

# 13. PERIODIC TABLE AND PERIODICITY

## 1. INTRODUCTION

You must have visited a library. There are thousands of books in a large library. In spite of this, if you ask for a particular book, the library staff can locate it easily. How is it possible? In a library, the books are classified into various categories and subcategories. They are arranged on the shelves accordingly. Therefore, locating the books becomes easy. Same is the story with chemical elements. A large number of elements and compounds are known today. But a systematic classification of these elements has made their study possible and easy. The well organized and tabulated classification of elements, as we know it today, is called the **Periodic Table**. It not only helps to locate, identify and characterize the element and its properties but also points out the directions in which new investigations are made.

## 2. GENESIS OF PERIODIC CLASSIFICATION

In 18<sup>th</sup> century, the number of elements was limited. In 19<sup>th</sup> century, scientists began to seek ways to classify elements because of their rapidly increasing number. They started recognizing patterns in properties and began to develop classification schemes. Some such early attempts of classification are described below.

### 2.1 Prout's Hypothesis

The atomic weights of all elements are simple multiples of atomic weight of hydrogen. Prout gave this hypothesis on the basis of Dalton's atomic theory and the atomic weights of some elements known at that time. But this hypothesis could not last longer, because there are some atomic weights which are fractional not in whole number.

### 2.2 Dobereiner's Triads

It was first attempt towards classification of elements. He arranged similar elements in groups of three elements called triad and the atomic mass of the middle elements of the triad is approximately the arithmetic mean of the other two.

**Table 13.1:** Example of dobereiner's triad

	Triad			Mean of at. Mass of (I) and (III) element
(i)	Li <sup>7</sup>	Na <sup>23</sup>	K <sup>39</sup>	$\frac{7+39}{2} = 23.00$
(ii)	Cl <sup>35.5</sup>	Br <sup>80</sup>	I <sup>127</sup>	$\frac{35.5+127}{2} = 81.25$
(iii)	P <sup>31</sup>	As <sup>75</sup>	Sb <sup>120</sup>	$\frac{31+120}{2} = 75.50$
(iv)	S <sup>32</sup>	Se <sup>79</sup>	Te <sup>127</sup>	$\frac{127+32}{2} = 79.50$
(v)	Ca <sup>40</sup>	Sr <sup>88</sup>	Ba <sup>137</sup>	$\frac{40+137}{2} = 88.50$

**Merits:** After Dobereiner, Chemists focused on chemicals in groups having similar physical and chemical properties.

**Demerits:** All the known elements did not follow this rule. Law of triads was rejected as some triads nearly had same atomic masses, e.g., (Fe, Co, Ni), (Ru, Rh, Pd), (Os, Ir, Pt)

## 2.3 Newland's Rule of Octaves

When the lighter elements are arranged in order of their increasing atomic weights, then every eighth element is similar to the first element in its properties, similarly as the eighth note of a musical scale is similar to the 1<sup>st</sup> one. e.g. Na, 8<sup>th</sup> element resembles in their properties with Li. Similarly K, the 8<sup>th</sup> element with Na, and so on.

	do	re	mi	pha	sol	la	si
Symbol of element	Li	Be	B	C	N	O	F
	7	9	11	12	14	16	19
Symbol of element	Na	Mg	Al	Si	P	S	Cl
	23	24	27	28	31	32	35.5

It is clear from the above table that sodium is the eighth element from lithium, whose properties resemble that of lithium.

This type of classification was limited up to only 20 elements.

### Demerits

- (i) Law of octave worked quite well for lighter elements but failed with heavier elements.
- (ii) Properties of elements were not taken into account and the elements were arranged in the order of their increasing atomic masses.
- (iii) No places were left for unknown elements and so, many elements occupied wrong positions. Thus, resulted in the rejection of the attempt.

## 2.4 Lothar Meyer's Volume Curve

The graphs of atomic volumes against weights are known as Lothar Meyer's volume curves.

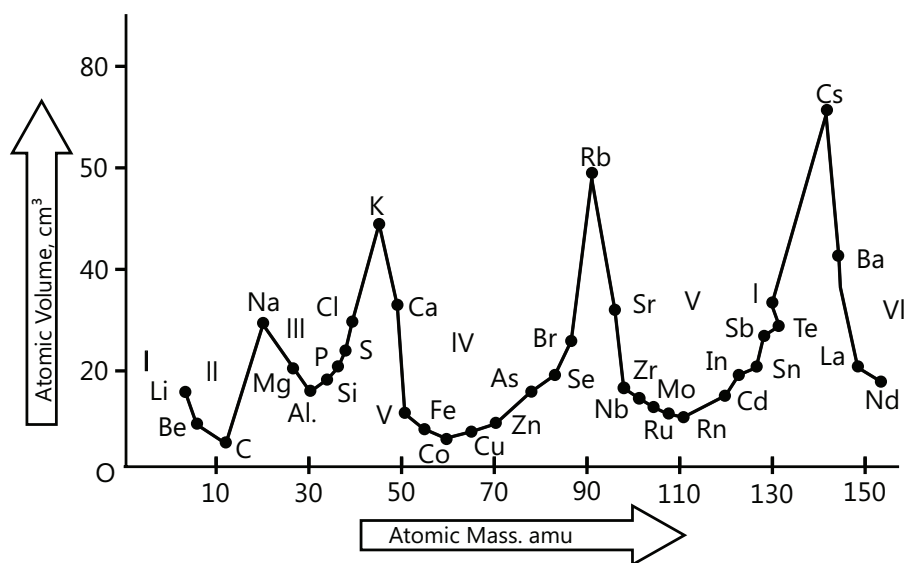


Figure 13.1: Lothar Meyer's volume curve

**Features of curve**

- (a) Alkali metals having the largest atomic volumes occupy the maxima of the curve.
- (b) Alkaline earth metals lie at about the mid points on the descending portions of the curve.
- (c) The halogens occupy positions on ascending portions of the curve before inert gases.
- (d) The transition metals occupy the minima of the curve.

**Demerits:** It lacked practical utility as it is not easy to remember the position of different elements on the curve.

**2.5 Mendeleev's Periodic Law**

According to Mendeleev's periodic law, the physical and chemical properties of elements are periodic functions of their atomic weights.

**Merits of Mendeleev's periodic table**

- (a) Study of elements and their compounds becomes easy and systematic, as by knowing the property of one element in a group, then the properties of the other elements present in the same group can easily be predicted.
- (b) Helps in the discovery of new elements. As Mendeleev left some blank spaces for some unknown elements and further, predicted the properties of these elements e.g. ekaluminium, ekasilicon.
- (c) Correction of doubtful atomic mass.
- (d) Correction in the valency of some elements.
- (e) Correction in the position of some elements.
- (f) Classification of elements then known, was done for the first time and the elements having similar properties were kept in the same group.
- (g) It encouraged research and led to discovery of newer elements.
- (h) Mendeleev had even predicted the properties of many elements not discovered at that time. This helped in the discovery of these elements.

For example: Mendeleev predicted the properties of the following elements.

- (i) Eka-boron - This was later called scandium (Sc)
- (ii) Eka- aluminium - This was later called gallium (Ga)
- (iii) Eka-silicon - This was later called germanium (Ge)

**Limitations of Mendeleev's periodic table**

- (a) The position of hydrogen was found to be anomalous due to its resemblance with the 1<sup>st</sup> group alkali metals and also with the 7<sup>th</sup> group halogens in their properties.
- (b) Position of isotopes: Isotopes must have different positions but they were placed in the same group.
- (c) Position of isobars: They were placed in different groups.
- (d) Dissimilar elements were placed together in the same group like K and Cu in 1<sup>st</sup> group.
- (e) Similar elements were placed in different groups.
- (f) Some higher atomic weight elements were placed before the lower atomic weight elements
- (g) e.g. Ar<sup>40</sup> precedes K<sup>39</sup>, Co<sup>58.9</sup> precedes Ni<sup>58.7</sup>, Te<sup>127.6</sup> precedes I<sup>127</sup>.
- (h) Position of metals and non-metals: Both were placed together in the same group.
- (i) Diagonal relationship could not be explained.

- (j) Position of lanthanides and actinides was not properly specified.
- (k) No proper position to VIII group elements.
- (l) There was no indication whether lanthanides and actinides were associated with group IIIA or group IIIB.
- (m) Position of Isobars- These elements had different groups when mass remained the same.
- (n) Lot of stress was given to the valence of elements.

## 2.6 Modern Periodic Law and Modern Periodic Table

**Mosley:** Proved that the square root of frequency ( $f$ ) of the rays, which are obtained from a metal on showering high velocity electrons is proportional to the nuclear charge of the atom.

This can be represented by the following expression.

$$\sqrt{f} = a(Z-b) \text{ where } Z \text{ is nuclear charge on the atom and } a \text{ and } b \text{ are constants.}$$

The nuclear charge on an atom is equal to the atomic number.

### Modern Periodic Table

According to modern periodic law, "The properties of elements are the periodic function of their atomic numbers".

**Period-**The details about the seven periods are as follows:-

Period	Atomic number		Number of elements
	From	to	
First	H (1)	He (2)	2
Second	Li (3)	Ne (10)	8
Third	Na (11)	Ar (18)	8
Fourth	K (19)	Kr (36)	18
Fifth	Rb (37)	Xe (54)	18
Sixth	Cs (55)	Rn (86)	32 (including lanthanides)
Seventh	Fr (87)	Ha (105)	19 (including actinides)

**Group:** The modern periodic table has 18 vertical columns and according to CAS system there are 16 groups having the following number of elements.

Group	Number of Elements
(a) I A group	7 (H, Li, Na, K, Rb, Cs, Fr) Alkali metals
(b) II A group	6 (Be, Mg, Ca, Sr, Ba, Ra) Alkaline earth metals
(c) III A group	5 (B, Al, Ga, In, Tl) Boron family
(d) IV A group	5 (C, Si, Ge, Sn, Pb) Carbon family
(e) V A group	5 (N, P, As, Sb, Bi) Nitrogen family
(f) VI A group	5 (O, S, Se, Te, Po) Oxygen family (Chalcogen)
(g) VII A group	5 (F, Cl, Br, I, At) Halogen family
(h) Zero group	6 (He, Ne, Ar, Kr, Xe, Rn) Inert elements 32 (Sc, Y, La, Ac & 14 lanthanide elements & 14 actinide elements.)
(i) III B group	These are elements of IIIB group, which could not be accommodated in one column and therefore written separately outside the periodic table.

(j)	IV B group	4 (Ti, Zr, Hf, Rf)
(k)	V B group	4 (V, Nb, Ta, Db)
(l)	VI B group	3 (Cr, Mo, W)
(m)	VII B group	3 (Mn, Tc, Re)
(n)	VIII (3) group	9 (Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, Pt)
(o)	I B group	3 (Cu, Ag, Au)
(p)	II B group	3 (Zn, Cd, Hg)

### Advantages of the Long Form of the Periodic Table

- (a) The table is based on a more fundamental property i.e. atomic number.
- (b) It correlates the position of elements with their electronic configuration more clearly.
- (c) The completion of each period is more logical. In a period, as the atomic number increases, the energy shells are gradually filled up until an inert gas configuration is reached.
- (d) It eliminates the even and odd series of IV, V and VI periods of Mendeleev's periodic table.
- (e) The position of VIII group is also justified in this table. All the transition elements have been brought to the middle as the properties of transition elements are intermediate between s- and p-block elements.
- (f) Due to the separation of two sub-groups, dissimilar elements do not fall together. One vertical column accommodates elements with same electronic configuration thereby showing same properties.
- (g) The table completely separates metals and non-metals. Non-metals are present in upper right corner of the periodic table.
- (h) There is a gradual change in properties of the elements with increase in their atomic numbers i.e., periodicity of properties can be easily visualized. The same properties occur after the intervals of 2, 8, 8, 18, 18 and 32 elements which indicates the capacity of various periods of the table.
- (i) The greatest advantage of this periodic table is that this can be divided into four blocks namely s-, p-, d- and f-block elements.
- (j) This arrangement of elements is easy to remember and reproduce.

### Defects of the Long Form of the Periodic Table

- (a) The position of hydrogen is still disputable as it was there in MENDELEEV periodic table in group IA as well as IVA & VIIA.
- (b) Helium is an inert gas but its configuration is different from that of the other inert gas elements
- (c) Lanthanide and actinide series could not be adjusted in the main periodic table and therefore they had to be provided with a place separately below the table.

### To Locate Group and Period if Atomic Number is given

**Locate period:** Write electronic configuration of each element for which the atomic number is given. The number of outermost shell suggests the period to which it belongs in the periodic table.

### Locate it's Block and Group

Group can be located after knowing the block of an element as follows:

For s-block elements,

gp. no. = No. of s-electrons in valence shell

For p-block elements,

gp. no. = No. of s-electrons + p-electrons in valence shell + 10

For d-block elements,

gp. no. = No. of  $(n - 1)d + ns$  electrons

**Illustration 1:** How many elements from the following atomic number are p-block elements?

83, 79, 42, 64, 37, 54 34

Use the following data for predicting answer – (Atomic Number of noble gases are given in the bracket)

**(JEE MAIN)**

He[2]            Ne[10]            Ar[18]            Kr[36]

Xe[54]            Rn[86]

**Sol:** 83 – p-block     $Xe^{54} 6s^2 5d^{10} 4f^{14} 6p^3$

79 – d-block     $Xe^{54} 6s^1 4f^{14} 5d^{10}$

42 – d-block     $Kr^{36} 5s^1 4d^5$

64 – f-block     $Xe^{54} 6s^2 5d^1 4f^7$

37 – s-block     $Kr^{36} 5s^1$

54 – p-block Xe

34 – p-block     $Ar^{18} 4s^2 3d^{10} 4p^4$

**Illustration 2:** (a) Write the electronic configuration of the elements given below:

A (At. No. = 9), B (At. No. = 12), C (At. No. = 29), D (At. No. = 54) and E (At. No. = 58)

(b) Also predict the period, group number and block to which they belong.

**(JEE MAIN)**

**Sol:** (a) Electronic configuration of the element A, B, C, D and E are as follows:

Element	At. No.	Electronic configuration
A	9	$1s^2 2s^2 2p^5$
B	12	$1s^2 2s^2 2p^6 3s^2$
C	29	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$
D	54	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6$
E	58	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 6s^2 5d^1 4f^1$

(b) **Element A:** Receives the last electron in 2p-orbital, therefore, it belongs to **p-block**.

**Group number** = 10 + No. of electrons in the valence shell = 10 + 7 = **17**.

**Period** = Principal quantum number of the valence shell = **2<sup>nd</sup>**.

**Element B:** Receives the last electron in 3s-orbital, thus, it belongs to **s-block**.

**Group number** = No. of electrons in the valence shell = **2**

**Period** = Principal quantum number of the valence shell = **3<sup>rd</sup>**

**Element C:** Receives the last electron in the 3d-orbital, thus, it belongs to **d-block**.

**Group number** = No. of electrons (penultimate shell + valence shell) = 10 + 1 = **11**

**Period** = Principal quantum number of the valence shell = **4<sup>th</sup>**

**Element D:** Receives its last electron in the 5p-orbital, thus, it belongs to **p-block**.

**Group number** = 10 + No. of electrons in the valence shell = 10 + 8 = **18**

**Period of the element** = Principal quantum number of the valence shell = **5<sup>th</sup>**

**Element E:** Receives its last electron in the 4f-orbital, thus, it belongs to **f-block**

It may be noted here, that, the filling of 4f-orbital occurs only when one electron has already entered the 5d-orbital. Therefore, element E belongs **to f-block** and not to **d-block**. Since it belongs to lanthanide series, there is no such group number of its own but is usually considered to lie in **group 3**.

**Period** = Principal quantum number of the valence shell = **6<sup>th</sup>**.

**Illustration 3:** Elements A, B, C, D and E have the following electronic configurations.

**A:**  $1s^2 2s^2 2p^1$

**B:**  $1s^2 2s^2 2p^6 3s^2 3p^1$

**C:**  $1s^2 2s^2 2p^6 3s^2 3p^3$

**D:**  $1s^2 2s^2 2p^6 3s^2 3p^5$

**E:**  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$

Which among these will belong to the same group in the periodic table?

**(JEE ADVANCED)**

**Sol:** We know that elements having similar valence electronic configuration belong to the same group of the periodic table. Therefore, elements **A** and **B** having three electrons in the valence shell, i.e.  $2s^2 2p^1$  and  $3s^2 3p^1$  respectively belong to the same group, i.e., group 13 of the periodic table.

### 3. NAMING OF ELEMENTS HAVING ATOMIC NUMBER GREATER THAN 100

(a) The name is derived directly from the atomic number of the elements using the following numerical roots:

**Table 13.2:** Naming of elements having atomic number greater than 100

Digit	Name	Abbreviation
0	nil	n
1	un	u
2	bi	b
3	tri	t
4	quad	q
5	pent	p
6	hex	h
7	sept	s
8	oct	o
9	oct	e

(b) The roots are put together in the order of the digits which make up the atomic number and are terminated by 'ium' to spell out the name. The final 'n' of 'enn' is removed when it occurs before 'nil' and the final 'i' of 'bi' and of 'tri' when it occurs before 'ium'

(c) The symbol of the element is composed of the initial letters of the numerical roots which make up the name.

**Illustration 4:** Eka-aluminium and eka-silicon were the names given by Mendeleev for the unknown elements gallium and germanium respectively. A recently discovered element was first named as eka-mercury. What is its atomic number? Write its group number, electronic configuration, IUPAC name. **(JEE MAIN)**

**Sol:** The element which comes after mercury in the periodic table is called eka-mercury. Its various parameters are:

$$Z = 80 + 32 = 112 \quad \text{IUPAC name: Uub}$$

Official name Cn(copernicium) E.C. =  $[\text{Rn}] 5f^{14} 8d^{10} 7s^2$

## 4. CLASSIFICATION OF PERIODIC TABLE BASED ON BLOCKS

**s-block Elements:** Elements of groups 1 and 2 including He in which the last electron enters the s-orbitals of the valence shell are called s-block elements. There are only **14 s-block elements** in the periodic table.

### Characteristics:

- The electronic configuration of outermost shell of s-block elements is  $ns^1$  (alkali metals; group 1) or  $ns^2$  (alkaline earth metals; group 2)
- The valence of group I elements is +1 and those of group II elements is +2.
- These are soft metals having low melting points and boiling points.
- Most of these form ionic compounds on account of their lower ionization energy.
- Most of these metals (except Be & Mg) and their salts impart characteristic colour to the flame e.g., sodium imparts a golden yellow colour; potassium imparts violet colour to the flame.
- These are highly reactive elements and are strong reducing agents.
- All are good conductors of heat and electricity.

**p-block Elements:** Elements of groups 13-18 in which the last electron enters the p-orbitals of the valence shell are called p-block elements.

### Characteristics:

- The electronic configuration of the outermost shell of p-block elements (group 13, 14, 15, 16, 17 and 18) is  $ns^2 np^{1-6}$ .
- These elements include metals and non-metals with a few metalloids. The metallic character, however, decreases along the period but increases down the group.
- These possess relatively higher ionization energy which tends to increase along the period but decreases down the group.
- Most of them form covalent compounds.
- Most of these elements show negative (except some metals) as well as positive oxidation states (except F).
- The oxidizing power of these elements increases along the period but decreases down the group.

**d-Block Elements:** There are three complete series and one incomplete series of d-block elements. These are: 1<sup>st</sup> or 3d-transition series which contains ten elements with atomic number 21-30 ( $_{21}\text{Sc}$ - $_{30}\text{Zn}$ ).

2<sup>nd</sup> or 4d-transition series which contains ten elements with atomic numbers 39-48 ( $_{39}\text{Y}$ - $_{48}\text{Cd}$ ).

3<sup>rd</sup> or 5d transition series which contains ten elements with atomic numbers 57 and 72-80

( $_{57}\text{La}$ ,  $_{72}\text{Hf}$ - $_{80}\text{Hg}$ ). 4<sup>th</sup> or 6d transition series which is incomplete at present and contains only nine elements. These are



$_{89}\text{Ac}$ ,  $_{104}\text{Rf}$ ,  $_{105}\text{Ha}$ , Unh (Seaborgium,  $Z = 106$ ),  $_{107}\text{Bh}$  (Bohrium),  $_{108}\text{Hs}$  (Hassium),  $_{109}\text{Mt}$  (Meitnerium), Ds (Darmstadtium,  $Z = 110$ ) and Cn (Copernicium,  $Z = 112$ ) or Ekamercury. The element,  $Z = 111$  has not been discovered yet. Thus, in all, there are 39 d-block elements.

### Characteristics:

- (a) The electronic configuration of outermost shell of d-block elements is  $ns^{0-2}$  followed with  $(n-1) s^2p^6d^{1-10}$ .
- (b) All (except Hg) are hard, ductile metals with high melting and boiling points.
- (c) All of these are good conductors of heat and electricity.
- (d) Their ionization energies are higher than s-block elements but lesser than p-block elements.
- (e) Most of the transition metals form coloured ions ( $\text{Zn}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Cd}^{2+}$  are colourless.)
- (f) These elements show variable oxidation states.
- (g) Most of these elements possess catalytic activity.
- (h) Metals and their ions are generally paramagnetic due to the presence of unpaired electrons.
- (i) Most of the transition metal ions possess the tendency to form complex ions.
- (j) Most transition metals form alloys.

**f-block Elements:** f-Block elements are also called inner-transition elements. In these elements, the f-subshell of the inner-penultimate is progressively filled up. There are two series of f-block elements each containing 14 elements. The fourteen elements from  $_{58}\text{Ce}$  -  $_{71}\text{Lu}$  in which, 4f-subshell is progressively filled up are called lanthanides or rare elements. Similarly, the fourteen elements from  $_{90}\text{Th}$  -  $_{103}\text{Lr}$  in which, 5f-subshell is progressively filled up are called actinides.

### Characteristics:

- (a) The electronic configuration of outermost shell of f-block elements is  $ns^2$ , followed with  $(n-2)f^{1-14}$ ,  $(n-1) d^{0-2}$ .
- (b) All are metals.
- (c) Lanthanoids are also known as **rare earth elements** whereas most of the members of actinoid series are known as **transuranic elements** (made artificially).
- (d) These show variable valency.
- (e) These form coloured ions.
- (f) Actinoids are radioactive.
- (g) These also form complexes.

## 5. POSITION OF METALS AND NON METALS IN PERIODIC TABLE

### Metals, Non Metals and Metalloids in Periodic Table

#### (a) Trends in metallic character in Periodic table

- (i) The metallic character increases down the group and decreases along the period.
- (ii) The non-metallic character decreases down the group and increases along the period.

**Note:** All the non-metals and metalloids belong to p-block (except H and He).

## 6. EFFECTIVE NUCLEAR CHARGE AND SHIELDING

In a polyelectronic atom, the internal electrons repel the electrons of the outermost orbit. This results in the decrease in the nuclear attraction on the electrons of the outermost orbit.

Therefore, only a part of the nuclear charge is effective on the electrons of the outermost orbit. Thus, the inner electrons protect or shield the nucleus and thereby decrease the effect of nuclear charge towards the electrons of the outermost orbit.

Thus, part of the nuclear charge works against outer electrons, and is known as effective nuclear charge  $Z^* = Z - S$   
 $Z^*$  = effective nuclear charge,  $S$  = shielding constant and  $Z$  = nuclear charge

A scientist named Slater, determined the value of shielding constant and put forward some rules which are listed below:

1. The shielding effect or screening effect of each electron of 1s orbital is 0.30.
2. The shielding effect of each electrons of ns and np i.e. electron of the outermost orbit, is 0.35.
3. The shielding effect of each electron of s, p or d orbitals of the penultimate orbit ( $n - 1$ ) is 0.85.
4. The shielding effect of each electron of s, p, d or f orbital of the inner penultimate orbit ( $n - 2$ ) and below this is 1.0

**Table 13.3:**  $Z^*$  for II period elements

Element	Atomic number	Calculation of			$\frac{349}{35.3}$	$Z^* = Z - S$
		$[0.35 \times \text{No. of nth electrons} - 1]$	$[0.85 \times \text{No. of (n-1)th electrons}]$	$[1.0 \times \text{No. of inner electrons}]$		
Li	3	—	$0.85 \times 2$	—	1.70	1.30
Be	4	$0.35 \times 1$	$0.85 \times 2$	—	2.05	1.95
B	5	$0.35 \times 2$	$0.85 \times 2$	—	2.40	2.60
C	6	$0.35 \times 3$	$0.85 \times 2$	—	2.75	3.25
N	7	$0.35 \times 4$	$0.85 \times 2$	—	3.10	3.90
O	8	$0.35 \times 5$	$0.85 \times 2$	—	3.45	4.55
F	9	$0.35 \times 6$	$0.85 \times 2$	—	3.80	5.20
Ne	10	$0.35 \times 7$	$0.85 \times 2$	—	4.15	5.85

**Illustration 5:** What is the screening constant for the last electron in Sc?

**(JEE MAIN)**

**Sol:**  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^1 4s^2$

Last electron is in 4s orbital.

The shielding effect for one electron of 4s = 0.35

Electrons of 3<sup>rd</sup> shell = 9; their contribution =  $9 \times 0.85$

Contribution of 2<sup>nd</sup> and 1<sup>st</sup> shell =  $10 \times 1$

Total =  $0.35 + 9 \times 0.85 + 10 \times 1 = 18$

$$\frac{349}{35.3} = 18$$

$$z^* = z - S = 21 - 18 = 3$$

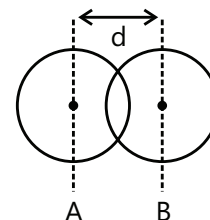
## 7. TRENDS IN PHYSICAL PROPERTIES

### 7.1 Atomic Radius

It refers to the distance between the centre of the nucleus of the atom to the outermost shell containing electrons. Since absolute value of the atomic size cannot be determined, it is usually expressed in terms of the following operational definitions.

#### (a) Covalent Radius

- (i) Normally, this term is used for non-metals.
  - (ii) It is defined as half of the distance between two successive nuclei of two covalently bonded atoms in a molecule.
  - (iii) bonded atoms in a molecule.
- $$\text{Covalent radius} = \frac{1}{2} \times \text{Internuclear distance between two covalently bonded like atom}(d)$$



**Figure 13.2-a:** Diagrammatic representation of covalent radius

In other words, covalent radius is the radius of a spherical atom that leads to observed bond lengths when the spheres are just touching each other.

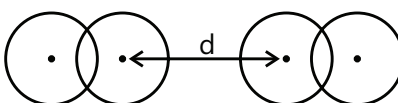
Covalent radius may be of following types

Single bond covalent radius

Double bond covalent radius

#### (b) Vander Waals Radius

- (i) Van der Waals radius is defined as half of the internuclear separation of two non-bonded atoms of the same element on their closest possible approach. The term is used for non-metals (covalent compound) and noble gases.
- (ii) It is half of the distance between two successive nuclei of two covalently bonded molecules of like atoms or two successive molecules of inert gases.



**Figure 13.2-b:** Diagrammatic representation of vander waal radius

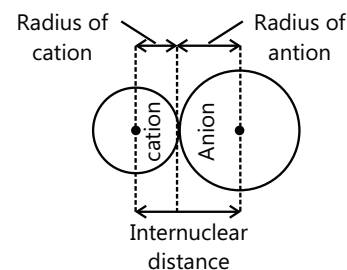
Vander Waals radius =  $\frac{1}{2} \times$  Internuclear distance between two successive nuclei of two covalent molecules (d)

#### (c) Crystal Radius or Metallic Radius

- (i) The term is usually used for metals.
- (ii) It is defined as half of the distance between two successive nuclei of two adjacent metal atoms in the metallic closed packed crystal lattice.

#### (d) Ionic Radius

- (i) This term is used in case of ions.
- (ii) It is the distance of outermost shell of an anion or cation from its nucleus. In other words, it is defined as the effective distance from the nucleus of the ion which is under influence in an ionic bond.



**Figure 13.2-c:** Diagrammatic representation of ionic radius

**MASTERJEE CONCEPTS**

It is evident that van der Waals radius is greater than Covalent radius of an atom because Vander Waals forces of attraction are weaker than covalent bond forces.

Vaibhav Krishnan JEE 2009, AIR 22

**Trends of Atomic Radius**

- (a) Along the period: On moving across a period, atomic radii decreases because effective nuclear charge increases.
- (b) Down the group: On moving down a group, atomic radii increases, because number of orbits increases.

**Factors Affecting Atomic Radii**

- (a) **Effective nuclear charge:** As the effective nuclear charge increases, the attractive force between nucleus and valence electron increases. Thus, across a period, atomic size/atomic radii decreases.

$$\text{So, Atomic radii} \propto \frac{1}{Z_{\text{eff}}}$$

- (b) **Size of valence shell:** Atomic radii is the measure of radius of valence shell. As the value of n (principal quantum no.) increases, for an orbit, its size increases, thus down a group, atomic radii increases.
- (c) **Multiplicity of bond:** Covalent radii decreases, as the multiplicity of bond increases.

For example, in case of carbon

	C – C	C = C	$\Delta_{\text{A-B}}$
$D_{\text{C-C}}$ (Å)	1.54	1.34	1.20
$r_{\text{C}}$ (Å)	0.77	0.67	0.60

- (d) **Percentage ionic character in bond:** Covalent radii of an atom in a bond depends upon % of ionic character. Increase in ionic character % leads in shortening of bond, decreasing the atomic radii.
- (e) **Cationic Radii:** Size of cation is always lesser than its parent atom and greater the charge on cation, smaller is its ionic radii. E.g.  $\text{Fe} > \text{Fe}^+ > \text{Fe}^{2+} > \text{Fe}^{3+}$  (decreasing ionic radii)
- Formation of cation involves loss of electron. Thus, effective nuclear charge increases, pulling the remaining electrons more tightly towards the nucleus.
- (f) **Anionic Radii:** Size of an anion is always larger than its parent atom. Formation of an anion involves gain of electrons by an atom and so, effective nuclear charge decreases. Thus, the valence shell electrons are less tightly held by the nucleus.

**MASTERJEE CONCEPTS**

Lanthanide contraction also plays an important role in deciding the trends of atomic radii accounting for the similar atomic radii of palladium and Pt.

Nikhil Khandelwal JEE 2009, AIR 94

**Illustration 6:** Which one of the following pairs would have a large size? Explain.

- (i) K or K<sup>+</sup> (ii) Br or Br<sup>-</sup> (iii) O<sup>2-</sup> or F<sup>-</sup> (iv) Li<sup>+</sup> or Na<sup>+</sup> (v) P or As (vi) Na<sup>+</sup> or Mg<sup>2+</sup>

(JEE MAIN)

**Sol:**

- (i) Due to higher effective nuclear charge, K<sup>+</sup> has smaller atomic size than K.  
 (ii) Due to lower effective nuclear charge, the size of Br<sup>-</sup> is greater than that of Br.  
 (iii) O<sup>2-</sup> and F<sup>-</sup> are isoelectronic species. Since effective nuclear charge of O<sup>2-</sup> is lower than that of F<sup>-</sup>, therefore, O<sup>2-</sup> has a greater atomic size than F<sup>-</sup>.  
 (iv) Li<sup>+</sup> and Na<sup>+</sup> both belong to group 1. Because of a greater number of shells (2, in case of Na<sup>+</sup> and 1, in case of Li<sup>+</sup>), Na<sup>+</sup> has a bigger atomic size than Li<sup>+</sup>.  
 (v) As has four shells while P has three. Therefore, atomic size of As is greater than that of P.  
 (vi) Na<sup>+</sup> and Mg<sup>2+</sup> are isoelectronic cations. Therefore, due to lower effective nuclear charge, the ionic radius of Na<sup>+</sup> is greater than that of Mg<sup>2+</sup>.

**Illustration 7:** Arrange the following in order of increasing radii?

- (i) I, I<sup>+</sup>, I<sup>-</sup> (ii) C, N, Si, P (iii) O<sup>2-</sup>, N<sup>3-</sup>, S<sup>2-</sup>, F<sup>-</sup>

(JEE MAIN)

**Sol:** The size of a neutral, positive and negative species is compared.

- (i) Size of a cation is always smaller while that of an anion is always bigger than the neutral atom, i.e. I<sup>+</sup> < I < I<sup>-</sup>  
 (ii) C and N lie in 2<sup>nd</sup> period while Si and P lie below them in the 3<sup>rd</sup> period. Since elements in the 3<sup>rd</sup> period have higher atomic size than those in the 2<sup>nd</sup> period. Therefore, atomic radii of Si and P are higher than those of C and N respectively. Since, atomic radii decreases across a period due to higher nuclear charge, therefore, C has higher atomic radius than N and Si has higher atomic radius than P. Thus, the overall order of increasing atomic radii is: N < C < P < Si.  
 (iii) Among isoelectronic ions, the size of anions increases as the nuclear charge decreases: F<sup>-</sup> < O<sup>2-</sup> < N<sup>3-</sup> < S<sup>2-</sup>.

**Illustration 8:** Select from each group the species which has the smallest radius stating appropriate reasons.

- (i) O, O<sup>-</sup>, O<sup>2-</sup> (ii) P<sup>3+</sup>, P<sup>4+</sup>, P<sup>5+</sup>

(JEE ADVANCED)

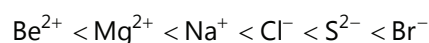
**Sol:** Ionic radius decrease on loss of electrons since the nuclear charge increases.

- (i) O has the smallest radius. The anion is larger than its parent atom. Also, the anion of the same atom with higher negative charge is bigger in size as compared to the anion with smaller negative charge as proton to electron ratio decreases. Thus, attraction between valence shell electrons and nucleus decreases. Hence, the electron cloud expands.  
 (ii) The ionic radius decreases as more electrons are ionized off. Thus, valency increases. So, the correct order is P<sup>5+</sup> < P<sup>4+</sup> < P<sup>3+</sup>.

**Illustration 9:** Arrange the following ions in the increasing order of their size: Be<sup>2+</sup>, Cl<sup>-</sup>, S<sup>2-</sup>, Na<sup>+</sup>, Mg<sup>2+</sup>, Br<sup>-</sup>?

(JEE ADVANCED)

**Sol:** Ionic radius  $\propto \frac{1}{\text{Nuclear charge}}$



Be<sup>2+</sup> is smaller than Mg<sup>2+</sup>, as, Be<sup>2+</sup> has one shell whereas, Mg<sup>2+</sup> has two shells. Mg<sup>2+</sup> and Na<sup>+</sup> are isoelectronic species.

Cl<sup>-</sup> is smaller than Br<sup>-</sup> as Cl<sup>-</sup> has three shells whereas Br<sup>-</sup> has four shells.

**MASTERJEE CONCEPTS**

- In isoelectronic ions, size decreases with increase in atomic number.

For e.g.  $N^{3-} > O^{2-} > F^- > Na^+ > Mg^{2+} > Al^{3+}$

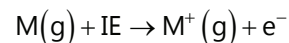
Although, Ne is also isoelectronic to them but its atomic radius is 1.60Å. It should not be compared to other radii because noble gases do not form ionic compounds and their radii are simply Van der Waals radii.

- In the end of the period, the atomic radii of inert gases are exceptionally higher because they do not form molecules and their radii are simply Van der Waals radii.

**Saurabh Gupta JEE 2010, AIR 443**

**7.2 Ionization Potential**

It is the amount of energy required to remove the most loosely bound electron from an isolated gaseous atom i.e.



The amount of energies required to remove the first, second, third etc. electrons from an isolated gaseous atom are called successive ionization energies and are designated as  $IE_1$ ,  $IE_2$ ,

$IE_3$  etc. It may be noted that  $IE_2$  is always greater than  $IE_1$ . Thus, the order is-  $IE_3 > IE_2 > IE_1$

**MASTERJEE CONCEPTS**

The removal of a second electron is relatively more difficult because after the removal of the first electron, remaining electrons in the cation are more effectively pulled by the nucleus due to increased effective nuclear charge, thus,  $IE_3 > IE_2 > IE_1$

**Neeraj Toshniwal (JEE 2009, AIR 21)**

**Factors affecting Ionisation Potential**

- Number of shells:** With the increase in the number of shells, the atomic radius increases i.e. the distance of outermost shell electron from the nucleus increases and hence the ionization potential decreases.
- Effective Nuclear Charge:** Atomic size decreases with the increase in effective nuclear charge because, higher the effective nuclear charge, stronger will be the attraction of the nucleus towards the electron of the outermost orbit and higher will be the ionization potential.
- Shielding Effect:** The electrons of the inner orbits repel the electrons of the outermost orbit due to which the attraction of the nucleus towards the electrons of the outermost orbit decreases and thus the atomic size increases and the value of ionization potential decreases.
- Stability of half-filled and fully filled orbitals:** The atoms whose orbitals are half-filled ( $p^3, d^5, f^7$ ) or fully-filled ( $s^2, p^6, d^{10}, f^{14}$ ) have greater stability than the other. Therefore, they require greater energy to remove an electron. However, stability of fully filled orbitals is greater than that of the half-filled orbitals.
- Penetration power:** In any atom, the s-orbital is nearer to the nucleus in comparison to p, and f orbitals. Therefore, greater energy is required to remove an electron from s-orbital than from p, d and f orbitals. The order is as follows-  $s > p > d > f$

## Periodic Trends in Ionisation Potential

**In a Period:** The value of ionization potential normally increase across a period, because effective nuclear charge increases and the atomic size decreases.

**Exceptions:** In the second period, ionization potential of Be is greater than that of B, and in the third period, ionization potential of Mg is greater than that of Al due to the high stability of fully filled orbitals. In the second period, ionization potential of N is greater than O and in the third period, ionization potential of P is greater than that of S, due to the stability of half-filled orbitals.

**In a Group:** The value of ionization potential normally decreases down the group because both, atomic size and shielding effect increase.

**Exception:** The value of ionization potential remains almost constant from Al to Ga in the III A group. ( $B > Al$ ,  $Ga > In$ ).

In IV B group i.e. Ti, Zr and Hf, the I.P. of Hf is higher than that of Zr due to Lanthanide contraction. Thus the I.P. of IV B group varies as  $Ti > Zr < Hf$ .

**Ionisation Potential of Transition Elements:** In transition elements, the value of ionization potential has changes very little across a period. This is because, the outermost orbit remains the same but electrons get filled up in the  $(n-1)d$  orbitals resulting in very little increase in the values of ionization potential.

In transition element series, the first ionization potential normally increases with increase in atomic number on going from left to right, but this periodicity is not uniform. The value of ionization potential of transition elements depends on two important factors-

- (a) The value of ionization potential increases with increase in effective nuclear charge.
- (b) The value of ionization potential decreases with increase in shielding effect when number of electrons increase in  $(n - 1)$  orbitals.
  - (i) In the first transition element series, the first ionization potential normally increases on going from left to right from Sc to Cr because shielding effect is much weaker in comparison to effective nuclear charge. The value of first ionisation potential of Fe, Co and Ni remains constant, because shielding effect and effective nuclear charge balance each other. The value of ionization potential shows a slight increase from Cu to Zn because they have fully filled s and d orbitals. The value of first ionisation potential of Mn is maximum because it has maximum stability due to fully filled s and half-filled orbitals.

**Inner Transition Elements:** The size of inner transition elements is greater than that of d block elements. Therefore, the value of ionization potential of f- block elements is smaller than that of d- block elements. Due to the almost constant atomic size of f- block elements in a period, the value of their ionisation potential remains more constant than that of d- block elements.

### MASTERJEE CONCEPTS

Ionization energy and the stable oxidation states of elements:

- (i) When difference in two successive IE values ( $\Delta^2$ ) for an atom is approximately 10-15 eV or less, then, the higher ox. state will be more stable.

E.g.

$$\text{For Al, } I.E_1 = 6.0 \text{ eV. } I.E_2 = 18.8 \text{ eV,}$$

$$I.E_3 = 28.4 \text{ eV and } I.E_4 = 120 \text{ eV,}$$

Then, for Al(II);  $\Delta I.E_{(1,2)} = 12.8 \text{ eV}$

$$\text{Al (III); } \Delta I.E_{(2,3)} = 9.6 \text{ eV}$$

$$\text{Al (IV); } \Delta I.E_{(3,4)} = 91.6 \text{ eV}$$

### MASTERJEE CONCEPTS

So, Al (III) is more stable than Al (I) or Al (II).

(ii) If the value of  $\infty$  is greater than 16.0 eV, then, the lower ox. state will be more stable.

E.g., For Na, I.E.<sub>1</sub> = 5.1 eV; I.E.<sub>2</sub> = 47.3 eV

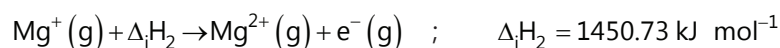
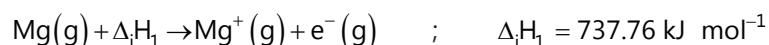
$$\therefore \Delta IE_{(1,2)} = 42.4 \text{ eV}$$

So, Na(I) is formed and not Na(II).

Aman Gour JEE 2012, AIR 203

**Illustration 10:** Calculate the energy required to convert all the atoms of magnesium to magnesium ions present in 24 mg of magnesium vapours? First and second ionization enthalpies of Mg are 737.76 and 1450.73 kJ mol<sup>-1</sup> respectively. **(JEE MAIN)**

**Sol:** According to the definition of successive ionization enthalpies,



$$\Delta \text{ Total amount of energy needed to convert Mg (g) atom into Mg}^{2+}(\text{g}) \text{ ion} = \Delta_i H_1 + \Delta_i H_2 \\ = (737.76 + 1450.73) \text{ kJ mol}^{-1} = 2188.49 \text{ kJ mol}^{-1}$$

$$24 \text{ mg of Mg} = \frac{24}{1000} \text{ g} = \frac{24}{1000 \times 24} \text{ mole} = 10^{-3} \text{ mole}$$

Therefore, amount of energy needed to ionize 10<sup>-3</sup> mole of Mg vapours = 2188.49 × 10<sup>-3</sup> = 2.188 kJ.

**Illustration 11:** The  $\Delta_i H_1$  and  $\Delta_i H_2$  of Mg(g) are 740 and 1450 kJ mol<sup>-1</sup>. Calculate the percentage of Mg<sup>+</sup>(g) and Mg<sup>2+</sup>(g) if 1 g of Mg(g) absorbs 50 kJ of energy. **(JEE MAIN)**

**Sol:**  $\Delta_i H_1$  and  $\Delta_i H_2$  is the ionization enthalpy i.e. heat energy used to remove the loosely bound electron.

No. of moles of Mg vapours present in 1 g = 1/24 = 0.0417

Energy absorbed in the ionization of 0.0417 mole of Mg(g) to Mg<sup>+</sup>(g) = 0.0417 × 740

= 30.83 kJ; Energy left unused = 50 – 30.83 = 19.17 kJ

Now, 19.17 kJ will be used to ionize Mg<sup>+</sup>(g) to Mg<sup>2+</sup>(g)

$$\underbrace{\text{Na} \quad \text{Mg} \quad \text{Al}}_{\text{Metals}} \quad \text{No. of moles of Mg}^+(\text{g}) \text{ converted into Mg}^{2+}(\text{g}) = 19.17/1450 = 0.0132$$

No. of moles of magnesium ions left as Mg<sup>+</sup>(g) = 0.0417 – 0.0132 = 0.0285

$$\underbrace{\text{Si}}_{\text{Metalloid}} \quad \% \text{ of Mg}^+(\text{g}) = (0.0285/0.0417) \times 100 = 68.35\% \text{ and } \% \text{ of Mg}^{2+}(\text{g}) = 100 - 68.35 = 31.65\%$$

**Illustration 12:** The first ( $\Delta_i H_1$ ) and the second ( $\Delta_i H_2$ ) ionization enthalpies (kJ mol<sup>-1</sup>) of a few elements designated by Roman numerals are shown below: **(JEE ADVANCED)**

Element	$\Delta_i H_1$	$\Delta_i H_2$
I	2372	5251
II	520	7300



III	900	1760
IV	1680	3380

Which of the above elements is likely to be (a) a reactive metal (b) a reactive non-metal (c) a noble gas (d) a metal that forms a stable binary halide of the formula  $AX_2$  (X = halogen).

**Sol:**

- (i) Since Element II has a very low  $\Delta_i H_1$  but a very high  $\Delta_i H_2$ , therefore, it has only one electron in the valence shell and hence is likely to be a reactive metal (i.e., an alkali metal).
- (ii) Since the  $\Delta_i H_1$  of Element IV is very high and its  $\Delta_i H_2$  is not so high (actually almost double), IV is likely to be a reactive non-metal (i.e. a halogen).
- (iii) Among the elements listed,  $\Delta_i H_1$  of element I is the highest and its,  $\Delta_i H_2$  is also not so high, therefore, it must be a noble gas.
- (iv) The  $\Delta_i H_1$  of element III is higher than that of element II, but unlike element II, its  $\Delta_i H_2$  is only about twice its  $\Delta_i H_1$ , therefore, it is likely that element III has two electrons in the valence shell (i.e., alkaline earth metal). As such it will form a stable binary halide of the formula  $AX_2$  where A is the metal and X is the halogen.

**Illustration 13:** From each set, choose the atom which has the largest ionization enthalpy and explain your answer.

- (i) F, O, N      (ii) Mg, P, Ar      (iii) B, Al, Ga

**(JEE MAIN)**

**Sol:** Largest ionization enthalpy is the highest amount of energy needed to remove the valence electron due to a stronger nuclear charge and a smaller atomic size.

- (i) F, O, N-All belong to 2<sup>nd</sup> period. Among these, F has the highest  $\Delta_i H_1$  because of its smallest size and highest nuclear charge.
- (ii) Mg, P, Ar-All lie in the 3<sup>rd</sup> period. Among these, Ar has the highest  $\Delta_i H_1$  because it has stable inert gas configuration.
- (iii) B, Al, Ga-All lie in group 13. B has the highest  $\Delta_i H_1$  due to its smallest size.

**Illustration 14:** Compare qualitatively the first and second ionization potentials of copper and zinc. Explain the observation.

**(JEE ADVANCED)**

**Sol:**

	$IE_1$ kJ mol <sup>-1</sup>	$IE_2$ kJ mol <sup>-2</sup>
Cu	744	1961
Zn	906	1736

$IE_1$  of copper is less than that of zinc, because removal of electron takes place from  $4s^1$  (attaining a more stable configuration  $3d^{10}$ ) whereas, in case of zinc, it is from completely filled  $4s^2$  (attaining the configuration  $4s^1$ )

$IE_2$  of copper is higher than zinc, because the removal of 2<sup>nd</sup> electron from a stable configuration ( $d^{10}$ ) requires higher energy.

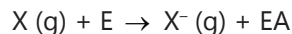
**Illustration 15:** The first four successive ionization energies for an element are (6.113, 11.871, 50.908, 67.01) respectively. What is the number of valence shell electrons?

**(JEE ADVANCED)**

**Sol:** The difference in second and third ionization is very large. Therefore, the no. of valence shell electrons should be 2. The element would attain the noble gas configuration after losing these 2 electrons.

## 7.3 Electron Affinity

It is the amount of energy released when a neutral isolated gaseous atom accepts an electron to form a gaseous anion.

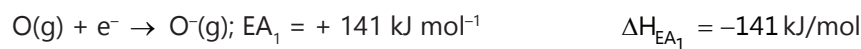


Similarly, second and third electron can be added to form gaseous dinegative and trinegative ions. The energy changes accompanying the addition of first, second, third etc. electrons to neutral isolated gaseous atoms are called successive electron affinities and are designated as  $EA_1$ ,  $EA_2$ ,  $EA_3$ , etc.

Since an atom has a natural tendency to accept an electron, therefore, the first electron affinity ( $EA_1$ ) is always taken as positive. However, the addition of second electron to the negatively charged ion is opposed by coulombic repulsion. Hence, energy has to be supplied for the addition of second electron.

Thus, second electron affinity ( $EA_2$ ) of an element is taken as negative.

For example,



### Factors Affecting Electron Affinity

**Atomic size or atomic radius:** When the atomic size/radius increases, the electrons entering the outermost orbit is more weakly attracted by the nucleus and the value of electron affinity is lower.

**Effective Nuclear charge:** When effective nuclear charge is more, then, the atomic size is less. Then, the atom can easily gain an electron and possess a higher value of electron affinity.

**Stability of Fully-Filled and Half-Filled orbitals:** The stability of the configuration having fully-filled orbitals ( $p^6$ ,  $d^{10}f^{14}$ ) and half-filled orbitals ( $p^3$ ,  $d^5$ ,  $f^7$ ) is relatively higher than that of other configurations. Hence, such type of atoms have a lesser tendency to gain an electron, therefore, their electron affinity values will be very low or zero.

**Trends in Electron Affinity:** In a period, atomic size decreases with the increase in effective nuclear charge and hence, increases the electron affinity.

#### Exception:

- (a) Ongoing from  $C^6$  to  $N^7$  in the second period, the values of electron affinity decrease instead of increasing. This is because there are half-filled ( $2p^3$ ) orbitals in the outermost orbit of N, which are more stable. On the other hand, the outermost orbit in C has a  $2p^2$  configuration.
- (b) In the third period, the value of electron affinity of Si is greater than that of P. This is because the electronic configuration of the outermost orbit in P atom is  $3p^3$ , which being half-filled, is relatively more stable. The values of electron affinity of inert gases are zero, because their outermost orbit has fully-filled p orbitals.
- (c) In a period, the value of electron affinity goes on decreasing on going from group IA to group IIA. The value of electron affinity of the elements of group IIA is zero because ns orbitals are fully-filled and such orbitals have no tendency to accept electrons.

**In a Group:** The values of electron affinity normally decrease down a group because the atomic size increases, decreasing the actual attractive force of the nucleus.

#### Exceptions:

- (a) The value of the electron affinity of F is lower than that of Cl, because the size of F is very small and compact and the charge density is high on the surface. Therefore, the incoming electron/s experience more repulsion in comparison to Cl accounting for the highest value of Cl in the periodic table.

- (b) The values of electron affinity of alkali metals and alkaline earth metals can be regarded as zero, because they do not have the tendency to form anions by accepting electron/s.

### MASTERJEE CONCEPTS

- (a) Cl has the highest electron affinity (3.7)
- (b) Higher the EA of an element, easier is the addition of an electron.
- (c) Following are some important observations derived from the general trend of electron affinity:
- (i) More the tendency to gain an electron, more is the non-metallic nature. Therefore, non-metallic nature increases along the period but decreases down the group.
  - (ii) More the tendency to form an anion, more is the tendency to show ionic bonding. Therefore, tendency of non-metals to show ionic bonding increases along the period but decreases down the group.
  - (iii) More the tendency to get reduced, more is the oxidizing nature. Therefore, oxidizing power increases along the period but decreases down the group

Order of Oxidizing power-  $F > Cl > Br > I$ .

**B Rajiv Reddy JEE 2012, AIR 11**

**Illustration 16:** The electron gain enthalpy of chlorine is  $-349 \text{ kJ mol}^{-1}$ . How much energy in kJ is released when 3.55 g of chlorine is converted completely into  $\text{Cl}^-$  ion in the gaseous state? **(JEE MAIN)**

**Sol:** According to the definition of electron gain enthalpy,  $\text{Cl}(\text{g}) + \text{e}^-(\text{g}) \rightarrow \text{Cl}^-(\text{g}) + 349 \text{ kJ mol}^{-1}$

$\text{C} \equiv \text{C}$  Energy released when 1 mole (=35.5 g) of chlorine atoms change completely into  $\text{Cl}^-(\text{g}) = 349 \text{ kJ}$

Energy released when 3.55 g of chlorine atoms change completely into  $\text{Cl}^-(\text{g}) = \frac{349}{35.5} \times 3.55 = 34.9 \text{ kJ}$

**Illustration 17:** Which of the following pairs of elements would have more negative electron gain enthalpy? Explain (i) N or O (ii) S or O (iii) C or Si **(JEE ADVANCED)**

**Sol:** (i) The electron gain enthalpy of O is highly negative while that of N is slightly positive.

**Reason:** The electronic configuration of N is quite stable ( $1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$ ) since it has exactly half-filled 2p-orbitals and hence has no tendency to accept an extra electron. In other words, energy has to be supplied to add an extra electron. Thus, electron-gain enthalpy of N is slightly positive. In contrast, the electronic configuration of O ( $1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$ ) is not so stable but it has a higher nuclear charge and smaller atomic size than N and hence, it has a higher tendency to accept an extra electron. In other words, electron gain enthalpy of O is highly negative.

(ii) S has more negative electron gain enthalpy than O.

**Reason:** The size of O is much smaller than that of S. As a result, the electron-electron repulsions in the smaller 2p-subshell of O are comparatively more than those present in the bigger 3p-subshell of S. Therefore, S has a higher tendency to accept an additional electron than O.

(iii) C has a more negative electron gain enthalpy than Si.

**Reason:** This is because C-atom has a smaller size than Si-atom. (Note that the electron-electron repulsions in these atoms are not very large because they contain only 4 electrons in the outermost shell.)

**Illustration 18:** (i) Arrange the following elements in order of decreasing electron gain enthalpy: B, C, N, O.

**(JEE ADVANCED)**

**Sol:** N has +ve electron gain enthalpy while, all others have -ve electron gain enthalpies. While moving from B → C → O, size decreases leading to -ve electron gain enthalpy in the same order. Thus, the overall decreasing order of electron gain enthalpies is N, B, C, O.

## 7.4 Electronegativity

The tendency of an atom to attract the shared pair of electrons of the covalent bond towards itself is called electronegativity of that atom.

### Factors Affecting Electronegativity

**Atomic size:** Electronegativity of a bonded atom decreases with increase in size since the attractive force on the valence electrons decreases and hence electronegativity decreases.

**Hybridisation state of atom:** Electronegativity increases with increase in the s-character of the hybrid orbital. This is because, the s-orbital is nearer to the nucleus and thus, suffers greater attraction leading to increased electronegativity. The number of covalent bonds present between two bonded atoms is known as its bond order. With increase in the bond order, the bond distance decreases, effective nuclear charge increases and thus electronegativity increases. Increasing order of electronegativity is as follows: C – C < C = C < C ≡ C. When effective nuclear charge is high, the nucleus will attract the shared electrons with greater strength to give high electronegativity.

**Oxidation number:** The electronegativity value increases with the increase in oxidation number since the radius decreases with the increase in oxidation number.

The increasing order of electronegativity is as follows: Fe < Fe<sup>+2</sup> < Fe<sup>+3</sup>

Electronegativity does not depend on stability of fully-filled or half-filled orbitals because it is simply the capacity of the nucleus to attract a bonded pair of electrons.

**Trends in Electronegativity:** Atomic size decreases across a period. Thus, electronegativity increases. Atomic size increases down a group decreasing the electronegativity.

F has maximum electronegativity value in the periodic table, while Cs has minimum.

According to the Pauling scale, the electronegativity value of F is 4.0, O is 3.5 N is 3.0 and Cl is 3.1

### Exceptions

- (a) The elements of group IIB i.e. Zn, Cd and Hg show increase in electronegativity value down the group.
- (b) The elements of group IIIA, i.e Al to Ga show increase in electronegativity value down the group.
- (c) The elements of group IVA, Si onwards, show no change in electronegativity value down the group.

### Measurement of Electronegativity

**Pauling Scale:** If two atoms, A and B, having different electronegativity values, get bonded to form a molecule, AB, then the bond between A and B in A–B will have both covalent and ionic properties.

$$\Delta_{A-B} = \text{Observed bond energy} - \text{Energy of 100\% covalent} \text{ or } \Delta_{A-B} = D - E_{A-B}$$

Where D = Observed bond energy

$E_{A-B}$  = Bond energy of pure covalent bond of A – B

The value of  $E_{A-A}$  and  $E_{B-B}$  is  $E_{A-B} = \frac{1}{2} [E_{A-A} + E_{B-B}]$

$$= 0.208 \sqrt{\Delta_{A-B}} = X_A - X_B \quad \text{where, } X_A > X_B \text{ or } 0.043 \times \Delta_{A-B} = (X_A - X_B)^2$$

**Mulliken Electronegativity Scale:** Mulliken suggested that the value of electronegativity of an element as an average of the values of ionization potential and electron affinity of the element.

$$X_M = \frac{\text{I.P.} + \text{E.A.}}{2} \text{ (in eV)}$$

Where  $X_M$  = Electronegativity value as given by Mulliken

$$X_p = \frac{X_M}{2.8} = \frac{\text{I.P.} + \text{E.A.}}{5.6}$$

Where  $X_p$  = Electronegativity value as given by Pauling or  $X_p = 0.336 (X_M - 0.615)$

### Allred-Roschow's Scale

$$X_{AR} = \frac{Z_{\text{eff}} \cdot e^2}{r^2}$$

$$X_p = 0.359 \frac{Z_{\text{eff}} \cdot e^2 + 0.744}{r^2}$$

$$Z_{\text{eff}} = Z - s^2, p^6, d^{10}, f^{14}$$

where  $Z$  = Nuclear charge

$\Delta IE$  = Shielding constant

$$\text{Or } X_p = 0.359 X_{AR} + 0.744$$

**Sanderson's Scale:** In Sanderson scale, the stability ratio of an atom itself has been regarded as its electronegativity.

$$X_s \text{ or S.R.} = \frac{\text{Average electron density of an atom}}{\text{Electron density of the isoelectronic inert gas}}$$

This is related to Pauling scale as follows-

$$\sqrt{X_p} = \frac{0.2}{\text{S.R. or } X_s} \times 0.77$$

### Applications of Electronegativity

**(a) Nomenclature:** Name of the more electronegative element is written at the end and 'ide' is suffixed to it. The name of the less electronegative element is written before the name of more electronegative element of the formula.

#### E.g. Correct formula

#### Name

- |                       |                   |
|-----------------------|-------------------|
| (a) IBr               | Iodine bromide    |
| (b) OF <sub>2</sub>   | Oxygen difluoride |
| (c) Cl <sub>2</sub> O | Dichlorine oxide  |

**(b) Nature of bond:** If the electronegativity difference between the two elements is 1.7 or more, then, an ionic bond is formed between them. Whereas, if it is less than 1.7, then, covalent bond is formed.

(HF is an exception in which a bond is covalent, although, difference of electronegativity is 1.9)

**(c) Metallic and non-metallic nature:** Low EN shows metallic nature and high EN shows non-metallic nature

Hydrolysis of AX – where A = Other element  
and X = Halogen

If electronegativity of X > Electronegativity of A, then, on hydrolysis, product will be HX.

Example In BCl<sub>3</sub>, EN of Cl > EN of B

- (d) **Partial ionic character in covalent bonds:** Partial ionic character is generated in covalent compounds due to the difference in electronegativities.

**Hanny and smith:** Calculates percentage of ionic character from the electronegativity difference. Percentage of ionic character =  $16(X_A - X_B) + 3.5(X_A - X_B)^2$

$$= 16\Delta + 3.5\Delta^2$$

$$= (0.16\Delta + 0.035\Delta^2) \times 100$$

Here,  $X_A$  is electronegativity of element A.

$X_B$  is electronegativity of element B.

$$\Delta = X_A - X_B$$

- (e) **Bond length:**  $d_{A-B} = r_A + r_B - 0.09(X_A - X_B)$

$$\text{or } d_{A-B} = \frac{1}{2}(D_{A-A} + D_{B+B}) - 0.09(X_A - X_B)$$

Here,  $X_A > X_B$

- (f) **Bond energy and stability:** Bond strength and stability of A-B increases on increase in difference of electronegativities of atoms A and B. Therefore, H-F > H-Cl > H-Br > H-I

- (g) **Acidic strength of hydrides:** Bond energy (Strength)  $\propto$  stability of molecule.

Order of stability of hydrohalides is HF > HCl > HBr > HI

So, Order of their acidic strength will be – HF < HCl < HBr < HI

Down the 5A group

NH <sub>3</sub> *Thermal	↓	stability decreases
PH <sub>3</sub> *Basic	↓	character decreases
AsH <sub>3</sub> *Acidic	↓	character increases

In PH<sub>3</sub> and AsH<sub>3</sub>, the difference in the electronegativities of  $X_A$  and  $X_B$  is very less, so their bond energy decreases and hence acidic character (losing H<sup>+</sup> ion) increases.

- (h) **Nature of oxides:** If the difference of the two electronegativities ( $X_O - X_A$ ) is 2.3 or more than 2.3, then the oxide will be basic in nature. Similarly, if value of  $X_O - X_A$  is lower than 2.3, then the compound will be first amphoteric and then acidic in nature.

Oxide	Na <sub>2</sub> O	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	SO <sub>3</sub>	Cl <sub>2</sub> O <sub>7</sub>
$(X_O - X_A)$	2.6	2.3	2.1	1.8	1.5	1.1	0.5
Nature	Strongly basic	Basic	Amphoteric	weakly acidic	Acidic	Strong acidic	Strongest acidic

- (i) **Nature of hydroxides:** According to Gallis, if electronegativity of A in a hydroxide (AOH) is more than 1.7, then, it will be acidic in nature whereas, it will be basic in nature, if electronegativity is less than 1.7.

<b>For example</b>	NaOH	and	ClOH
Electronegativity ( $X_A$ )	0.9		3.00
Nature	Basic		Acidic

If the value is more than  $X_O - X_H$ , then that hydroxide will be basic, otherwise, it will be acidic.

**Illustration 19:** Among the following, how many elements have lower electronegativity than oxygen atom-F, Cl, Br, I, H, S, P, K, Ca **(JEE MAIN)**

**Sol:** F is the most electronegative element. Order of electronegativity-  $F > O > N = Cl > \dots$  Except F, all will have electronegativity less than oxygen.

**Illustration 20:** What is the difference in the electronegativity of two atoms, when the percentage ionic character is 19.5%? **(JEE ADVANCED)**

**Sol:** Hanny – Smith equation

$$\text{Percentage of ionic character} = (16\Delta + 3.5\Delta^2)$$

$\Delta$  = difference in electronegativity

$$19.5 = 16\Delta + 3.5\Delta^2$$

$$3.5\Delta^2 + 16\Delta - 19.5 = 0$$

Solving quadratic, we get,  $\Delta = 1$

## 8. TRENDS IN CHEMICAL PROPERTIES

**Valency/valence**, also known as **valence number**, is the number of valence bonds a given atom has formed, or can form, with one or more atoms.

**Table 13.4:** Variation of valence in a group:

Group	1	2	13	14	15	16	17	18
Number of valence electron/s	1	2	3	4	5	6	7	8
Valence	1	2	3	4	3,5	2,6	1,7	0,8

**Variation of valence in a period:** On moving along the period, the number of valence electrons increases from 1 to 8. Consequently, the valence of the elements with respect to hydrogen increases from 1 to 4 up to group IV and then decreases to 1 as shown in the table. However, valence with respect to oxygen increases from one to seven along the period.

**Variation of valence in group:** On moving down the group, the number of valence electrons remains the same. Therefore, all the elements in a group have the same valence. For example, elements of group I have valency 1 and elements of group II have valency 2.

**Variation of valence in transition elements:** Transition metals show variable valence of 1, 2 or 3 as they can use electrons from their outermost as well as penultimate shell, during chemical reactions as energy difference between them is small.

### Some anomalous properties of second period elements

Consider the elements of II period.

II period:      Li      Be      B      C      N      O      F      Ne

The elements of gp. 1, 2 (Li & Be) and of gp. 13–17 (B to F) differ in many respects from other members of their group. (These points of difference will be later studied in detail.) Some anomalous properties of 2<sup>nd</sup> period elements are given below with their explanation.

**(a) Covalence:** The maximum covalency of 2<sup>nd</sup> period elements is four while, other members may also show higher covalency. e.g.,  $\text{BF}_4^-$  exists but  $[\text{BF}_6]^{3-}$  is known. Similarly  $\text{OF}_2$  is known but  $\text{OF}_4$ ,  $\text{OF}_6$  are not while,  $\text{SF}_4$  are known, N is never pentavalent etc.

**Explanation:** These elements have only two shells in their atom and the valence shell contain 4 orbitals only (one 2s and three 2p) so, a maximum of four bonds can be formed. In the 3<sup>rd</sup> period and onwards, the valence shell contain empty d-orbitals also. So, covalency may be more than four.

(b)  $p\pi - p\pi$  **Multiple bonding:** Bonds like C=C, C $\equiv$ C, N $\equiv$ N, C=O etc. exist due to  $p\pi - p\pi$  multiple bonding. These elements are smaller in size and mostly electronegative in their respective groups thus forming multiple bonds.

(c) **Diagonal relationship:** Diagonal relationship between elements of II & III periods.

Li Be B C

Na Mg Al Si

Diagonal relationship between these elements can be explained on the basis of approximately similar charge/size ratio of diagonally related elements.

## 9. PERIODIC PROPERTIES OF ELEMENTS

### 9.1 Periodicity Along the Period

(a) **Ionization enthalpy:** Increases along the period (with exception).

(b) **Electron gain enthalpy:** Increases along the period (with exception).

(c) **Electronegativity:** Increases along the period.

(d) **Atomic radius:** Decreases along the period.

(e) **Ionic radius:** The radii of isoelectronic ions decrease with increase in atomic number.

(f) **Atomic volume:** Volume occupied by 1 g-atom of an element in solid state is Atomic Volume.

Atomic volume decreases up to metals and then increases:

	Na	Mg	Al	Si	P	S	Cl	Ar
Atomic volume (cm <sup>3</sup> )	24	14	10	12	17	16	19	23.7

(g) **Melting point, Boiling point:** Increases along the period for metals.

	Na	Mg	Al
M.P (°C)	98	649	660
B.P (°C)	883	1100	1800

(h) **Density:** Increases along the period.

(i) **Reducing behavior:** Decreases along the period.

Na	Mg	Al	Si	P	S	Cl
Strong reductants					Strong oxidants	

(j) **Metallic character:** Decreases along the period.

Na	Mg	Al	Si	P	S	Cl
Metals			Metalloid	Non-metals		

Increasing non-metallic nature  
Decreasing metallic nature →

(k) **Electropositive character:** Decreases along the period.



**(l) Nature of oxides:** The basic character of oxides decreases and acidic character increases along the period.

Elements: Na Mg Al Si P S Cl

Oxides:  $\underbrace{\text{Na}_2\text{O} \quad \text{MgO}}_{\text{Basic}} \quad \underbrace{\text{Al}_2\text{O}_3}_{\text{Amphoteric}} \quad \underbrace{\text{SiO}_2 \quad \text{P}_2\text{O}_5 \quad \text{SO}_3 \quad \text{Cl}_2\text{O}_7}_{\text{Acidic}}$

**(m) Nature of hydrides:** The basic character of hydrides decreases along the period.

**(n) Valency:** (i) Valency with respect to oxygen increases from one to seven along the period (table 1.9). (ii) Valency with respect to hydrogen increases first from one to four & then decreases to one (table 1.9)

**Table 13.5:** Valence of Elements

Group	I	II	III	IV	V	VI	VIII
Valency with respect to oxygen	1	2	3	4	5	6	7
Formula of the oxide	$\text{R}_2\text{O}$	$\text{RO}$	$\text{R}_2\text{O}_3$	$\text{RO}_2$	$\text{R}_2\text{O}_5$	$\text{RO}_3$	$\text{R}_2\text{O}_7$
Valency with respect to hydrogen	1	2	3	4	3	2	1
Formula of the hydride	$\text{RH}$	$\text{RH}_2$	$\text{RH}_3$	$\text{RH}_4$	$\text{RH}_3$	$\text{RH}_2$	$\text{RH}$

## 9.2 Periodicity along the Group

- (a) Ionisation enthalpy : Decreases
- (b) Electron gain enthalpy : Decreases
- (c) Electronegativity : Decreases
- (d) Atomic radii : Increases
- (e) Ionic radii : Increases
- (f) Atomic volume : Increases
- (g) M.P./B.P : Decreases
- (h) Density : Increases
- (i) Oxidant-Reductant nature :
- \* Reducing nature of metals : Increases
- \* Oxidizing nature of non-metals : Decreases
- (i) Metallic character : Increases
- (j) Electro positive character : Increases
- (k) Basic character of oxide : Increases
- (l) Basic character of hydride : Decreases

## MASTERJEE CONCEPTS

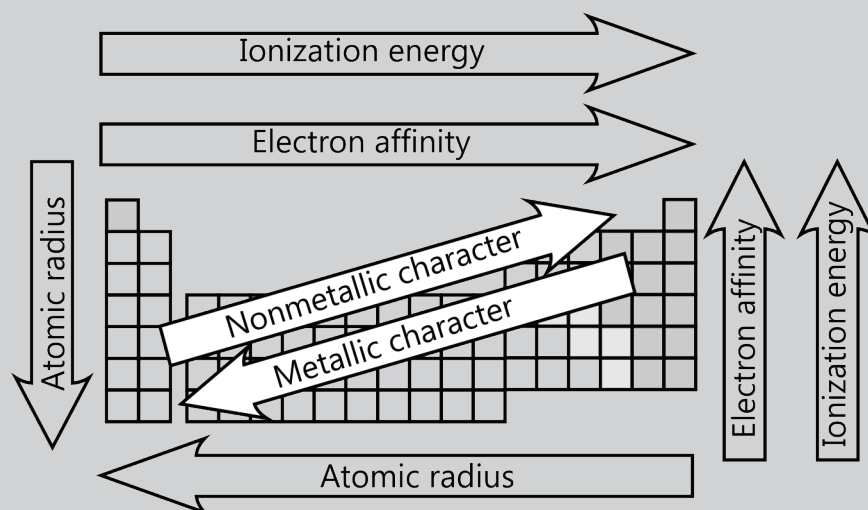


Figure 13.3: Variation of properties across the table

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### Some Important Things to Remember

1. Liquid radioactive element: Francium (Fr)
2. Rarest element in earth crust: Astatine (At)
3. Most poisonous metal: Plutonium (Pu)
4. Element with the maximum number of natural isotopes: Tin(Sn)
5. First man-made element: Technetium (Tc)
6. The size of the largest atom (Cs) is approximately 4.4 times to that of the smallest (H) atom.
7. Out of 17 non-metals known, 11 are gases, one is liquid (Br) and 5 are solids (C, P, S, Si and I)
8. Element with highest M.P.: Carbon (C in diamond)
9. Metal with highest M.P.: Tungsten (W)
10. Metal with maximum density: Iridium(Ir) (22.61 g/cc)
11. Metal with minimum density: Lithium(Li)
12. Lightest element: Hydrogen(H)
13. Most acidic oxide: Dichlorine heptoxide ( $\text{Cl}_2\text{O}_7$ )