as a drying and oxygen-removing agent. |

## Compounds of Group II Elements

The compounds of alkaline-earth metals are white and ionic. Those of beryllium have considerably covalent character.

The covalent nature of most of the compounds of beryllium is brought about by the fact that beryllium ion has small ionic radius and this gives the cation a high charge density and hence, high polarising power.

The ionic character in the compounds increases as the group is descended. This is due to increase in the ionic radius of the metal ions, $M^{2+}$ (where M is group II metal).

The compounds of group II elements are less ionic, less soluble, less stable to heat compared to those of corresponding group I members.

### A. Hydrides

- The hydrides are ionic solids except beryllium hydride and magnesium hydride which are both covalent.
- Beryllium hydride is made by reacting beryllium chloride with *lithium tetrahydroaluminate(III)* (or simply lithium aluminium hydride), $LiAlH_4$.
  $2BeCl_2(s) + LiAlH_4(s) \longrightarrow 2BeH_2(s) + LiCl(s) + AlCl_3(s)$
- The hydrides react with water to form a metal hydroxide in solution with evolution of hydrogen gas.

$MH_2(s) + 2H_2O(l) \longrightarrow M(OH)_2(aq) + H_2(g)$

### B. Oxides

- All the elements form normal oxides of the general formula MO.
- However, strontium and barium form peroxides when burnt in excess. This is because their cations are have larger ionic radii and this allows formation of stable lattices with the peroxide ions. The peroxides have the general $MO_2$ and contain the anion $O_2^{2-}$.
- The normal oxides can be obtained in the following ways:
  - (i) Burning the metals directly in air (oxygen).
  - (ii) Heating the metal hydroxide, carbonate or nitrate strongly in an open vessel to allow the corresponding gases to escape.
    $Mg(OH)_2(s) \rightarrow MgO(s) + H_2O(g)$; $MgCO_3(s) \rightarrow MgO(s) + CO_2(g)$
    $2Mg(NO_3)_2(s) \rightarrow 2MgO(s) + 4NO_2(g) + O_2(g)$

**Note**:
Barium carbonate requires very high temperatures to decompose thus, its oxide is made by heating its nitrate.

- All the oxides are white crystalline solids.
- Beryllium oxide is partially covalent and is amphoteric while the rest are ionic and basic.

### Reactions of the oxides

- Beryllium oxide is insoluble in water (due to its high covalent character); the rest react with water to form the corresponding hydroxide in solution. A lot of heat is evolved.
  $MO(s) + H_2O(l) \longrightarrow M(OH)_2(aq)$
- The peroxides of barium ($BaO_2$) and strontium ($SrO_2$) dissolve in water forming the corresponding hydroxides and hydrogen peroxide.
  For example: $BaO_2(s) + 2H_2O(l) \rightarrow Ba(OH)_2(aq) + H_2O(aq)$
- Barium peroxide reacts dilute sulphuric acid at 0℃ to form hydrogen peroxide in addition to barium sulphate.
  $BaO_2(s) + H_2SO_4(aq) \rightarrow BaSO_4(s) + H_2O_2(aq)$
- The normal oxides of group II elements also react with heated carbon to form carbides. The most important and common carbide is calcium carbide (refer to reactions of the metals with non-metals page 20).
- The basic oxides react with acidic oxides such as carbon dioxide, sulphur trioxide, silicon dioxide and phosphorus(V) oxide to form the corresponding salts on heating.
  For example: $SiO_2(g) + CaO(s) \rightarrow CaSiO_3(s/l)$

## C. Hydroxides, $M(OH)_2$

- All the hydroxides are white solids prepared by precipitation method.
  Precipitation method involves adding aqueous sodium hydroxide solution to an aqueous solution of the soluble salt of the metal.
  $M^{2+}(aq) + 2OH^-(aq) \longrightarrow M(OH)_2(s)$
- Beryllium hydroxide is essentially covalent and amphoteric. The rest are ionic and basic.
  The amphoteric nature of beryllium hydroxide can be illustrated as follows:
  As an acid: $Be(OH)_2(s) + 2OH^-(aq) \longrightarrow Be(OH)_4^{2-}(aq)$
  As a base: $Be(OH)_2(s) + 2H^+(aq) \rightarrow Be^{2+}(aq) + 2H_2O(l)$.
  Thus, the hydroxide resembles aluminium hydroxide, in this respect.
- At very high temperatures, the hydroxides decompose to give metal oxides and water vapour.
  $M(OH)_2(s) \rightarrow MO(s) + 2H_2O(g)$

**Question**:
Explain why hydroxides of group II metals are decomposed by heat whereas hydroxides of group I metals are not.

- Solubility of the hydroxides increases down the group; beryllium hydroxide is insoluble in water and barium hydroxide is sparingly soluble/fairly soluble in water.

| Hydroxide | $Be(OH)_2$ | $Mg(OH)_2$ | $Ca(OH)_2$ | $Sr(OH)_2$ | $Ba(OH)_2$ |
|---|---|---|---|---|---|
| Solubility (g/100g of water at 20°C) | Insoluble | 0.002 | 0.15 | 0.9 | 4.0 |

**Trend**:
The solubility of the hydroxides increases in the order:
$Be(OH)_2 < Mg(OH)_2 < Ca(OH)_2 < Sr(OH)_2 < Ba(OH)_2$

**Explanation**:
Beryllium hydroxide is covalent and this makes it insoluble in water.
From beryllium hydroxide to barium hydroxide, the charge on the cation remains the same but the radius increases. Thus, both lattice energy and hydration energy decrease in the same order. But the lattice energy decreases more rapidly than the hydration energy. This makes the heat of solution to become more negative from $Be(OH)_2$ to $Ba(OH)_2$ and hence, solubility increases.
The solubility also increases from $Be(OH)_2$ to $Ba(OH)_2$ due decrease in the charge density (polarizing power) of the cation from beryllium ion to barium ion. This makes the hydroxides to become more ionic form $Be(OH)_2$ to $Ba(OH)_2$.

**Note:**
The hydroxides of group II metals are much less soluble in water the corresponding hydroxides of group I metals. Thus, the hydroxides of group II metals are less basic than those of group I elements.

**Uses of the hydroxides of group II elements**

- Calcium hydroxide is the most important and has the following uses:
  - ✓ To remove acidic gases in industries and treating acidic soils.
  - ✓ Softening water and production of ammonia.
  - ✓ Making bleaching powder (e.g. calcium hypochlorite), sodium hydroxide, sodium carbonate, mortar and calcium hydrogensulphite used in paper industries.
  - ✓ Refining sugar (sucrose); strontium hydroxide can also be used for this purpose.
- Magnesium hydroxide is to make indigestion tablets since magnesium is non-toxic.

## D. Carbonates, $MCO_3$ and hydrogencarbonate, $M(HCO_3)_2$

- All form carbonates of the general formula $MCO_3$.
- The carbonates are insoluble in water and thus, are prepared by precipitation method. Use of aqueous sodium hydrogencarbonate is preferred to aqueous sodium carbonate during the precipitation process.

  For example:

$$4Mg^{2+}(aq) + \underbrace{3CO_3^{2-}(aq) + 2OH^-(aq)}_{\text{sodium carbonate solution}} + 4H_2O(l) \longrightarrow \underbrace{3MgCO_3.Mg(OH)_2.4H_2O(s)}_{\substack{\text{basic magnesium carbonate}\\ \text{(white precipitate)}}}$$

**Or** $$2Mg^{2+}(aq) + \underbrace{CO_3^{2-}(aq) + 2OH^-(aq)}_{\text{sodium carbonate solution}} \longrightarrow \underbrace{MgCO_3.Mg(OH)_2(s)}_{\substack{\text{basic magnesium carbonate}\\ \text{(white precipitate)}}}$$

$$Mg^{2+}(aq) + \underbrace{2\,HCO_3^-(aq)}_{\substack{\text{sodium hydrogencarbonate}\\ \text{solution}}} \longrightarrow \underbrace{MgCO_3(s)}_{\substack{\text{normal magnesium carbonate}\\ \text{(white precipitate)}}} + H_2O(s) + CO_2(g)$$

- All carbonates are thermally unstable (i.e. decompose on heating).

$$MCO_3(aq) \rightarrow \underbrace{MO(s)}_{\text{residue}} + CO_2(g)$$

- The decomposition temperature increases as the from beryllium carbonate to barium carbonate.

| Carbonate | $BeCO_3$ | $MgCO_3$ | $CaCO_3$ | $SrCO_3$ | $BaCO_3$ |
|---|---|---|---|---|---|
| Decomposition temperature | 25 | 540 | 900 | 1290 | 1360 |

**Explanation**:

Beryllium carbonate is thermally unstable and decomposes at room temperature. This is because beryllium ion has a very small ionic radius. Thus, the cation has a high charge density and hence, high polarizing power. Beryllium ion greatly polarizes the electron cloud of the carbonate ion making the carbonate covalent and thermally unstable.

As the group is descended, the radius of the cation increases but the cationic charge remains the same. The charge density and hence, the polarising power of the cations decrease. The ability of the cation to polarize the carbonate ions decreases in the same order. This makes the ionic character and hence, thermal stability of the carbonates to increase from beryllium carbonate to barium carbonate.

- The hydrogencarbonates only exist in aqueous solution and are very unstable.
  Both magnesium hydrogencarbonate and calcium hydrogencarbonate cause temporary hardness of water and can be decomposed by boiling of water. This sets water free of hardness.
  For example: $Ca(HCO_3)_2(aq) \xrightarrow{boil} CaCO_3(s) + CO_2(g) + H_2O(l)$

**Uses of the carbonates of group II elements**

- Calcium carbonate is used in Solvay process (ammonia-soda process), as flux in the iron and steel industry, in glass industry, in neutralising acidic soils, in making quicklime, cement, tiles, laboratory mortar and pestle.
- $CaCO_3.MgCO_3$ is used as building stones.

## E. Nitrates, $M(NO_3)_2$

- All the elements form nitrates.
- The nitrates are prepared in the laboratory by action of dilute nitric acid on either the metal oxide, hydroxide or carbonate and then crystallising the resultant hot saturated solution by cooling.
- All the nitrates decompose on strong heating to give metal oxide, nitrogen dioxide and oxygen.
  $2M(NO_3)_2(s) \rightarrow 2MO(s) + 4NO_2(g) + O_2(l)$

**Uses of the nitrates of group II elements**

- The nitrates are used as fertilisers, for example, calcium nitrate mixed with calcium oxide.
- They are also used in fireworks for example, barium nitrate gives a green flame and strontium nitrate gives a crimson flame.
- An aqueous solution of barium nitrate acidified with dilute nitric acid is used in the detection and identification of sulphate ions in solution.

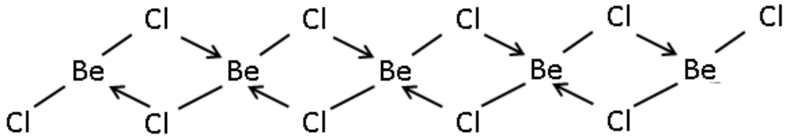
## F. Chlorides, $MCl_2$.

- Anhydrous chloride is obtained by heating the metal in a current of dry chlorine or dry hydrogen chloride.
  For example: $Mg(s) + Cl_2(g) \rightarrow MgCl_2(s)$ ; $Mg(s) + 2HCl(g) \rightarrow MgCl_2(s) + H_2(g)$

- Anhydrous beryllium chloride is a **covalent** polymeric solid while the rest are predominantly **ionic**. This is because charge density and hence, the polarizing power of the cations decrease down the group. This can be seen in the melting points of the chlorides.

| Chloride | $BeCl_2$ | $MgCl_2$ | $CaCl_2$ | $SrCl_2$ | $BaCl_2$ |
|---|---|---|---|---|---|
| M.pt (°C) | 405 | 708 | 722 | 873 | 962 |

The structure of polymerized beryllium chloride is as follows:



- Hydrated chlorides can be made by reacting the metal, its oxide, hydroxide or carbonate with dilute hydrochloric acid and carefully evaporating the resultant solution to dryness.
  $MO(s) + 2HCl(aq) \longrightarrow MCl_2(aq) + H_2O(l)$
  For example, the chloride of magnesium can be obtained as $MgCl_2.6H_2O$.
- When the hydrated chlorides of magnesium and calcium are heated, some hydrolysis takes place to give basic chlorides and evolve hydrogen chloride gas. Strong heating causes the formation of an oxide.
  For example:
  $MgCl_2.6H_2O(s) \xrightarrow{gentle\ heating} Mg(OH)Cl(s) + HCl(g) + 5H_2O(l)$
  $Mg(OH)Cl(s) \xrightarrow{strong\ heating} MgO(s) + HCl(g)$
  Hydrated calcium chloride behaves in a similar way but is less hydrolysed compared to hydrated magnesium chloride.
- The chlorides of beryllium and magnesium hydrolyse in water forming acidic solutions. The rest are resistant to hydrolysis since they are ionic. In fact, beryllium chloride fumes readily in moist air due to evolution of hydrogen chloride gas.
  $BeCl_2(s) + 2H_2O(s) \longrightarrow Be(OH)_2(s) + 2HCl(g)$
- Beryllium chloride readily dissolves in the organic solvents (such as ethanol) and this further confirms its covalent character.
- In vapour phases, beryllium chloride dimerises to form $Be_2Cl_4$.

**Uses of the chlorides of group II elements**

- Anhydrous calcium chloride is used as a drying agent.
- Barium chloride solution acidified with dilute hydrochloric is used confirm the presence of sulphate ions in aqueous solution.
- Fused chlorides are sources of a number of metals.

## G. Sulphates, $MSO_4$.

- The sulphates of group II metals occur naturally except, beryllium sulphate; for example, $CaSO_4.2H_2O$ (gypsum in soils, rocks and tap water) and $MgSO_4.7H_2O$ (in Epsom salt in tap water).
- $BeSO_4$ and $MgSO_4$ are prepared in the laboratory by reacting the metal, oxide, hydroxide or carbonate with dilute sulphuric acid.
  For example: $Be(s) + \underbrace{H_2SO_4(aq)}_{(warm)} \longrightarrow BeSO_4(aq) + H_2O(g)$
- $CaSO_4$, $SrSO_4$ and $BaSO_4$ are insoluble in water and are prepared by precipitation method.
  For example, barium sulphate can be made by adding a solution of a soluble sulphate or dilute sulphuric acid to an aqueous solution of a soluble salt of barium.
  $Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s)$
- The solubility of sulphates in water decreases down the group.
  (*$BeSO_4$ and $MgSO_4$ are very soluble; $CaSO_4$ is only sparingly soluble and the rest are insoluble in water*)

| Sulphate | $BeSO_4$ | $MgSO_4$ | $CaSO_4$ | $SrSO_4$ | $BaSO_4$ |
|---|---|---|---|---|---|
| Solubility (g/100g of water at 25°C) | 43.00 | 33.50 | 0.18 | 0.10 | 0.0024 |

**Explanation**:

This is because both the lattice energy and hydration energy decrease from $BeSO_4$ to $BaSO_4$.

Lattice energy of the sulphates decreases less rapidly down the group since the radius of the anion is so large compared to the radius of the cation. Thus, the increase in the radius of the cations does not greatly affect the lattice energy. However, the hydration energy of the sulphates of group II elements decreases more rapidly down the group due to increase in the cationic radius.

This makes the heat of solution become less exothermic down the group and thus, the solubility of the sulphates decreases down the group.

- The solubilities of their carbonates, oxalates (ethanedioates) and chromates vary in a similar way as that of the sulphates. This is because these anions are large compared to the constituent cations. Thus, the effect of the radius of the cations on the lattice energy of such salts can be regarded as insignificant and ignored.

**Note:**

Because both barium sulphate and barium chromate have low solubility in water, barium ions can be identified by precipitating it as barium sulphate or barium chromate.

$Ba^{2+}(aq) + SO_4^{2-}(aq) \longrightarrow \underbrace{BaSO_4(s)}_{white\ ppt};\quad Ba^{2+}(aq) + CrO_4^{2-}(aq) \longrightarrow \underbrace{BaCrO_4(s)}_{yellow\ ppt}$

**Uses of sulphates of group(II) elements**

- The sulphates have a number of applications. These include:
  (i) Aqueous solution of magnesium sulphate is used in the lab to distinguish between carbonate and hydrogencarbonate ions in solution.

  **Observations**:
  - ✓ Immediate white precipitate confirms carbonate ions in solution.
    $Mg^{2+}(aq) + CO_3^{2-}(aq) \longrightarrow MgCO_3(s)$
  - ✓ No observable change at room temperature (or white precipitate on boiling/heating) confirms hydrogencarbonate ions in solution.
    $Mg^{2+}(aq) + 2HCO_3^-(aq) \xrightarrow{boil} MgCO_3(s) + CO_2(g) + H_2O(l)$

  (ii) $MgSO_4.7H_2O$ is used in medicine as an intestine purgative, a filler in making glazed paper and, in tanning and dyeing.

  (iii) $CaSO_4.\ H_2O$ forms plaster of paris used in building, making cast and keeping the broken limbs/bones in place while healing. The dihydrate is used in the manufacture of fertilisers (for example ammonium sulphate).

  (iv) Both $MgSO_4.7H_2O$ and $CaSO_4.2H_2O$ are present in hard water and are useful for healthy bone and teeth growth, hardening of shells of water animals like snails.

  (v) $BaSO_4$ is used in 'X-rays meals' since it is relatively opaque to the rays, in paint manufacture and, as a filler for paper and rubber.

**Effects of heat on the sulphates**

- On gentle heating, hydrated sulphates ($BeSO_4.4H_2O$, $MgSO_4.7H_2O$, $CaSO_4.2H_2O$) lose their water of crystallisation and form powder (anhydrous salts).
- On strong heating to high temperatures, the sulphates decompose leaving metal oxides as a residue and oxides of sulphur ($SO_2$, $SO_3$) are evolved.
- Thermal stability of ionic compounds depends on majorly two factors; **ionic charge** and **ionic radius**.
  - ✓ The higher the charge on the ions, the greater will be the electrostatic forces of attraction between the oppositely charged ions and the more stable the compound will be due to greater lattice energy.

    For example magnesium sulphate is more stable on heat than magnesium hydroxide; since the sulphate ion is doubly charged while the hydroxide ion is singly charged.
  - ✓ The smaller the ionic radii, the more closely the ions will approach each other in the crystal lattice and the more stable will the compound be due to greater lattice energy.

    For example magnesium oxide is more stable than magnesium sulphate because the oxide ion is much smaller than the sulphate ion. This explains why the sulphates of group II elements readily decompose leaving the metal oxides. Sulphates of group I metals however are not decomposed by heat.

## H. Orthophosphates, $M_3(PO_4)_2$

- The only most important orthophosphate is calcium calcium phosphate(V) (calcium orthophosphate); $Ca_3(PO_4)_2$. The salt naturally occurs in rock phosphate.
- The salt is precipitated by mixing a solution containing calcium ions with disodium hydrogenphosphate(V) solution and an alkali. The alkali liberates the phosphate ions in solution.

  $HPO_4^{2-}(aq) + OH^-(aq) \rightarrow PO_4^{3-}(aq) + H_2O(l)$

  $3Ca^{2+}(aq) + 2PO_4^{3-}(aq) \rightarrow \underbrace{Ca_3(PO_4)_2(s)}_{white\ solid}$

  Overall equation: $3Ca^{2+}(aq) + 2HPO_4^{2-}(aq) + 2OH^-(aq) \rightarrow Ca_3(PO_4)_2(s) + 2H_2O(l)$
- The salt is used as a fertilizer but has a slow action due to its low solubility in pure water.

**Explanation:**

The low solubility of the salt in pure water is due to the strong attraction between the highly charged phosphate ions and calcium ions. This gives the salt a high lattice energy that cannot be offset by the hydration energy of the ions produced.

In pure water, the salt establishes the following equilibrium:

$Ca_3(PO_4)_2(s) + (aq) \rightleftharpoons 3Ca^{2+}(aq) + 2PO_4^{3-}(aq)$………………………………….(∗)

However, the salt readily dissolves in aqueous solutions of strong acids like dilute hydrochloric acid or nitric acid.

This is because the phosphate ions in solution combine with hydrogen ions from the acid to form a **weak acid** called phosphoric(V) acid.

$3H^+(aq) + PO_4^{3-}(aq) \rightarrow H_3PO_4(aq)$

The removal of phosphate ions to form a weak acid disturbs the equilibrium position in (∗). In order to restore the equilibrium position, more solid calcium phosphate dissolves. This makes the salt readily dissolve in aqueous solutions of strong acids than in pure water.

*For similar reasons, calcium carbonate and calcium oxalate are insoluble in pure water but readily dissolve in aqueous solutions of hydrochloric and nitric acids.*

- Calcium phosphate(V) can be converted to a better fertilizer; super phosphate of lime (calcium dihydrogenphosphate(V)) by treating it with 70% sulphuric acid.

  $Ca_3(PO_4)_2(s) + 2H_2SO_4(aq) \rightarrow Ca(H_2PO_4)_2(s) + 2CaSO_4(s)$

  Calcium dihydrogenphosphate(V) is a better fertiliser because it is more soluble and thus, it action is rapid.
- Triple super phosphate (one containing no $CaSO_4$) is made by treating calcium phosphate(V) with phosphoric acid.

  $Ca_3(PO_4)_2(s) + 4H_3PO_4(aq) \rightarrow 3Ca(H_2PO_4)_2(s)$

## Effects of ionic radii and ionic charge of the cations of group II elements on their compounds

- The cations of group II elements are doubly charged and have much smaller ionic radii than their corresponding cations of group I elements which are singly charged.
  Thus, cations of group II elements have a much higher charge density and hence, much higher polarizing power than their corresponding cations of group I elements.
- As a result, compounds of group II elements exhibit the following properties:
  (i) The salts of group II elements are less thermally stable than the corresponding salts of group I elements.
  For example, magnesium carbonate decomposes on heating whereas sodium carbonate does not.
  **Explanation**:
  Cations of group II elements are more highly charged with smaller ionic radii than the corresponding cations of group I elements. Thus, cations of group II elements have higher charge density than the corresponding cations of group I elements. Hence, cations of group II elements greatly polarize the neighbouring anions than the cations of group I elements can do.
  This makes the salts of group II elements less ionic (more covalent) while the salts of group I elements are more ionic. The less ionic/more covalent a salt is, the less stable to heat the salt is.

  (ii) The salts of group II elements are generally less soluble in water than the corresponding salts of group I elements.
  This is because the solubility of salts depends on the magnitude of both lattice energy and hydration energy.
  The higher the magnitude of lattice energy, the lower the solubility of the salt. This is because the heat of solution of such a salt will be less negative/ more positive.
  Group II elements form cations which are doubly charged with much smaller ionic radii than those of the corresponding cations of group I elements.
  Thus, the cations of group II elements strongly attract and hold the neighbouring anions more than the corresponding cations of group I elements can do. This makes salts of group II elements to have a much higher lattice energy which cannot be easily offset by the hydration energy of the ions produced. This reduces the solubility of the salts of group II elements as compared to that of group I elements.

(iii) Salts of group II elements generally have lower melting and boiling points than the corresponding salts of group I elements.

Cations of group II elements are more highly charged with much smaller ionic radii than the corresponding cations of group I elements. Thus, cations of group II elements have higher charge density than the cations of group I elements. The cations of group II elements greatly polarize the neighbouring anions than the cations of group I elements can do.

Salts of group II elements are less ionic (more covalent) and the salts of group I elements are more ionic/less covalent. The less ionic/more covalent a salt is, the lower the melting and boiling points of the salt.

(iv) Soluble salts of group II elements tend to go under hydrolysis in aqueous solution. Hydrolysis is much more pronounced in soluble salts of beryllium and to a less extent in soluble salts of magnesium.

$Be(H_2O)_4^{2+}(aq) + H_2O(l) \rightleftharpoons [Be(H_2O)_3(OH)]^{+}(aq) + H_3O^{+}(aq)$

Similarly for magnesium salts,

$Mg(H_2O)_6^{2+}(aq) + H_2O(l) \rightleftharpoons [Mg(H_2O)_5(OH)]^{+}(aq) + H_3O^{+}(aq)$

The ability for the soluble salts of group II elements to undergo hydrolysis decreases down the group. This is because of decrease in charge density of the cation resulting from increase in cation radius in the same order as the charge on the cations remain the same.

The resultant solutions of soluble salts of beryllium and magnesium are normally acidic to litmus due to hydrolysis of the cations.

Cations of group I elements do not undergo hydrolysis in aqueous solution. This is because of their low charge density/polarizing power brought about by their low charge and large ionic radii.

## Manufacture of cement

- Cement is a complex mixture of calcium silicates, aluminates, ferrites of calcium and other ingredients. It's a fine powder which sets a few hours when mixed with water and then hardens in a few days into a solid, strong material. Thus, cement is a binder.
- The common raw materials used in cement manufacture are limestone, sea shells, chalk or marl combined with shale, clay, slate, blast furnace slag, silica sand and iron ore.
- Cement can be manufactured through either **dry process** or **wet process**. The two processes are essentially the alike except in the wet process, the raw materials are ground with water before being fed into the kiln.
- **Steps involved in cement production are:**
  - ✓ The basic raw materials mainly limestone, clay and other materials obtained from quarrying are crushed through several stages to form a homogeneous mixture.

- ✓ The crushed material is mixed with other ingredients such as iron ore or fly ash and ground to form a homogenous mixture ('kiln feed' or 'raw feed' or 'slurry') which is fed into a rotary cement kiln and heated to a temperature of about 1500°C.

  Some reactions that take place in the kiln are:

  $CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$

  $CaO(s) + SiO_2(s) \longrightarrow CaSiO_3(s)$

  $CaO(s) + Al_2O_3(s) \longrightarrow Ca(AlO_2)_2(s)$
- ✓ In the kiln, certain elements are oxidised and driven off in form of gases. The remaining elements form **clinker** which comes out as grey balls.
- ✓ Clinker is cooled, powdered and mixed with small amounts of gypsum and limestone to form a fine and homogeneous powder called cement.

  The gypsum slows down the reaction between cement and water (i.e. slows down the setting properties when water is added to cement).

> Write short notes on each of the following terms:
> **(a) Mortar**
> **(b) Concrete**

## Complex compounds

- A complex is either an ion or a neutral compound consisting of a metal cation or atom directly bonded to a number of neutral molecules with lone pairs of electrons or negatively charged ions via dative/co-ordinate bonds.
- A complex ion is a positive or negative ion in which an atom or group of atoms with a negative charge or lone pair of electrons form dative bonds with the central metal ion.
- The neutral molecules or negatively charged ions are called **ligands**.
- Examples of some common complexes formed by group II elements are:

| **Complex** | $Be(H_2O)_4^{2+}$ | $Be(OH)_4^{2-}$ | $Be(NH_3)_4^{2+}$ | $BeF_4^{2-}$ | $Mg(H_2O)_6^{2+}$ |
|---|---|---|---|---|---|
| **C.N (no of ligands directly bonded to the central atom/ion)** | **4** | **4** | **4** | **4** | **6** |

- Complex formation is favoured by:
  - (i) Availability of empty orbitals (of suitable energy) to accommodate lone pairs of electrons from the ligands.
  - (ii) Charge density of the cation; cations with high charge density strongly attract and hold the lone pairs from the ligands.
  - (iii) Cation radius; the smaller the cation ionic, the higher the charge density.
- Group II elements have a tendency to form complexes.

  The tendency decreases in the order: $Be > Mg > Ca > Sr > Ba$

**Explanation:**
The radius of the cations increases from $Be^{2+}$to $Ba^{2+}$ but the charge on the cations remains the same. The charge density of the cations and hence, the attraction for the lone pairs of electrons on the ligands decrease from $Be^{2+}$to $Ba^{2+}$.
Beryllium forms the largest number of complexes because it forms beryllium ion with a very small ionic radius. Thus, the cation has a high charge density and hence, high polarizing power.
Magnesium forms a fair number of complexes but are less stable. Calcium, strontium and barium form very few complexes.

## Identification of group II cations in aqueous solution.

**Table showing effect of different reagents when separately treated with aqueous solutions containing magnesium, calcium and barium ions.**

| **Reagent added to the aqueous solution** | **Cation in aqueous solution** | | |
|---|---|---|---|
| | **$Mg^{2+}$** | **$Ca^{2+}$** | **$Ba^{2+}$** |
| Addition of dilute sodium hydroxide solution | White precipitate insoluble in excess | White precipitate insoluble in excess | White precipitate insoluble in excess |
| Addition of dilute ammonia solution | White precipitate insoluble in excess | No precipitate | No precipitate |
| Addition of sodium sulphate solution **or** dilute sulphuric acid | No precipitate | White precipitate | White precipitate |
| Addition of sodium (ammonium) carbonate solution | White precipitate | White precipitate | White precipitate |
| Addition of ammonium (potassium) oxalate solution followed by ethanoic acid | No precipitate | White precipitate insoluble in ethanoic acid.<br>(*The precipitate dissolves in mineral acids*) | White precipitate dissolves in hot/warm ethanoic acid |

| | | | |
|---|---|---|---|
| Addition of potassium chromate solution followed by ethanoic acid | No precipitate | Yellow precipitate soluble in ethanoic acid | Yellow precipitate insoluble in ethanoic acid.<br>(*The ppt is also insoluble in excess sodium hydroxide solution*) |
| Addition of little solid ammonium chloride followed by 3-4 drops of disodium hydrogenphosphate solution followed by excess ammonia solution.<br>***This is the confirmatory test for magnesium ions in aqueous solution.*** | White precipitate insoluble in excess ammonia solution.<br>(*The precipitate however dissolves in dilute hydrochloric or and dilute nitric acid*) | | |

Some ionic equations for reactions taking place during the identification of the cations in aqueous solution are:

$$M^{2+}(aq) + 2OH^{-}(aq) \longrightarrow \underbrace{M(OH)_2(s)}_{white\ ppt}\ ; \quad M^{2+}(aq) + SO_4^{2-}(aq) \longrightarrow \underbrace{MSO_4(s)}_{white\ ppt}$$

$$M^{2+}(aq) + CO_3^{2-}(aq) \longrightarrow \underbrace{MCO_3(s)}_{white\ ppt}\ ; \quad M^{2+}(aq) + C_2O_4^{2-}(aq) \longrightarrow \underbrace{MC_2O_4(s)}_{white\ ppt};$$

$$M^{2+}(aq) + CrO_4^{2-}(aq) \longrightarrow \underbrace{MCrO_4(s)}_{yellow\ ppt}; \quad Mg^{2+}(aq) + NH_4^{+}(aq) + HPO_4^{2-}(aq) \longrightarrow \underbrace{MgNH_4PO_4(s)}_{white\ ppt} + H^{+}(aq)$$