

CHAPTER 7

CHEMISTRY OF THE GROUP 1, 2 AND 3 ELEMENTS

S – BLOCK ELEMENTS

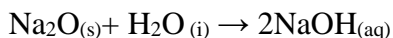
The alkali and alkaline earth metals are the s-block elements because their outermost electrons are found in the s-subshells. The alkali metals are in the group one and they have one electron in their outermost s-subshell while the alkaline earth metal have two electrons and are in group two.

7.1 GENERAL OBSERVATIONS ABOUT THE MAIN – GROUP ELEMENTS

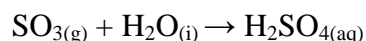
In studying the chemistry of the main group elements, there are some general trends observed. These periodic trends are discussed below:

Elements of the left side of the periodic table are mainly metals, while those on the right side of the periodic table are non-metals. Ionization energies and electronegativities are low for metal as compared to nonmetals. So the metal tend to lose their valence electrons to form cations (e.g. Na^+ , Ca^{2+} , Al^{3+}) in compounds or in aqueous solution. On the other hand, nonmetals react by gain of electrons to form monoatomic anions (O^{2-} , Cl^-) and Oxoanions (NO_3^- , SO_4^{2-}).

Also, oxides of metals are basic; they dissolve in water to give basic solution.



It should be noted however that oxides of metal in high oxidation states e.g. in some transition metals, can be acidic; chromium (IV) oxide, CrO_3 is an acidic oxide. Oxides of nonmetals are acidic they dissolve in water to give an acidic solution



Generally, metals have oxidations states equal to the group number, which corresponds to a loss of the valence electrons in forming compounds. Some metallic elements in the fifth and sixth periods also have oxidation states equal to the group number minus two (e.g. Pb^{2+}). On the other hand, non-metals (apart from fluorine and oxygen which are highly electronegative) have variable oxidation states, stretching from the group number (the most positive value) to the group number minus eight (the most negative value). As an illustration, Chlorine (a Group VII element) has the following oxidations states in compounds; +7, +5, +3, +1, and -1.

The metallic and nonmetallic character of elements changes gradually, in definite ways from left to right across the period and down the group. Generally, metallic character decreases from left to right across the period. While the metallic character increases down the group. This trend is

more obvious with the Group III A – VA elements. For examples, in group VA, Carbon is a nonmetal, silicon and Gallium are metalloids, while tin and lead are metals. Reactivity increases down the metallic group. For example, in the Group IA elements; lithium is much less reactive than sodium and potassium. For nonmetals, reactivity decreases down the nonmetallic group, for example fluorine is far more reactive than bromine and iodine.

A second-period element is often rather different from the other elements in its group. The reason for this is that the second period elements generally have small atoms that tend to hold electrons strongly, resulting to high electronegativity. For example while the electronegativity of nitrogen is 3.1, the other member of the group VA have electronegativities values within 1.9 – 2.1.

Another reason why the second – period elements behave differently from the remaining members of their group is that the second period elements involves only the s-and p orbital's in bond formation, which places a limit on the types of compounds they form. The remaining elements in the group involve the use of the s, p and d-orbital indicating that more types of compounds can be formed by these elements. For example, Nitrogen as a second-period element forms only the trihalides (e.g. NCl_3) while phosphorus has both the trihalides (PCl_3) and pentahalides (PCl_5) which it forms using the 3d orbital.

7.2 GROUP 1 – THE ALKALI METALS

The alkali metals are member of the group 1 elements. They have valence shell electronic configuration as ns^1

The alkali metals are chemically the most reactive metal and their reactivity increases as the group descend. This is because the single outer electron is increasingly screened from the positive charge of the nucleus by successive electron shells and so is lost more and more readily. Because the metal is very reactive, it occurs in nature combined with other elements.

The alkali metals are soft and white with a characteristic luster or sheen when freshly cut, this surface tarnishes very rapidly with the formation of a thin layer of the oxide. Table 7.1 shows members of the alkali metals and their electronic configuration.

Table 7.1 Group 1 elements and their electronic configuration

ELEMENTS	ELECTRONIC CONFIGURATION
Lithium Li	3 - $1s^2 2s^1$
Sodium Na	11 - $1s^2 2s^2 2p^6 3s^1$
Potassium K	19 - $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$
Rubidium Rb	37 - (Kr) $5s^1$
Caesium Cs	55 - (Xe) $6s^1$
Francium	87 - (Rn) $7s^1$

The atoms of the elements get larger down the group as more shells of electrons are added, screening the outer electrons from the increasing nuclear charge. Atoms of elements down the group are more likely to have electrons densities transferred away from them in a chemical reaction than atoms of element up the group. This is reflected in the decreasing electronegativity of the elements down the group.

Atoms of the elements down the group are held together less strongly than those higher up, leading to lower melting points and also reducing the strength of the metallic bond. Table 7.2 shows the physical properties of the group 1 elements.

Table 7.2 The physical properties of the group 1 elements

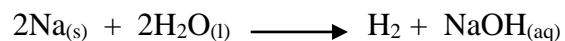
Element	Li	Na	K	Rb	Cs
Metallic radius/nm	0.16	0.19	0.24	0.25	0.27
Ionic radius/nm	0.074	0.102	0.138	0.149	0.170
Electronegativity	1.0	0.9	0.8	0.8	0.7
1 st Ionization energy/kJ mol	520	496	419	403	376
2 nd Ionization energy	7298	4563	3051	2632	2420
Melting points/ ^o c	181	98	63	39	29
Boiling points/ ^o c	1342	883	760	686	669
Density/gcm ⁻³	0.53	0.97	0.86	1.53	1.88

The group 1 elements have similar electronic configuration in which each has a single electron outside a full shell of inner electrons. This similarity in their electronic configuration directly influences their chemical properties since it determines the way in which they form chemical bond. The similarities in chemical behaviour on them includes

- (a) **Reactivity:** - They are chemically the most reactive metals. They are so reactive that they are generally found in nature combined with other elements and the pure metals are usually stored in an inert liquid out of contact with air or water.

The alkali metals react with cold water, displacing hydrogen and forming an alkaline hydroxide solution





- (b) **Univalence:-** They all have a single electron in their outer s-subshell which is readily lost to form ions with a noble gas configuration and a single positive charge e.g. Na^+ , Li^+ etc. The alkali metals thus have only one oxidation state, +1
- (c) **Formation of ionic Compound:** - Evidence from the ionization energies of elements suggests that there is a particular stability associated with the electronic configuration of the noble gases. In order for the group 1 elements to achieve this full shell configuration, they give away the single electron in their sub-shell to become M^+ ion. This involves the complete transfer of electron from the atom of the group one element to another atom of another group of element. This relationship is called ionic or electrovalent bond and the compound formed is called ionic compound.
- (d) **Strong Reducing Agent:** - As a reducing agent, they are oxidized in the course of a chemical reaction by
- Loss of electron
 - Increase in oxidation number
 - Addition of oxygen

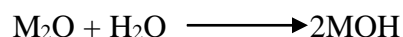
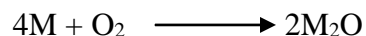


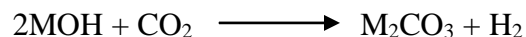
From the equation, electrons are removed from sodium and transferred to oxygen. Also oxygen is added to sodium. Therefore we say that sodium is oxidized while oxygen is reduced.

- (d) **Low Ionization Energy:** - Ionization energy is the energy needed to remove one mole of electron from one mole of a gaseous atom or gaseous cation. Ionization energy increases across the period, as it becomes harder to remove an electron due to the increasing positive charge across the period without the additional electron shells to screen the outer electrons. The atomic radius gets smaller and electrons are held more firmly.
- (e) They all burn in air in strongly exothermic reaction producing typical flame colours.

7.3 CHEMICAL PROPERTIES OF THE ALKALI METALS

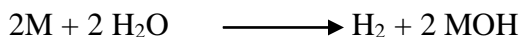
- They tarnish in damp air to form their oxides when these oxides react with water; it forms the corresponding hydroxides, which slowly absorb atmospheric carbon dioxide to form crystals of hydrated trioxocarbonate(iv) salt of the corresponding metal.





(M = alkali metal)

2. They react with water, liberating hydrogen and forming the corresponding hydroxide solutions which are very basic.



The vigour of this reaction increases down the group. While lithium reacts slowly with water, sodium react vigorously, potassium reacts violently with water that the hydrogen formed catches fire. Rubidium and caesium reacts explosively.

3. They react with dilute acids vigorously liberating hydrogen gas and forming the corresponding salt.



4. When heated, they react with hydrogen to form the corresponding, hydrides.



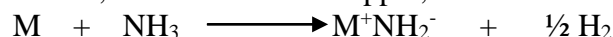
5. They react violently with halogens forming the corresponding halides



6. They dissolve in mercury forming the corresponding amalgams which are used as reducing agent



7. They dissolve in liquid ammonia and some amines to form a blue solution. At higher concentration, the solutions are copper, coloured



7.4 THE GROUP II ELEMENTS: – THE ALKALINE EARTH METALS

The group II elements are also very reactive metals in which the electropositive character increases down the metallic group. The element in this group has two electrons in their outer shell hence less reactive and harder than the group I elements, as they need more energy to lose the outer two electrons to achieve a noble gas configuration. They all burn in air in strongly exothermic reaction. Some of them produce typical flame colours. Apart from beryllium, which differs from the other alkaline earth metals in its lack of reactivity, alkaline earth metals react with cold water, displacing hydrogen and forming an alkaline hydroxide. Also, apart from beryllium, the alkaline earth metals are white, relatively soft metals, which are good conductors of heat and electricity. Table 7.3 shows the members of the group and their electronic configuration.

Table 7.3 The group II element and their electronic configuration.

ELEMENT		ELECTRONIC CONFIGURATION
Beryllium	Be	$4 - 1s^2 2s^2$
Magnesium	Mg	$12 - 1s^2 2s^2 2p^6 3s^2$
Calcium	Ca	$20 - 1s^2 2s^2 2p^2 3s^2 3p^2 4s^2$
Strontium	Sr	$38 - (\text{Kr}) 5s^2$
Barium	Ba	$56 - (\text{Xe}) 6s^2$
Radium	Ra	$88 - (\text{Rn}) 7s^2$

They form basic oxides and hydroxides with general formula MO and $\text{M}(\text{OH})_2$. Their oxides and hydroxides are either sparingly soluble or insoluble.

The freshly cut surfaces are shiny, but they quickly oxidize and the oxide film protects the metal from further reaction.

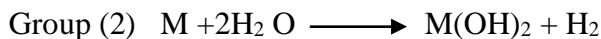
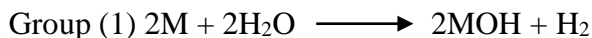
The group II element ionizes with the loss of two electrons to form ions with oxidation number of +2 e.g. Ca^{2+} , Mg^{2+} etc.

Like the alkali metal, the ionization energy and the electronegativity of the alkaline earth metals decrease down the group-as the number of shell increases, the attractive pull of the nucleus to the outer electrons decreases, as the electron are screened more effectively from the positive charge of the nucleus.

Like the alkali metals, metals down the group are held together less strongly than those higher up, leading to lower melting point. The strength of the metallic bond also decreases down the group as the density of the positive ions in the metal lattice decreases as the ion get larger. Also reactivity increase down the group as the element at the bottom of the group are more reactive and softer than those on top.. For example, Barium in the six period react with water much like the alkali metals. It is also a soft metal much like the alkali metals. Magnesium in the third period is a less reactive and harder metal.

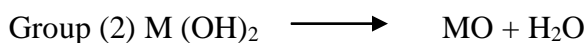
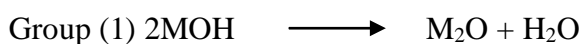
7.5 SIMILARITIES BETWEEN ALKALI AND ALKALINE EARTH METALS.

1. They are both high up in the electrochemical series hence good reducing agent.
2. They both react with water, reducing it to hydrogen and the metal hydroxide.



3. They both have their valence shell electrons in the s-subshell.

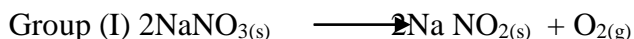
4. They both show one oxidation state.
5. The nitrates of all the s-block elements decompose on heating with a bunsen flame.
6. The s-block elements are so reactive that they are not found free in nature. And they are extracted from there ore by electrolysis.
7. Their hydroxides decompose to form the corresponding oxide and water.



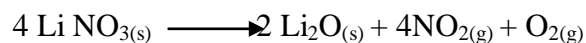
8. They are soft and easily cut with a knife
9. They both have low melting and boiling points
10. They have low densities (Li, Na, K,) are less dense than water
11. They have low standard enthalpies (heats) of melting and vapourisation
12. They show typical flame colours; Li – red, Na – yellow, K, - lilac, Rb – , Cs, - blue, Be – colourless, Mg, - Brilliant white, Ca – Brick red, Sr – crimson

7.6 DIFFERENCE BETWEEN ALKALI AND ALKALINE EARTH METALS.

1. The alkali metals are more electropositive than the alkaline earth metals.
2. The alkali metals have one electron in their outer shell while the alkaline earth metals have two.
3. The group II elements show stronger metallic bonding than the group I. This is reflected in their properties
4. All common group I metal salts are soluble in water. All group II salts where the anions have a charge of – 1 are soluble, with the exception of hydroxides. All group II salts where the anion has a charge of – 2 are insoluble with the exception of a few magnesium and calcium salts.
5. Group I nitrates except Lithium decompose on heating to give stable nitrite while group II nitrates give oxide

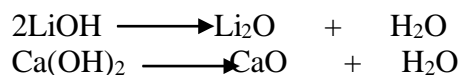
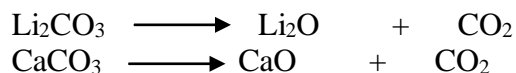


Group (II) and Lithium



6. The compounds of Group I metals are thermally more stable than those of group II metals. The carbonates and hydroxides of Group 1 metals (except Li_2CO_3 and LiOH) do

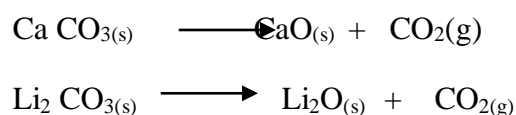
not decompose at 1000°C, but those of group II metals decompose to their oxides on heating.



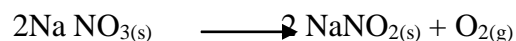
As stated earlier (section 7.1), a second period element shows properties that are different from its group. These differences are more obvious in the right side of the periodic table. For example:

Lithium though in group I resembles group II because it shows similar properties with the group II elements.

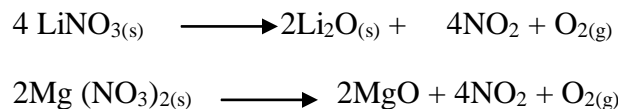
1. When heated in an ordinary Bunsen flame the group I carbonates are stable with the exception of lithium carbonate, Li_2CO_3 . The group II carbonates together with lithium carbonate decompose to form stable oxides, with the liberation of carbon dioxide gas



2. Group I nitrates, with the exception of lithium nitrate LiNO_3 decompose on heating on a Bunsen flame to give their corresponding nitrite and these (NaNO_2) are stable to heat.



In contrast, lithium nitrate and all the group II nitrates decompose on heating to form the corresponding oxide.



3. Li_2CO_3 is only slightly soluble in water at room temperature, whereas sodium carbonate and other group I elements carbonate are soluble

Also, beryllium differs from the other members of its group by its lack of reactivity. Furthermore, while the hydroxides of magnesium and barium are basic, beryllium hydroxide is amphoteric, reacting with both acids and bases.

7.7 THE GROUP III ELEMENTS

The group III elements mark the beginning of the p-block elements. These elements have three electrons in their outer shell, two in the s-subshell and one p-subshell. Their valence shell

electronic configuration is represented as $ns^2 np^1$. The principal oxidation state of the Group III elements is +3. Table 7.4 below shows the members of the group and their electronic configuration.

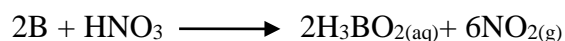
Table 7.4 The Group III elements and their electronic configurations.

Elements	Symbol	Electronic Configuration
Boron	B	$5 - 1s^2 2s^2 2p^1$
Aluminium	Al	$13 - 1s^2 2p^6 3s^2 3p^1$
Gallium	Ga	$31 - (\text{Ar}) 3d^{10} 4s^2 4p^1$
Indium	In	$49 - (\text{Kr}) 4d^{10} 5s^2 5p^1$
Thallium	Tl	$81 - (\text{Xe}) 5d^{10} 6s^2 6p^1$

There is a gradation in the properties of these elements as we go down the group. This gradation of properties can be explained in terms of:

7.7.1. METALLIC CHARACTERISTICS: - Metallic character increases down the group, from Boron which shows clearly non-metallic properties, through aluminium which shows amphoteric properties to the rest of the elements (gallium, indium and thallium) which are metals and also show metallic character.

In common with other reactive metals, aluminium will give off hydrogen gas with hydrochloric or sulphuric acids. But it does not react with nitric acid because the acid renders the aluminium surface passive. Boron does not give off hydrogen with sulphuric and nitric acid instead the boron reduces the acid



Boron, aluminium and gallium all show an oxidation state of +3 in their compounds while indium and especially thallium prefers an oxidation number of +1. These properties of the group show clearly that metallic property of the elements increases as one goes down the group.

7.7.2 NATURE OF THEIR BOND

Bonding in boron is covalent. The atom shares its $2s^2 2p^1$ valence electrons to attain a full valence shell configuration, with oxidation state of +3. Aluminium also forms many covalent compounds (e.g. AlCl_3) as well as ionic ones e.g. AlF_3 with +3 oxidation state. But gallium, indium and thallium form predominantly ionic compounds with oxidation states of +1.

The elements in this group all form halides with the general formula MX_3 e.g. BCl_3 , AlCl_3 , GaCl_3 . Some of these chlorides dimerise e.g. aluminium trichloride gives Al_2Cl_6 with a mixture of both covalent and coordinate bonding. Boron chloride (BCl_3) and aluminium chloride (AlCl_3) are covalent, hence they show nonmetallic character. Indium and especially thallium which prefer an oxidation state of +1 will prefer an ionic bond.

7.7.3. RELATIVE STABILITY OF THEIR OXIDATION STATES: -

The metallic behavior of an element decreases as the positive oxidation number of its elements in compound increases. Thus as the +1 oxidation state becomes more stable down the group so is

the increase in their metallic properties.

The +1 oxidation state increases down the group because increase in electronic shell screens the valence shell electrons from the attractive nuclear pull. Therefore, covalent bonding does not form between large atoms. Here, the s-electrons remain inert and do not take part in bonding, while the p-electron becomes easily lost to form ionic bond. So the +1 oxidation state becomes more stable than the +3 oxidation state down the group.

7.7.4 ACIDIC / BASIC NATURE OF THEIR OXIDES: - All the elements give oxides with general formula E_2O_3

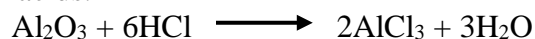
Boron burns in oxygen at 700°C to form boric oxide B_2O_3 which dissolves in hot water to form boric acid. $B_2O_3 + 3H_2O \longrightarrow 2H_2BO_3$

Boric acid and boric oxide reacts with metal oxide or hydroxide to form borates (borates are salts of oxyacid of boron). This clearly shows that boron exhibits nonmetallic properties

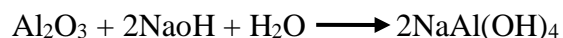
Aluminum reacts with oxygen to form aluminium oxide (alumina)



Aluminum oxide shows amphoteric properties as it reacts with both acids and bases. It forms simple aluminium salts with acids.



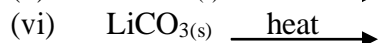
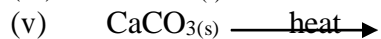
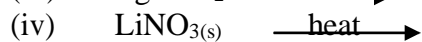
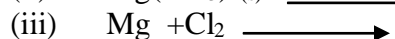
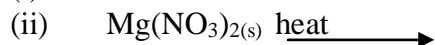
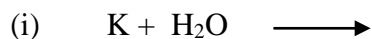
While it reacts with bases to form the corresponding metal aluminates.



PRACTICE QUESTIONS

1. (a) Give an account of how lithium, though in Group 1 behave like the Group II elements.

2. (a) Write balanced chemical equation for the following reactions:



3. Explain why and how beryllium though a group II element does not behave like the other members of its group

Explain why the ionization $\text{M}^+ + \text{e}^-$ takes place more readily as you pass down the group I elements.