

# 18

## GENERAL CHARACTERISTICS OF MAIN GROUP ELEMENTS

### 18.1 INTRODUCTION

The elements in Groups 1, 2, 13, 14, 15, 16, 17 and 18 are generally called the “*main group*” elements. They are made up of “s” block (Group 1 and 2) and “p” block elements (Groups 13, 14, 15, 16, 17 and 18).

The main group elements show simple trends with respect to a number of physical properties. These properties vary in a regular manner as we move from left to right across a row of elements called ‘period’. On the other hand, if we move from top to bottom in a column of elements, called ‘group’, we observe significant similarities in their properties with a few changes in the properties as we move down to heavier elements. We may explain these observations in terms of properties of individual atoms.

In this lesson we shall study some important physical properties and will try to explain the observed periodicity in atomic properties in terms of electronic configuration of the atoms. Finally, we shall relate the periodicity in atomic properties to the observed chemical behaviour of their compounds with special reference to their *oxides, hydrides and halides*.

### 18.2 OBJECTIVES

After reading this lesson you will be able to:

- Describe the variation in some important physical properties such as:
-

- size, ionization energy, electron affinity, electronegativity and, metallic behaviour along a group or a period among main group elements in terms of their given electronic configurations.
- Correlate the variation in the composition and properties of (i) oxides (ii) hydrides (iii) halides of main group elements with their position in the periodic table.
- Explain with reason for the similarities in properties between diagonal elements of main group elements especially those between Li and Mg.

### 18.3 SIZES OF ATOMS

Among the different physical properties of atoms, an important property that varies in a regular fashion with increasing atomic number is the *atomic size*. The relative sizes of main group elements are given in Fig. 18.1. We observe two important trends. These are:

1. In moving across a given period of elements, the atomic radius decreases. This is because the addition of electrons takes place in the same valence shell and are subjected to an increased pull of the nuclear charge at each step.

Period	Group							
	1	2	13	14	15	16	17	18
1	(H) <sub>37</sub>							He
2	(Li) <sub>152</sub>	(Be) <sub>111</sub>	(B) <sub>88</sub>	(C) <sub>77</sub>	(N) <sub>78</sub>	(O) <sub>66</sub>	(F) <sub>64</sub>	Ne
3	(Na) <sub>186</sub>	(Mg) <sub>168</sub>	(Al) <sub>143</sub>	(Si) <sub>117</sub>	(P) <sub>110</sub>	(S) <sub>104</sub>	(Cl) <sub>99</sub>	Ar
4	(K) <sub>231</sub>	(Ca) <sub>197</sub>	(Ga) <sub>122</sub>	(Ge) <sub>122</sub>	(As) <sub>121</sub>	(Se) <sub>117</sub>	(Br) <sub>114</sub>	(Kr) <sub>111</sub>
5	(Rb) <sub>244</sub>	(Sr) <sub>215</sub>	(In) <sub>162</sub>	(Sn) <sub>148</sub>	(Sb) <sub>141</sub>	(Te) <sub>135</sub>	(I) <sub>133</sub>	(Xe) <sub>130</sub>

Fig 18.1: Relative atomic sizes of main group elements.  
The radii are given in picometers.

The valence electrons are pulled closer to the nucleus. This results in a decrease in atomic size from as we move left to right in a period of elements (table 18.1).

SIZE DECREASES  $\longrightarrow$ 

ELEMENT	Li	Be	B	C	N	O	F
Atomic size (pm)	152	111	88	77	70	66	64
Nuclear charge	+3	+4	+5	+6	+7	+8	+9
Effective nuclear charge ( $Z^*$ )	+1.3	+1.95	+2.60	+3.25	+3.90	+4.55	+5.20
Electronic configuration	$1s^2, 2s^1$	$1s^2, 2s^2$	$1s^2, 2s^2, 2p^1$	$1s^2, 2s^2, 2p^2$	$1s^2, 2s^2, 2p^3$	$1s^2, 2s^2, 2p^4$	$1s^2, 2s^2, 2p^5$

Table 18.1: Variation of properties of main group elements along a period.

2. In going down a column of elements, i.e., a "group" the atomic size, *increases*. (table 18.2).

	Elements of Group 1	Atomic Size (pm)	Nuclear Charge (Z)	Effective Nuclear Charge ( $Z^*$ )	Electronic Configuration
SIZE INCREASES $\downarrow$	Li	152	3	1.3	[He], $2s^1$
	Na	186	11	2.2	[Ne], $3s^1$
	K	231	19	2.2	[Ar], $4s^1$
	Rb	244	37	2.2	[Kr], $5s^1$
	Cs	267	55	2.2	[Xe], $6s^1$

Table 18.2: Variation of properties of main group elements along a group.

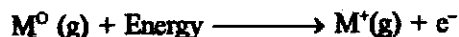
This increase may be explained in terms of a new electronic shell which is added when we move from one element to the next in a group. The additional increase in the energy level, more than compensates for the added nuclear charge.

## 18.4 IONIZATION ENERGY

The first ionization energy is the energy needed to remove the most loosely bound electron from an atom of the element in the gaseous state for one mole of the substance. As the

\* It is more appropriate to use effective nuclear charge,  $Z^*$  rather than simple nuclear charge,  $Z$ . This is calculated as  $Z^* = Z - S$  where  $S$  is called the screening constant. The value of  $S$  is determined by the extent of shielding of an electron by inner low lying electrons. The numerical value of  $S$  is determined by a set of empirical rules proposed by Slater and are known as Slater's rules. The effective nuclear charge faced by the outer electrons is lower than the nuclear charge,  $Z$ .

force of attraction between an electron and the nucleus increases, the energy required to remove the electron, i.e., the ionization energy also increases.



The first ionization energies ( $\text{kJ mol}^{-1}$ ) of main group elements are given in Fig. 18.2. In order to understand the variation in ionization energies given in Fig. 18.2, it is essential to understand the important factors which determine its magnitude, which are discussed below:

Period	Group							
	1	2	13	14	15	16	17	18
1	H (1312)							He (2372)
2	Li (520)	Be (900)	B (800)	C (1086)	N (1402)	O (1314)	F (1681)	Ne (2080)
3	Na (496)	Mg (738)	Al (578)	Si (787)	P (1012)	S (1000)	Cl (1251)	Ar (1521)
4	K (419)	Ca (590)	Ga (579)	Ge (762)	As (944)	Se (941)	Br (1140)	Kr (1351)
5	Rb (403)	Sr (550)	In (558)	Sn (709)	Sb (832)	Te (869)	I (1008)	Xe (1170)

IONIZATION ENERGY DECREASES ↑

↓ IONIZATION ENERGY INCREASES

Fig. 18.2: First ionization energies ( $\text{kJ mol}^{-1}$ ) of main group elements.

### 1. Magnitude of Nuclear Charge

If all other factors remain constant, the greater the nuclear charge, the greater is the attraction of the nucleus for the electron. Thus more energy is required to remove this electron from the pull of the nucleus. Ionization energy increases with increase in the value of nuclear charge.

### 2. The size of the atom

The force of attraction between the positively charged nucleus and the negatively charged electron is electrostatic. According to Coulomb's law, the force of attraction between two charges depends inversely on the square of the distance between them. This means the force of attraction decreases rapidly as the radius (size) of the atom increases. Thus ionization energy decreases as the size of the atom increases (other factors remaining constant).

### Ionization Energy and Main Group Elements

1. Within each period, for example, in moving from Li to Ne, atomic size decreases and nuclear charge increases. Both factors lead to an increase in the force of attraction between the nucleus and the electrons in the outermost orbit. Thus ionization energy value increases as we move from left to right in a period. It reaches a maximum value

at neon which has  $2s^2 2p^6$  configuration, i.e., a stable octet. It is most difficult to pull out an electron from a closed shell ( $ns^2 np^6$ ) configuration and that is why noble gases have the highest ionization energy value. (table 18.3)

**Table 18.3: Variation of ionization energy along a period.**

ELEMENT	Li	Be	B	C	N	O	F	Ne
Radius (pm)	152	111	88	77	70	66	64	—
Nuclear Charge	+3	+4	+5	+6	+7	+8	+9	+10
Ionization Energy ( $\text{kJ mol}^{-1}$ )	520	900	800	1090	1400	1310	1680	2080

However, there are a few irregularities in the general trend ! For example, the I.E. value of Boron is less than that of Beryllium. This is just the opposite of what was normally expected. Why?

This unusual behaviour can be explained in terms of their electronic configurations; Be:  $1s^2 2s^2$  and boron is  $1s^2, 2s^2 2p^1$ . In Be the outer electron is to be removed from a filled 2s orbital whereas in boron the electron to be ionized is a single 2p electron. Also the 2s electrons penetrate the nucleus more effectively and are thus more strongly attracted to the nucleus while the 2p electron is less penetrating and therefore, its force of attraction from the nuclear charge is less.

Similarly, a small decrease in the first ionization energy in going from Nitrogen to Oxygen may be attributed to the extra stability of the half-filled p-orbitals in the Nitrogen atom.

The extra stability attributed to half-filled or completely filled configuration can be explained in terms of gain in exchange energy. In these configurations, the system has maximum number of electrons in parallel spins. Since electrons of parallel spins like to stay away from each other, they do not shield each other from the nucleus effectively. Thus electron to nucleus attraction is large. Thus the energy of the system is lowered.

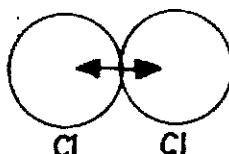
2. On moving down a group, ionization energy decreases (Fig. 18.2) This can be easily explained in terms of size alone. As we move down a group the size increases, therefore, the attraction of the nucleus for the outermost electron decreases. Thus ionization energy is lowered.

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## INTEXT QUESTIONS 18.1

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1. The bond length in  $\text{Cl}_2$  is 198 pm. The covalent radius of carbon
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is 77 pm ( $1 \text{ pm} = 10^{-9} \text{ m}$ ). Calculate the C-Cl bond length in  $\text{CCl}_4$ .

.....

2. Which atom of the following is expected to have smaller size?

(i)  ${}_9\text{F}$  and  ${}_{17}\text{Cl}$  (ii)  ${}_6\text{C}$  and  ${}_{14}\text{Si}$  (iii)  ${}_5\text{B}$  and  ${}_6\text{C}$  (iv)  ${}_6\text{C}$  and  ${}_7\text{N}$

.....

3. The bond length in  $\text{Cl}_2$  is 198 pm and C-Cl bond length in  $\text{CCl}_4$  is 176 pm. Calculate the atomic radii of carbon and chlorine.

.....

4. Which element in the following pairs of atoms is expected to have higher ionization energy?

(i)  ${}_4\text{Be}$  and  ${}_5\text{B}$  (ii)  ${}_{11}\text{Na}$  and  ${}_{12}\text{Mg}$  (iii)  ${}_2\text{He}$  and  ${}_{10}\text{Ne}$  (iv)  ${}_8\text{O}$  and  ${}_{16}\text{S}$

.....

5. Arrange the following atoms in order of increasing ionization energy:  ${}_2\text{He}$ ,  ${}_4\text{Be}$ ,  ${}_7\text{N}$ ,  ${}_{11}\text{Na}$ .

.....

6. Define ionization energy. How much energy is required to convert 1.0 g of sodium atom to  $\text{Na}^+$  ions?

.....

## 18.5 ELECTRON AFFINITY

It is evident from the values given in Fig 18.2 that elements on the extreme right say Group 17 (known as halogens) exhibit very high ionization energies. These elements are not keen to lose electrons and form positive ions. Instead these elements are observed to form negative ions by accepting an electron. In this process, they acquire electronic configuration of the noble gases. The energy change,  $\Delta E$ , for this process is called the electron affinity (EA) of the atom:



Electron affinity is the energy released when a neutral atoms in gaseous state accept electrons for one mole of the substance.

For example, the electron affinity of Cl atom is  $-349 \text{ kJ mol}^{-1}$ . This means that  $349 \text{ kJ}$  of energy is released when one mol of Cl atoms combine with 1 mol of electrons to give 1 mol of  $\text{Cl}^-$  ions:



Thus Electron affinity (EA) of chlorine is  $349 \text{ kJ mol}^{-1}$ . The greater the EA value the more stable is the anion formed. Electron affinity values are given in Fig. 18.3.

PERIOD ↓	GROUP							
	1	2	13	14	15	16	17	18
1	H (-73)							He (0)
2	Li (-59.6)	Be (0)	B (-26.7)	C (-154)	N (-7)	O (-141)	F (-328)	Ne (0)
3	Na (-53)	Mg (0)	Al (-42.5)	Si (-134)	P (-72)	S (-200)	Cl (-349)	Ar (0)
4	K (-48)	Ca (0)	Ga (-29)	Ge (-119)	As (-78)	Se (-195)	Br (-325)	Kr (0)
5	Rb (-47)	Sr (0)	In (-28.9)	Sn (-107)	Sb (-103)	Te (-190)	I (-295)	Xe (0)

Fig. 18.3: Electron Affinities Of Some Gaseous Main Group Atoms ( $\text{KJ mol}^{-1}$ )

The most important observations are:

1. Elements with high ionization energies, such as the halogens, also show large electron affinities.
2. Elements with low ionization energies, such as Group 1 elements (alkali metals) also show small electron affinities.

Therefore, a halogen atom easily gains an electron to form a negative ion. In contrast an alkali metal atom shows no tendency to gain an electron to form a negative ion, rather it tends to lose an electron to form a positive ion.

3. As we move down a group, the change in electron affinity is very small, i.e., the values do not show any change. Normally, we may expect the electron affinity value to decrease as we move down a group. The atoms undergo an increase in size and since the added electron is further away from the nucleus therefore it is attracted less strongly. But as the size of the atoms gets larger, the distance between the electrons in the valence shell increases. Therefore, electron-electron repulsion decreases and this gets balanced by the decreased nuclear-electron attraction.
4. Fluorine and other Period 2 elements show unexpectedly low values of electron affinity. Their low values may be explained in terms of the extremely small sizes of these atoms. In their cases, addition of an electron produces a negative ion which has a high electron density. This may lead to instability in terms of increased interelectronic repulsion.

## 18.6 ELECTRONEGATIVITY

In a homonuclear (two atoms of the same elements) diatomic molecule such as  $H_2$ ,  $F_2$ ,  $Cl_2$  the electron pair of the covalent bond is shared equally between the two atoms since they are identical and therefore attract the electrons of the bond equally strongly. However, in heteronuclear diatomic molecules such as  $HCl$ ,  $ICl$ ,  $ClF$ , the electron pair forming the covalent bond is not shared equally between the two atoms. One atom always attracts the electron pair more strongly than the other. This tendency of an atom is defined in terms of a parameter, defined as the electronegativity of an atom. The greater the electronegativity of an atom, the more strongly it attracts the electron pair in a covalent bond. For example fluorine atom is the most electronegative and will attract the electron pair towards itself when bonded to an atom of any other element.

*Electronegativity is defined as a measure of the ability of an atom to attract the electron pair in a covalent bond to itself.*

Electronegativity is a qualitative concept. Its quantitative value for an atom cannot be measured experimentally. Several methods have been suggested to assign approximate values to different atoms or species. Electronegativity is a useful concept and the difference between the electronegativities of two atoms helps us in identifying the nature of the bond. Electronegativities of main group elements are given in Fig. 18.4.

Period	Group							
	1	2	13	14	15	16	17	18
1	H 2.2							He —
2	Li 1.0	Be 1.5	B 2.0	C 2.5	N 3.1	O 3.5	F 4.1	Ne —
3	Na 1.0	Mg 1.2	Al 1.3	Si 1.7	P 2.1	S 2.4	Cl 2.8	Ar —
4	K 0.9	Ca 1.0	Ga 1.8	Ge 2.0	As 2.2	Se 2.5	Br 2.7	Kr 3.1
5	Rb 0.9	Sr 1.0	In 1.5	Sn 1.7	Sb 1.8	Te 2.0	I 2.2	Xe 2.4

Electronegativity Increases →

Fig. 18.4: Electronegativities of main group elements.

We observe two important trends:

1. Electronegativity increases across a period. As the effective nuclear charge increases along a period the pull of the nucleus for an electron of the other atom increases strongly.
2. Electronegativity decreases from top to bottom in a group. As the atomic size increases, the bond electrons are further from the nucleus and thus the force of attraction between the nucleus of an atom and the bond electrons decreases.

Elements on the right-hand side of the periodic table have high electronegativities and elements on the left-hand side have low electronegativities.

*Fluorine* is the most electronegative of all the elements. The second most electronegative element is *oxygen* followed by *nitrogen* in the third position.

If two atoms forming a diatomic molecule have same electronegativities, then the bonding pair is shared equally between the two atoms and the bond is said to be a *non-polar covalent bond*. On the other hand, when the difference in the electronegativities between two atoms forming a bond is not zero, i.e. they have different electronegativities, the bonding pair is shared unequally and the bond between such atoms is called a *polar covalent bond*. For example, H-H bond in  $H_2$  is a non-polar bond while H-Cl bond in HCl



is a polar bond, and is often represented as  $H-\overset{\delta+}{Cl}^{\delta-}$  (since electronegativity of chlorine atom is greater than that of hydrogen atom).

## 18.7 METALLIC BEHAVIOUR

The elements can be broadly classified into *metals* and *nonmetals*. This classification is based on certain physical properties which are characteristic of each type. Metals are electropositive in character and have a ready tendency to lose electrons (which make them good conductors):



This reaction is closely related to the ionization energy of an element, therefore, we may say that these two properties are inter-linked. The lower the value of ionization energy of an element, greater will be its tendency to undergo this reaction and therefore more electropositive and metallic the element is.

Two prominent observations are:

1. Elements on the left hand side in Fig. 18.2, show lower ionization energies than elements on the extreme right. Therefore, they act as metals in their behaviour. On moving down a group, the ionization energy decreases and so metallic character also increases.

*Metals* exist on the left-hand side and exhibit low ionization energies. Metallic character increases as we go down a group. Thus Cs is the most electropositive metallic element.

2. Elements on the right-hand side show high ionization energies and thus lose their outermost electron with difficulty. These elements prefer to accept electrons (large electron affinities) and are called *non-metals*.

Elements on the right-hand side are called non-metals. They show high ionization energies and large electron affinities.

Between these two extremes, i.e. metallic or nonmetallic behaviour, there are some elements which show properties that are intermediate between those of metals and

nonmetals. They are generally called '*metalloids*'. For example, silicon and arsenic are generally classified as metalloids.

Elements exhibiting properties intermediate between those of metals and nonmetals are called *metalloids*.

A classification of main group elements in these categories is shown in Fig. 18.5.

Period	Group							
	1	2	13	14	15	16	17	18
1								He
2	Li	Be	B	C	N	O	F	Ne
3	Na	Mg	Al	Si	P	S	Cl	Ar
4	K	Ca	Ga	Ge	As	Se	Br	Kr
5	Rb	Sr	In	Sn	Sb	Te	I	Xe
6	Cs	Ba	Tl	Pb	Bi	Po	At	Rn

Metal ←
Metalloids

} Non - metals

Fig. 18.5: Classification of main group elements into metal, non-metals and metalloids.

## INTEXT QUESTIONS 18.2

- Why does fluorine have lower electron affinity than chlorine?  
.....
- Which atom in the following pairs of atoms has greater electron affinity?  
(i) F, Cl (ii) Br, I (iii) I, Xe (iv) O, F (v) O, S  
.....
- Define electron affinity.  
.....
- On the basis of electronegativity values, classify the following molecules into polar and non-polar molecules.  
(i) HCl (ii) ICl (iii) H<sub>2</sub> (iv) N<sub>2</sub>  
.....

5. Which atom among the main group elements is expected to be least electronegative (consult Fig. 18.4).
- .....

6. Arrange the following elements into metals, non-metals and metalloids: Na, Al, S, I, Pb, Cs, Se and As.
- .....

## 18.8 PERIODICITY IN PROPERTIES OF COMPOUNDS OF MAIN GROUP ELEMENTS

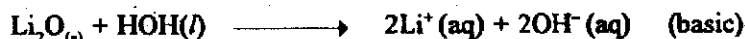
### 18.8.1 Oxides

Most of you may have already learnt that Periodic Table is a valuable aid in predicting the formulas of compounds with different anions. The periodicity in the formulas of oxides is shown in Fig. 18.6. We may also expect periodicity in their chemical behaviour.

↑ Increasing basicity of oxides ↓	Li <sub>2</sub> O Basic	BeO Amphoteric	B <sub>2</sub> O <sub>3</sub> Acidic	CO <sub>2</sub> Acidic	N <sub>2</sub> O <sub>5</sub> Acidic	-	F <sub>2</sub> O Acidic
	Na <sub>2</sub> O Basic	MgO Basic	Al <sub>2</sub> O <sub>3</sub> Amphoteric	SiO <sub>2</sub> Acidic	P <sub>4</sub> O <sub>6</sub> Acidic	SO <sub>3</sub> Acidic	Cl <sub>2</sub> O Acidic
	K <sub>2</sub> O Basic	CaO Basic	Ga <sub>2</sub> O <sub>3</sub> Amphoteric	GeO <sub>2</sub> Amphoteric	As <sub>4</sub> O <sub>6</sub> Amphoteric	SeO <sub>3</sub> Acidic	Br <sub>2</sub> O Acidic
	Rb <sub>2</sub> O Basic	SrO Basic	In <sub>2</sub> O <sub>3</sub> Basic	SnO <sub>2</sub> Amphoteric	Sb <sub>4</sub> O <sub>6</sub> Amphoteric	TeO <sub>3</sub> Acidic	I <sub>2</sub> O <sub>5</sub> Acidic
	Cs <sub>2</sub> O Basic	BaO Basic	Tl <sub>2</sub> O <sub>3</sub> Basic	PbO <sub>2</sub> Amphoteric	Bi <sub>2</sub> O <sub>3</sub> Basic	-	-
	Increasing Acidity of Oxides →						

Fig. 18.6: Periodicity of oxides of main group elements.

Oxides such as Li<sub>2</sub>O and CaO dissolve in water and yield basic solutions.



(HOH and H<sub>2</sub>O are same)

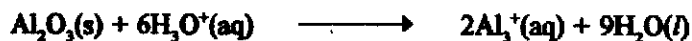
Nonmetallic oxides such as CO<sub>2</sub> and SO<sub>2</sub> dissolve in water and yield acid solutions and are called acid oxides.



**Basic Oxides** are formed by the combination of oxygen with highly electropositive elements called metals.

**Acidic Oxides** are formed by the combination of oxygen with electronegative elements called nonmetals.

Oxides which react with either acids or bases are called *amphoteric oxides*. For example,  $\text{Al}_2\text{O}_3$  does not dissolve appreciably in water. It, however, dissolves in acids and bases.



In the first equation  $\text{Al}_2\text{O}_3$  is behaving as a base and in the second equation as an acid and yields aluminate ion  $\text{AlO}_2^-$ .

### 18.8.2 Hydrides

Hydrogen forms stable hydrides with main group elements except noble gases. They are classified into two types:

**Ionic hydrides** are formed by the reaction of hydrogen with highly electropositive elements (Groups 1 and 2). They are ionic compounds and possess very high melting and boiling points. They dissolve in water to give basic solutions.



**Covalent hydrides** are formed by the reaction of hydrogen with p-block elements. These compounds are volatile in nature. Their acid strength increases as we move from left to right. Hydrides of main group elements are listed in Fig. 18.7.

GROUPS						
1	2	13	14	15	16	17
IONIC HYDRIDES ←			COVALENT HYDRIDES →			
LiH	$\text{BeH}_2$	$\text{B}_2\text{H}_6$	$\text{CH}_4$	$\text{NH}_3$	$\text{H}_2\text{O}$	HF
NaH	$\text{MgH}_2$	$(\text{AlH}_3)_x$	$\text{SiH}_4$	$\text{PH}_3$	$\text{H}_2\text{S}$	HCl
KH	$\text{CaH}_2$	$\text{Ga}_2\text{H}_6$	$\text{GeH}_4$	$\text{AsH}_3$	$\text{H}_2\text{Se}$	HBr
RbH	$\text{SrH}_2$	$\text{InH}_3$	$\text{SnH}_4$	$\text{SbH}_3$	$\text{H}_2\text{Te}$	HI
CsH	$\text{BaH}_2$	$\text{TlH}_3$	$\text{PbH}_4$	$\text{BiH}_3$	$\text{H}_3\text{PO}$	—

ACIDIC CHARACTER INCREASES →

ACIDIC CHARACTER INCREASES ↓

Fig. 18.7: Hydrides of main group elements.

The increase in acid strength of the hydrides as we move from left to right may be attributed to the increasing electronegativity of the metal, i.e., the increase in the polarity of the  $H^{\delta+} - X^{\delta-}$  bond.

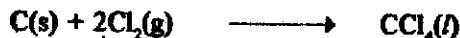
### 18.8.3 Halides

All main group elements (except He, Ne and Ar) react with halogens ( $F_2$ ,  $Cl_2$ ,  $Br_2$  and  $I_2$ ) to form halides. The compounds formed by reactions of halogens with metals are quite different from those of the non-metals. For example,

#### Metals



#### Non-metals



Metals halides are ionic compounds consisting of oppositely charged ions ( $Na^+$ ,  $Cl^-$ ). They are colourless crystalline solids with high melting points.

On the other hand, nonmetal halides are generally gases, liquids or solids of low melting points. The bonds in these compounds are covalent. These are two extreme types of bonds. Bonds in many other halides are of an intermediate nature. The nature of the bonds depends upon the electronegativities of the two combining atoms.

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### INTEXT QUESTION 18.3

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1. Which of the following oxides of main group elements is the most acidic? Which elements form the most basic oxides?

(i)  $Al_2O_3$             (ii)  $CO_2$             (iii)  $SO_2$

.....

2. Which of the following hydrides of main group elements is the most acidic?

(i)  $H_2Se$             (ii)  $H_2O$             (iii)  $HCl$             (iv)  $HI$

.....

3. Which of the following elements form (i) ionic (ii) covalent halides?

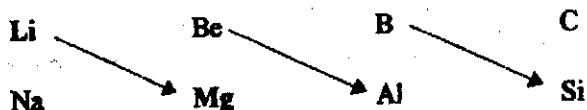
Ca, Cs, Li, C, Si, P, Mg.

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## 18.9 DIAGONAL RELATIONSHIP BETWEEN Li AND Mg

An important feature of the second period elements is that they resemble with the elements to their lower right element of the third period, i.e., diagonally opposite element. The reasons for this similar behaviour:



1. The electropositive nature of the elements increases on moving down a column but decreases when we move from left to right.

Electropositive nature of two diagonal elements will be quite similar.

2. On moving from left to right in a row, the charge increases but their size decreases, while in moving down a group the size increases. Thus on moving diagonally, *size to charge ratio remains almost the same*. The variation of different properties of main group elements is given in Fig 18.8.

		GROUP							
PERIOD		1	2	13	14	15	16	17	18
↓ BASIC CHARACTER OF OXIDES INCREASES ↓ METALLIC PROPERTIES INCREASE ↓ IONIZATION ENERGIES DECREASE ↓ ATOMIC RADII INCREASE	1	H							He
	2	Li	Be	B	C	N	O	F	Ne
	3	Na	Mg	Al	Si	P	S	Cl	Ar
	4	K	Ca	Ga	Ge	As	Se	Br	Kr
	5	Rb	Sr	In	Sn	Sb	Te	I	Xe
	6	Cs	Ba	Tl	Pb	Bi	Po	At	Rn
		← METALS					METALLOIDS		
		↓ NONMETALLIC PROPERTIES INCREASE ↓ ACID CHARACTER OF OXIDES INCREASES ↓ BASIC TO ACID CHARACTER OF HYDRIDES INCREASES ↓ ATOMIC RADII DECREASE ↓ IONIZATION ENERGIES INCREASE ↓ ELECTRON AFFINITIES INCREASE							

Fig 18.8: Variation of properties of main group elements.

### 18.9.1 Diagonal Similarities between Li and Mg

Lithium resembles more with its diagonally opposite member magnesium than with the other members of its own family, i.e., Na, K, Rb and Cs. The following properties show behaviour:

- (i) The radii of  $\text{Li}^+$  (60 pm) and  $\text{Mg}^{2+}$  (65 pm) are almost similar.
- (ii) Electronegativities of Li (1.0) and Mg (1.2) are comparable.
- (iii) Lithium when burnt in air forms  $\text{Li}_2\text{O}$ . Magnesium also burns in air to form  $\text{MgO}$ . Other alkali metals form peroxides ( $\text{Na}_2\text{O}_2$ ) and superoxides ( $\text{KO}_2$ ).
- (iv) Of all the alkali metal carbonates and nitrates, only  $\text{Li}_2\text{CO}_3$  and  $\text{LiNO}_3$  are unstable and decompose on heating. Similarly,  $\text{MgCO}_3$  and  $\text{Mg}(\text{NO}_3)_2$  decompose on heating to form  $\text{MgO}$ .
- (v) Lithium is the only alkali metal which forms  $\text{Li}_3\text{N}$  (lithium nitride) when lithium is burnt in an atmosphere of  $\text{N}_2$ . Similarly, Mg when burnt in  $\text{N}_2$  forms  $\text{Mg}_3\text{N}_2$ .
- (vi) Lithium hydroxide is the only alkali metal hydroxide which has low solubility in water, is weakly basic and decomposes on heating to form  $\text{Li}_2\text{O}$ . Magnesium hydroxide is also sparingly soluble, has low basicity and decomposes on heating to form  $\text{MgO}$ .
- (vii) Both lithium and magnesium metals combine with carbon to form carbides.

## 18.10 WHAT YOU HAVE LEARNT

- The elements comprising 's' block and 'p' block elements are called **main group or representative elements**.
- The elements of groups 1 and 2 are called 's' block elements, their valence electrons are  $ns^1$  and  $ns^2$ , respectively.
- A *period* is a horizontal row of elements of the periodic table.
- A *group* is a vertical column of elements of the periodic table.
- Many physical and chemical properties of the main group elements show periodic variation with atomic number and are called *periodic properties*.
- The atomic radius (or size) of an atom is one-half the distance between two similar atoms.
- The *effective nuclear charge* ( $Z^*$ ) is the net nuclear charge exerted on an electron in an atom. It is equal to nuclear charge ( $Z$ ) reduced by an amount that makes up for the screening ( $S$ ) by the intervening electrons,  $Z^* = Z - S$ .
- The *ionization energy* is the energy required to remove the outermost electron from a gaseous atom.
- The *electron affinity* is the energy released when a neutral atom in a gaseous state accepts an electron.
- *Electronegativity* is the ability of an atom in a molecule to attract the electrons of a covalent bond to itself.

A *metalloid* is an element whose properties are intermediate between those of a metal and those of nonmetal.

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**18.11 TERMINAL EXERCISE**


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1. Which elements of the 'periodic Table' constitute main group elements ?  
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2. List some important factor which determine the magnitude of ionization energy of an atom.  
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3. How does electronegativity change along a row of elements ?  
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4. Explain 'Metallic character decreases along a period but increase on moving down a group'.  
.....
5. Discuss the trends in the chemistry of main group elements with respect to:
  - (i) acidic and basic nature of the oxides;
  - (ii) ionic and covalent nature of the hydrides.
 .....
6. What is the cause of diagonal relationship amongst certain elements ?  
.....
7. Give reasons for the following:
  - (i) Electron affinity of fluorine is less than that of chlorine.
  - (ii) Ionization energy of B is less than that of Be.
  - (iii) Caesium is used in photoelectric cells.
  - (iv) Lithium resembles magnesium in its chemical behaviour.
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**CHECK YOUR ANSWERS**


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**INTEXT QUESTIONS 18.1**

- (1)  $r_{\text{Ca}} = 198/2 = 99 \text{ pm}$ ,  $r_{\text{F}} = 77 \text{ pm}$  .  $r_{\text{Ca-F}} = 99+77 = 176 \text{ pm}$
  - (2) (i) F (ii) C (iv) N
  - (3)  $r_{\text{Ca}} = 198/2 = 99 \text{ pm}$  .  $r_{\text{F}} = r_{\text{Ca-F}} - r_{\text{Ca}}$ , i.e,  $176-99=77 \text{ pm}$
  - (4)  ${}_{3}\text{Li}$  (ii)  ${}_{12}\text{Mg}$  (iii)  ${}_{2}\text{He}$  (iv)  ${}_{8}\text{O}$
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- (5)  $\text{Na} < \text{Be} < \text{N} < \text{He}$
- (6) Ionization energy of an atom is the energy needed to remove the most loosely bound electron from a gaseous atom.

$$\text{I.E. of Na} = 496 \text{ kJ mol}^{-1}$$

$$\text{I.E. of 1 g atom of Na} = \frac{496}{23} = 21.4 \text{ kJ}$$

(Atomic wt. of Na = 23)

### INTEXT QUESTIONS 18.2

- (1) The unexpectedly low value of F as compared to that of Cl atom may be attributed to the extremely small size of F atom vis-a-vis Cl atom. The addition of another electron produces a negative ion which has a high electron density and leads to increased interelectronic repulsions.
- (2) (i) Cl (ii) Br (iii) I (iv) F (v) S
- (3) It is the amount of energy released when a neutral atom in a gaseous state accepts an electron



- (4) Polar molecules:  $\text{H}^{\delta+} \text{Cl}^{\delta-}$ ;  $\text{I}^{\delta+} \text{Cl}^{\delta-}$

Non-polar molecules :  $\text{H}_2$ ;  $\text{N}_2$

- (5) Caesium (Cs)
- (6) Metals : Na, Pb, Cs; Nonmetals : S, I, Se; Metalloids : At, As

### INTEXT QUESTIONS 18.3

- (1)  $\text{SO}_2$

Compounds of oxygen with highly electropositive elements, i.e., s-block elements (Groups 1 and 2)

- (2) HI

- (3) Ionic halides : Ca, Cs, Li, Mg

Covalent halides : C, Si, P

### TERMINAL EXERCISE

- s-block and p-block elements are called main group or representative elements.
- Magnitude of nuclear charge
  - The size of the atom

3. It increases as we move from left to right in a row (or period) of elements.
4. Metallic behaviour of an element is associated with its ready tendency to lose electrons ( $M \longrightarrow M^+ + e^-$ ). Since ionization energy increases as we move across a row of elements from left to right, therefore, metallic character decreases as we move to the right of the period. Since I.E. decreases as we go down a group of elements, therefore, metallic behaviour becomes more pronounced as we go down the group.
5. (i) Acidic character of oxides of main group elements increases along a period and basic character becomes more pronounced as we go down a group.  
(ii) Since elements on the left side of the main group elements are metallic therefore they form hydrides which are ionic in nature. On the other hand, elements towards the right side are non-metallic therefore they form covalent hydrides.
6. Similar value for charge / radius ratio.
7. (i) Fluorine has lower electron affinity than chlorine because addition of another electron in the smaller 2p orbitals produces ( $F(g) + e^- \longrightarrow F^-(g)$ ) greater interelectronic repulsion which causes instability. However, 3p orbitals of chlorine can accommodate ( $Cl(g) + e^- \longrightarrow Cl^-(g)$ ) the additional electron with more ease and therefore greater energy is released for the formation of  $Cl^-(g)$  ion than  $F^-(g)$  ion.  
(ii) Boron atom ( $1s^2 2s^2 2p^1$ ) has lower I.E. value than Be(g) atom ( $1s^2; 2s^2$ ) although the former is expected to show greater I.E. value due to its increased Z value. This may be attributed to the reason that p electron penetrate less effectively and are not attracted to the nuclear charge as strongly as are the s-electrons. Therefore, it is easier to remove the last electron of boron than that of beryllium.  
(iii) Caesium has the lowest ionization energy, i.e., it can readily lose an electron and is therefore used in photoelectric cells.  
(iv) Due to diagonal relationship these two elements have the same charge / radius ratio.