## PERIODIC TABLE

<u>INTRODUCTION</u>: Periodic table helps us to undergo a systematic study of the various elements found in nature, Without which it would have been impossible for us to study all the elements. By classifying the elements into various groups and periods a comparative study of the elements and their compounds can be done. It also help us to analyze the periodic trend in various properties such as ionization potential, electron affinity, electronegativity etc.

### **DEVELOPMENT OF PERIODIC TABLE**

#### 1. PROUT'S HYPOTHESIS

He simply assumed that all the elements are made up of hydrogen, so we can say that

Atomic weight of element = n (Atomic weight of one hydrogen atom)

Atomic weight of H = 1

where n = number of hydrogen atom = 1, 2, 3,...

#### Drawback or Limitation:

- (a) Every element can not be formed by Hydrogen.
- (b) The atomic weights of all elements were not found as whole numbers.

Ex. Chlorine (atomic weight 35.5) and Strontium (atomic weight 87.5)

#### 2. DOBEREINER TRIAD RULE

J.W. Dorbereiner pointed out that within a group of three elements having similar chemical and physical properties, the atomic weight of the middle element is the mean of the other two. Some examples of such triads are given below. He also pointed out the triad - iron, cobalt and nickel in which the atomic weights of the elements are almost the same.

Some representative triads of Dobereiner

Triad	Li	Na	K	Ca	Sr	Ba	S	Se	Te	Cl	Br	I
Elements												
Atomic weight	7	23	39	40	88	137	32	80	128	35.5	80	127
Mean value		23			88.5			80			81.25	

Other example. (K, Rb, Cs), (P, As, Sb) (H, F, Cl) (Sc, Y, La).

Though it was the first successful attempt to rationalise the problem, it could not be generalised or extended.

Drawback or Limitation: All the known elements could not be arranged as triads.

#### 3. NEWLAND'S OCTET LAW

John Alexander Reina newland in England made the first attempt to correlate the chamical properties of the elements with their atomic weight. According to him -

(a) If the elements are arranged in order to their increasing atomic weights, every eighth element had similar properties to first one like the first and eighth note in music. For example

Sa	Re	Ga	Ma	Pa	Dha	Ni	Sa
Li	Be	В	С	N	Ο	F	Na
Na	Mg	Al	Si	P	Dha O S	Cl	K

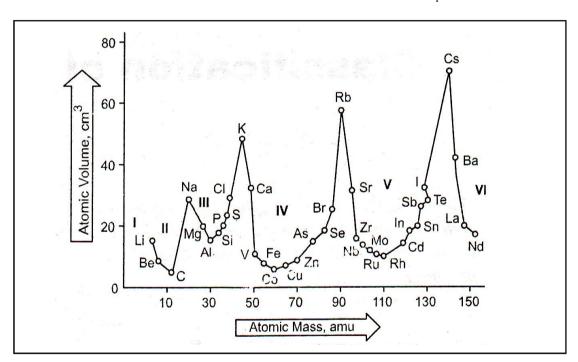
- (b) Inert gases were not discovered till then.
- (c) All the elements could not be classified on this basis.

### 4. LOTHER MEYER'S CURVE:

- (a) He plotted a curve between atomic weight and atomic volume of different elements.
- (b) The following observation can be made from the curve -
- (i) Most electropositive elements i.e. alkali metals (Li, Na, K, Rb, Cs etc.) occupy the peak positions on the curve.
- (ii) Less electropositive i.e. alkali earth metal (Be, Mg, Ca, Sr, Ba) occupy the descending position on the curve.
- (iii) Metalloids (B, Si, As, Te, At etc.) and transition metals occupy bottom part of the curve.
- (iv) Most electronegative i.e. halogens (F, Cl, Br, I) occupy the ascending position on the curve.

Note: Elements having similar properties occupy similar position on the curve.

**Conclusion :** On the basis of this curve Lother Meyer proposed that the physical properties of the elements are periodic function of their atomic wt. and this become the base of Mendeleef's periodic table.



5. TELLURIC HELIX: A three dimensional periodic table given by De-chan-chortois.

#### 6. MENDELEEF'S PERIODIC TABLE:

- (a) **Mendeleef's periodic law**: The physical and chemical properties of elements are the periodic function of their atomic weight
- (b) Characteristic of Mendeleef's periodic table :
- (i) It is based on atomic weight
- (ii) 63 elements were known, noble gases were not discovered.
- (iii) He was the first scientist to classify the elements in a systamatic manner i.e. in horizontal rows and in vertical columns.
- (iv) Horizontal rows are called periods and there were 7 periods in Mendeleev's Periodic table.

- (v) Vertical columns are called groups and there were 8 groups in Mendeleev's Periodic table.
- (vi) Each group upto VII<sup>th</sup> is divided into A & B subgroups.'A' sub groups element are called normal elements and 'B' sub groups elements are called transition elements.
- (vii) The VIII<sup>th</sup> group was consists of 9 elements in three rows (Transitional metals group).
- (viii) The elements belonging to same group exhibit similar properties.
- (c) Merits or advantages of Mendeleef's periodic table :
- (i) Study of elements: First time all known elements were classified in groups according to their similar properties. So study of the properties of elements become easier.
- (ii) **Prediction of new elements :** It gave encouragement to the discovery of new elements as some gaps were left in it.

Sc (Scandium) Ga (Gallium) Ge (Germanium) Tc (Technetium)

These were the elements for whom position and properties were well defined by Mendeleev even before their discoveries and he left the blank spaces for them in his table.

Ex. Blank space at atomic weight 72 in silicon group was called Eka silicon (means properties like silicon) and element discovered later was named Germanium.

Similarly other elements discovered after mendeleef periodic tabel were.

Eka aluminium – Galium(Ga)	Eka Boron – Scandium (Sc)
Eka Silicon – Germanium (Ge)	Eka Mangense – Technetium (Tc)

(iii) Correction of doubtful atomic weights: Correction were done in atomic weight of some elements.

Initially, it was found that equivalent weight of Be is 4.5 and it is trivalent (V = 3), so the weight of Be was 13.5 and there is no space in Mendeleev's table for this element. So, after correction, it was found that Be is actually divalent (V = 2). So, the weight of Be became 2 - 4.5 = 9 and there was a space between Li and B for this element in Mendeleev's table.

- Corrections were done in atomic weight of elements are U, Be, In, Au, Pt.
- (d) Defects of Mendeleef's Periodic Table:
- (i) Position of hydrogen is uncertain. It has been placed in IA and VII A groups because of its resemblance with both the groups.
- (ii) No separate positions were given to isotopes.
- (iii) It is not clear whether the lanthanides and actinides are related to IIA or IIB group.
- (iv) Although there is no resemblance except valency of subgroups A and B, they have been put in the same group.
- (v) Order of increasing atomic weights is not strictly followed in the arrangement of elements in the periodic table. For e.g. Co (At. wt. 58.9) is placed before I (127) and Ar (39.9) before K (39).

### 7. MODERN PERIODIC TABLE (MODIFIED MENDELEEF PERIODIC TABLE) :

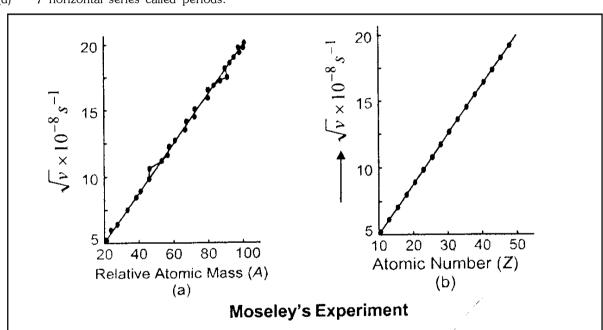
- (a) It was proposed by Moseley.
- (b) Modern periodic table is based on atomic number.
- (c) Moseley did an experiment in which he bombarded high speed electron on different metal surfaces and obtained X-rays.

He found out that  $\sqrt{v} \propto Z$  where v = frequency of X-rays, Z = atomic number.

(d) **Modern periodic law**: The physical & chemical properties of elements are the periodic function of their atomic number.

### Characteristics of modern periodic table

- (a) 9 vertical columns called groups.
- (b) Ist to VIII group + 0 group of inert gases.
- (c) Inert gases were introduced in periodic table by Ramsay.
- (d) 7 horizontal series called periods.



#### 8. LONG FORM / PRESENT FORM OF MODERN PERIODIC TABLE:

(It is also called as 'Bohr, Bury & Rang, Werner Periodic Table)

- (a) It is based on the Bohr-Bury electronic configuration concept and atomic number.
- (b) This model is proposed by Rang & Werner
- (c) 7 periods and 18 vertical columns (groups)
- (d) According to I. U. P. A. C. 18 vertical columns are named as  $I^{st}$  to  $18^{th}$  group.
- (e) Elements belonging to same group having same number of electrons in the outermost shell so their properties are similar.
- (f) Elements belonging to same group having same no. of electrons in the outermost shell so their properties are similar.

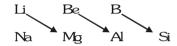
### Description of periods

Period	n	Sub shell	No. of elements	Element	Name of Period
1.	1	1s	2	<sub>1</sub> H, <sub>2</sub> He	Shortest
2.	2	2s, 2p	8	<sub>3</sub> Li – <sub>10</sub> Ne	Short
3.	3	3s, 3p	8	<sub>11</sub> Na – <sub>18</sub> Ar	Short
4.	4	4s, 3d, 4p	18	<sub>19</sub> K – <sub>36</sub> Kr	Long
5.	5	5s, 4d, 5p	18	<sub>37</sub> Rb - <sub>58</sub> Xe	Long
6.	6	6s, 4f, 5d, 6p	32	<sub>55</sub> Cs – <sub>86</sub> Rn	Longest
7.	7	7s, 5f, 6d,	26	<sub>87</sub> Fr – <sub>112</sub> Uub	Incomplete

### Important Points:

(a) 2<sup>nd</sup> period elements (Li, Be, B) Shows diagonal relationship with 3rd period elements (Mg, Al, Si) so (Li, Be, B) are called Bridge elements. Because of same ionic potential value they shows similarity in properties.

### (Ionic potential = Charge/Radius)



- (b) 3<sup>rd</sup> period elements (Na, Mg, Al, Si, P, S, Cl) are called typical elements because they represent the properties of other element of their respective group.
- (c) Atomic number of last inert gas element is 86.
- (d) Number of Gaseous elements 11 (H, N, O, F, Cl + Noble gases)

Number of Liquid elements - 6 (Cs, Fr, Ga, Hg, Br, Uub)

Bromine is the only non-metal which exists in liquid form.

Number of Solid elements - 95 (if discovered elements are 112)

(e) 2nd period contains maximum number of gaseous elements. They are 4 (N, O, F, Ne)

#### Nomenclature of elements

(a) IUPAC gave names to elements above atomic number 100 as follows -

	0	1	2	3	4	5	6	7	8	9
n	nil	un	bi	tri	quad	pent	hex	sept	oct	enn

(b) In all the elements, suffix is - ium. Ex.

Atomic No.	IUPAC Name	Symbol	IUPAC Official Name	IUPAC Symbol
101	Un nil unium	Unu	Mendelevium	Md
102	Un nil bium	Unb	Nobelium	No
103	Un nil trium	Unt	Lawrencium	Lr
104	Un nil quadium	Unq	Rutherfordium	Rf
105	Un nil pentium	Unp	Dubnium	Db
106	Un nil hexium	Unh	Seaborgium	Sg
107	Un nil septium	Uns	Bohrium	Bh
108	Un nil octium	Uno	Hassnium	Hs
109	Un nil ennium	Une	Meitnerium	Mt
110	Un un nilium	Uun	Darmstadtium	Ds

#### CLASSIFICATION OF ELEMENTS

#### s-BLOCK ELEMENTS

- (a) The elements of the periodic table in which the last electron enters in s-orbital, are called s-block elements.
- (b) s-orbital can accommodate a maximum of two electrons.
- (c) Their general formulae are  $ns^1$  and  $ns^2$  respectively, where n = (1 to 7)
- (d) IA group elements are known as alkali metals because they react with water to form alkali. II A group elements are known as alkaline earth metals because their oxides react with water to form alkali and these are found in the soil or earth.
- (e) Total number of s-block elements are 14.
- (f) Fr<sup>57</sup> and Ra<sup>88</sup> are radioactive elements while H and He are gaseous elements.
- (g) Cs and Fr are liquid elements belonging to s-block.

#### p-BLOCK ELEMENTS

- (a) The elements of the periodic table in which the last electron gets filled up in the p-orbital, called p-block elements.
- (b) p-orbital can accommodate a maximum of six electrons. Therefore, p-block elements are divided into six groups which are III A, IV A, V A, VI A, VII A and zero group.
- (c) The general formula of p-block elements is  $ns^2 p^{1.6}$  (where n = 2 to 6)
- (d) The zero group elements having general formula  $ns^2p^6$  are inert, because their energy levels are fully filled.
- (e) The total number of p-block elements in the periodic table is 30 (excluding He).
- (f) There are nine gaseous elements (Ne, Ar, Kr, Xe, Rn,  $F_2$ ,  $Cl_2$ ,  $O_2$  and  $N_2$ ) belonging to p-block. Gallium (Ga) and bromine (Br) are liquids.
- (g) The step-like thick lines drawn in the periodic table in the p-block divides elements into metals, nonmetals and metalloids.

#### d-BLOCK ELEMENTS

- (a) The elements of the periodic table in which the last electron gets filled up in the d-orbital, called d-block elements.
- (b) The d-block elements are placed in the groups named III, IV B, V B, VI B, VII B, VIII, I B and II B.
- (c) In d-block elements the electron gets filled up in the d-orbital of the penultimate shell.
- (d) d-block elements lie between s & p block elements.
- (e) The general formula of these elements is  $(n-1)s^2$ ,  $p^6$ ,  $d^{1-10}$   $ns^{1-2}$  where n=4 to 7.
- (f) All of these elements are metals.
- (g) Out of all the d-block elements, mercury is the only liquid element.

#### f-BLOCK ELEMENTS

(a) The element of the periodic table in which the last electron gets filled up in the f-orbital, called f-block elements.

- (b) The f-block elements are from atomic number 58 to 71 and from 90 to 103.
- (c) The lanthanides occur in nature in low abundance and therefore, these are called rare earth elements.
- (d) There are 28 f-block elements in the periodic table.
- (e) The elements from atomic number 58 to 71 are called lanthanides because they come after lanthanum (57). The elements from 90 to 103 are called actinides because they come after actinium (89).
- (f) All the actinide elements are radioactive.
- (g) All the elements after atomic number 92 (i.e. U92) are transuranic elements.
- (h) The general formula of these elements is (n-2) s<sup>2</sup> p<sup>6</sup> d<sup>10</sup> f<sup>(1-14)</sup> (n-1) s<sup>2</sup> p<sup>6</sup> d<sup>0-1</sup> ns<sup>2</sup> where n = 6 & 7.

### TYPE OF ELEMENTS

Using electronic configuration as the criteria, we generally recognize four general type of elements; the inert gas elements, the representative elements, the transition elements, and the inner transition elements. The classification of the elements into these groups is dependent on the extent to which the s, p, d and f orbitals are filled.

#### Inert Gases

- (a) s and p orbitals of the outer most shell of these elements are completely filled. The outermost electronic configuration is  $ns^2np^6$ .
- (b) Helium is also inert gas but its electronic configuration is 1s<sup>2</sup>

#### Representative or Normal Elements

- (a) Outermost shell of these elements is incomplete. The number of electrons in the outermost shell is less than eight.
- (b) Inner shell are complete.
- (c) s-and p-block elements except inert gases are called normal or representative elements.

#### Transition Elements

- (a) Last two shells of these elements namely outermost and penultimate shells are incomplete.
- (b) The last shell contains one or two electrons and the penultimate shell may contain more than eight or up to eighteen electrons.
- (c) Their outermost electronic configuration is similar to d-block elements i.e. (n-1)  $d^{1-10}$   $ns^{1-2}$ .
- (d) According to definition of transition elements, those elements which have partly filled d-orbitals in neutral state or in any stable oxidation state are called transition elements. According to this definition Zn, Cd and Hg (IIB group) are d-block elements but not transition elements because these elements have d<sup>10</sup> configuration in neutral as well as in stable +2 oxidation state.
- (e) Because of the extra stability which is associated with empty, half-filled, and fully filled subshells, there are some apparent anomalies in electronic arrangements in the transition series. This empirical rule is illustrated by the chromium and copper configuration in the first d series of elements:

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
3d	1	2	3	5	5	6	7	8	10	Zn 10 2
4s	2	2	2	1	2	2	2	2	1	2

#### Inner Transition Elements

- (a) In these elements last three shells i.e. last, penultimate and prepenultimate shells are incomplete.
- (b) These are related to IIIB i.e. group 3.
- (c) The last shell contains two electrons. Penultimate shell may contain eight or nine electrons and prepenultimate shell contains more than 18, up to 32 electrons.
- (d) Their outemost electronic configuration is similar to f-block element i.e.  $(n-2)f^{1-14} (n-1)s^2 (n-1)p^6 (n-1)d^{0-1}ns^2$

#### PREDICTING ATOMIC NUMBER OF SUCCESIVE MEMBER IN A GROUP OR FAMILY

#### Magic Numbers

32

VII

32

32

(a) Knowing the atomic number of the first member of a group, we can write the atomic number of the subsequent elements by adding given magic number

Ex. Group 2 3 4, 5, 6, 7, 8, 9 10, 11, 12, 13, 14, 15, 16, 17 18 IΑ IΙΑ IIIB IIIA IV V VI VII 'O'gp. I + 8 8 8 II+III+ 18 18 18 18 18 18 18 18 18 18 32 32 32

(b) In group IA - Atomic number of H is 1 and atomic number of other element will be as follows -

32

### Determination of period, block and group of an element

- (a) **Period number:** The period no. of the element can be predicted from the principal quantum no. (n) of the valence shell.
- (b) Block number: Last electron enter in which orbital is knows as block no. .
- (c) Group number: It is predicted from the number of electrons in the valence shell and penultimate shell.

#### Example:

S.No.	Electronic Configuration	Period number	Block number	Prediction of Group	Group number
1.	$[Ar]4s^2 3d^{10}4p^6, 5s^1$	5	S	No. of ns e⁻	1
2.	[Kr] 5s <sup>2</sup> , 4d <sup>10</sup> 5p <sup>2</sup>	5	р	ns e <sup>-</sup> + 10 + np e <sup>-</sup>	2+10+2 =14
3.	[Rn] $7s^2$ , $6d^4$ $5f^{14}$	7	d	ns e <sup>-</sup> + (n–1)d e <sup>-</sup>	2+4 = 6
4.	[Xe] 6s²,5d¹, 4f¹²	6	f	_	3/III B

#### **PERIODICITY**

- (a) The regular gradation in properties from top to bottom in a group and from left to right in a period is called periodicity in properties.
- (b) In a period, the ultimate orbit remain same, but the number of e- gradually increases.
- (c) In a group, the number of e- in the ultimate orbit remains same, but the values of n increases.

### Causes of periodicity

- (a) The cause of periodicity in properties is due to the same outermost shell electronic configuration coming at regular intervals.
- (b) In the periodic table, elements with similar properties occur at intervals of 2, 8, 8, 18, 18 and 32. These numbers are called as magic numbers.

### Periodic Properties

**Valency:** It is defined as the combining capacity of the elements. The word valency is derived from an Italian word "Valentia" which means combining capacity.

Old concept: Given by: Frankland

Valency with respect to Hydrogen: Valency of H = 1

It is defined as the number of hydrogen atoms attached with a particular element.

	IA	IIA	IIIA	IVA	VA	VIA	VIIA
	NaH	${\sf MgH}_2$	$AlH_3$	$SiH_4$	$PH_3$	$H_2S$	H-Cl
Valency	1	2	3	4	3	2	1

Note: Valency w.r.t. H across the period increases upto 4 and then again decreases to 1.

Valency with respect to oxygen: Valency of 'O' = 2

It is defined as twice the number of oxygen atoms attached with a particular atom.

	IA	IIA	IIIA	IVA	VA	VIA	VIIA
	$Na_2O$	MgO	$Al_2O_3$	$SiO_2$	$P_2O_5$	$SO_3$	$\text{Cl}_2\text{O}_7$
Valency	1	2	3	4	5	6	7

**Note**: Valency with respect to oxygen increases from 1 to 7 across the period. Valency w.r.t. 'O' is equal to the group number.

**New concept**: This concept is based on the electronic configuration. According to this concept valency for IA to IVA group elements is equal to number of valence shell e<sup>-</sup> and from VA to zero group, it is -

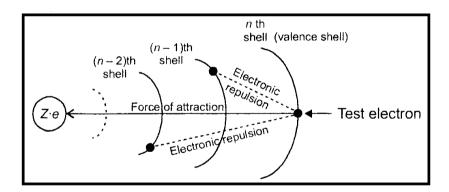
[8- (number of valence e-)].

	Valen	icy = No	o. of valenc	e e-	V	/alency = (8- r	no. ot valence	e e-)
	+			•	+			•
	IA	IIA	IIIA	IVA	VA	VIA	VII	0
	$ns^1$	$ns^2$	$ns^2np^1$	$ns^2np^2$	$ns^2np^3$	$ns^2np^4$	$ns^2np^5$	ns <sup>2</sup> np <sup>6</sup>
Valence shell e	1	2	3	4	5	6	7	8
Valency	1	2	3	4	3	2	1	0
					(8 - 5) = 3			(8 - 8) = 0

Note: All the elements of a group have same valencies because they have same number of valence shell electrons.

## SCREENING EFFECT ( $\sigma$ ) AND EFFECTIVE NUCLEAR CHARGE ( $Z_{eff}$ )

- (a) Valence shell e suffer force of attraction due to nucleus and force of repulsion due to inner shell electrons.
- (b) The decrease in force of attraction on valence  $e^-$  due to inner shell  $e^-$  is called screening effect or shielding effect.(i.e. total repulsive force is called shielding effect.)
- (c) Due to screening effect. valence shell  $e^-$  experiences less force of attraction exerted by nucleus.(i.e. total attraction force experienced by valence  $e^-$  is called Zeff.)
- (d) There is a reduction in nuclear charge due to screening effect. Reduced nuclear charge is called effective nuclear charge.
- (e) If nuclear charge = Z, then effective nuclear charge = Z  $\sigma$  (Where  $\sigma$  (Sigma)= Screening constant) So, Zeff = (Z -  $\sigma$ )



#### Slater's rule to know screening constant ( $\sigma$ ):

- (a) Screening effect (S.E.) of one  $e^-$  of the 1s is 0.30. **Ex.** In He (1s<sup>2</sup>) Screening effect of one 1s  $e^-$ , where  $\sigma = 0.30$
- $\therefore$  Zeff = Z  $\sigma$  = 2 0.30 = 1.7
- (b) Screening effect of ns and np (Outermost orbit) electron is 0.35
- (c) Screening effect of (n 1) penultimate orbit s, p, d electrons is 0.85
- (d) Screening effect of (n 2) and below all the  $e^{\scriptscriptstyle -}$  present in s, p, d, f is 1.0

	(Effective Nuclear charge of elements of second period)												
Element	Electronic Configaration	Z	σ of ns & np electron	σ (n-1) orbital	Total Screeing Constant	Effective nuclear charge							
			(a)	(b)	(a + b)	Z*=Z - σ							
<sub>3</sub> Li	$1s^2 2s^1$	3	-	0.85 2=1.70	1.70	1.30							
<sub>4</sub> Be	$1s^2, 2s^2$	4	1 0.35=0.35	0.85 2=1.70	2.05	1.95							
<sub>5</sub> B	$1s^2, 2s^2, 2p^1$	5	2 0.35=0.70	0.85 2=1.70	2.40	2.60							
<sub>6</sub> C	$1s^2, 2s^2, 2p^1$	6	3 0.35=1.05	0.85 2=1.70	2.75	3.25							
<sub>7</sub> N	$1s^2, 2s^2, 2p^3$	7	4 0.35=1.40	0.85 2=1.70	3.10	3.90							
<sub>8</sub> O	$1s^2, 2s^2, 2p^4$	8	5 0.35=1.75	0.85 2=1.70	3.45	4.55							
<sub>9</sub> F	$1s^2, 2s^2, 2p^5$	9	6 0.35=2.10	0.85 2=1.70	3.80	5.20							

#### Periodic variation

- (a) From left to right in a period Zeff increases
- (i) That is why in a period Zeff increases by 0.65 and hence atomic size decreases considerably.
- (ii) In transition series Z increase by + 1 but screening effect increases by 0.85 So Zeff is 0.15 (1- 0.85 = 0.15) [Because  $e^-$  enters in (n 1) orbit which has value of  $\sigma = 0.85$ ]

In transition series Zeff increases very less amount, by 0.15 from left to right and hence atomic size remains almost constant.

Element	Sc	Ti	V	Cr	Mn	Fe	Со	Ni	Cu	Zn
Zeff	3.00	3.15	3.30	3.45	3.60	3.75	3.90	4.05	3.70	4.35

(b) From top to bottom in a group Zeff remain constant

Element	Li	Na	K	Rb	Cs	Fr
Zeff	1.30	2.20	2.20	2.20	2.20	2.20

### ■ ATOMIC RADIUS

The average distance of valence shell  $e^-$  from nucleus is called atomic radius. It is very difficult to measure the atomic radius because –

- (i) The isolation of single atom is very difficult.
- (ii) There is no well defined boundary for the atom. (The probability of finding the  $e^-$  is 0 only at infinity). So, the more accurate definition of atomic radius is –
- Half the inter-nuclear distance(d) between two atoms in a homoatomic molecule is known as atomic radius.
- This inter-nuclear distance is also known as bond length. Inter-nuclear distance depends upon the type of bond by which two atoms combine.

Based on the chemical bonds, atomic radius is divided into four categories -

1. Covalent radius 2. Ionic radius 3. Metallic radius 4. Vander waal radius

#### 1. Covalent radius

One half of the distance between the nuclei (internuclear distance) of two covalently bonded atoms in homodiatomic molecule is called the covalent radius of that atom. The covalent bond must be single covalent bond. The covalent radius  $(r_A)$  of atom A in a molecule  $A_2$  may be given as:

$$r_A = \frac{d_{A-A}}{2}$$

i.e. the distance between nuclei of two single covalently bonded atoms in a homodiatomic molecule is equal to the sum of covalent radii of both the atoms

$$d_{A-A} = r_A + r_A$$

In a heterodiatomic molecule AB where the electronegativity of atoms A and B are different, the experimental values of internuclear distance  $d_{A-B}$  is less than the theoretical values  $(r_A + r_B)$ .

According to Schomaker and stevenson -

$$D_{A-B} = r_A + r_B - 0.09 \Delta_x$$

Where  $\Delta_{_{\! X}}$  is the difference of electronegativities of the atoms A and B.

According to Pauling – If the electronegativities of the two atoms A and B are  $x_{_{A}}$  and  $x_{_{B}}$  respectively then

$$D_{A-B} = r_A + r_B - (C_1 x_A - C_2 x_B)$$

 $\mathrm{C_{\scriptscriptstyle{1}}}$  and  $\mathrm{C_{\scriptscriptstyle{2}}}$  are the Stevenson's coefficients for atoms A and B respectively.

#### 2. Metallic Radius

Metal atoms are assumed to be closely packed spheres in the metallic crystal. These metal atom spheres are considered to touch one another in the crystal. One half of the internuclear distance between the two closest metal atoms in the metallic crystal is called metallic radius.

Metallic > Covalent radius

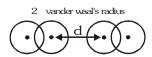
For example - Metallic radius and covalent radius of potassium are 2.3 Å and 2.03 Å respectively.

#### 3. Van Der Wall's Radius or Collision radius

The molecules of non metal atoms are generally gases. On cooling, the gaseous state changes to solid state.

In the solid state, the non metallic elements usually exist as aggregations of molecules are held together by van der wall forces. One half of the distance between the nuclei of two adjacent atoms belonging to two neighbouring molecules of a compound in the solid state is called van der walls radius.

It may also be defined as half of the inter nuclear distance of two non bonded neighbouring atoms of two adjacent molecules.



van der Wall's radius =  $\frac{1}{2}$  Internuclear distance between two successive nuclei of two covalent molecules (d)

Van der wall's radius > Metallic radius > Covalent radius

The vander walls radius and covalent radius of chlorine atom are 1.80 Å and 0.99 Å respectively

#### 4. Ionic Radius

A neutral atom changes to a cation by the loss of one or more electrons and to an anion by the gain of one or more electrons. The magnitude of charge on cation and anion is equal to the number of electrons lost or gained respectively. The ionic radii of the ions present in an ionic crystal may be calculated from the inter molecular distance between the two ions.

#### (a) Radius of Cation

Radius of cation is smaller than that of corresponding atom.

#### Reasons

- (i) During the formation of cation either one shell is removed or
- (ii) After removing an electron effective nuclear charge increase.

#### (b) Radius of an Anion

Radius of an anion is invariably bigger than that of the corresponding atom.

#### Reasons

- (i) The effective nuclear charge decrease in the formation of anion. Thus the electrostatic force of attraction between the nucleus and the outer electrons decreases as the size of the anion increases.
- (ii) Interelectronic repulsion increases.

#### Factors affecting atomic radius are

(a)	Atomic radius $\propto \frac{1}{\text{Effective nuclear charge (Zeff)}}$ Li > Be > B > C > N > O > F	(b)	Atomic radius ∝ number of shells Li < Na < K < Rb < Cs
(c)	Atomic radius $\propto$ Screening effect	(d)	Atomic size ∝ Magnitude of -ve charge
			$O < O^{-} < O^{-2}$
(e)	Atomic radius $\propto \frac{1}{\text{Magnitude of +ve charge}}$	(f)	Atomic radius $\propto \frac{1}{Bond\;order}$
	$M_n > M_n^{+2} > M_n^{+3} > M_n^{+4}$		$N - N > -N = N - N \equiv N$

#### Periodic variation of atomic radius

(a) Across a period : It decreases from left to right in a period as nuclear charge increases

Ex. Li  $\rightarrow$  Be  $\rightarrow$  B  $\rightarrow$  C  $\rightarrow$  N  $\rightarrow$  O  $\rightarrow$  F  $\leftarrow$  Ne

(b) In a group : It increases from top to bottom in a group as number of shell increases

Ex. Li < Na < K < Rb < Cs

### Exceptions

(a) Transition elements

### (b) Lanthanide Contraction

- (i) Outermost electronic configuration of inner transition elements is (n-2) f<sup>1-14</sup>,  $(n-1)s^2p^6d^{0-1}$ ,  $ns^2$  (n=6 or 7)
- (ii)  $e^-$  enters in (n-2) f orbitals
- (iii) Mutual screening effect of e- is very less, because of complicated structure of f-orbital
- (iv) Nuclear charge increases by one (+1) in lanthanides and actinides so atomic size of these elements slightly decreases. It is known as lanthanide contraction. Its effect is also observe in 5d transition series.

Here Nuclear charge > Screening effect.

(v) In Ist,  $2^{nd}$  and  $3^{rd}$  transition series, Radii –  $3d < 4d \approx 5d$  (except IIIrd B)

	IIIB	IVB
size	Sc	$Ti \downarrow$ size increases
increases	Y	$\left\{\begin{array}{c} Zr \\ Hf \end{array}\right\}$ Equal due to lanthanide contraction
	La	Here to lanthanide contraction

### (c) Transition contraction:

IIIA  $\rightarrow$  B<Al  $\approx$  Ga Note: While atomic size should increases down the group.

- (i) At. size of Ga = At. size of Al, due to transition contraction.
- (ii) In transition elements nuclear charge increases by 1.
- (iii) but e⁻ enters in (n −1)d orbital exerts screening effect.
- (iv) Screening effect of  $(n 1)d e^-$  balance the nuclear charge by 85%
- (v)  $Z_{eff}$  on increasing each electron = 1 0.85 = 0.15
- (vi) Increase in nuclear charge is only 0.15 so atomic size remains almost constant.

Group Period	1	2											13	14	15	16	17	18
1	H ~0.30																H ∼0.30	He • 1.20*
2	Li • 1.23	Be • 0.89											B • 0.80	C 0.77	N • 0.75	O 0.73	F 0.72	Ne ● 1.60*
3	Na • 1.57	Mg • 1.36	3	4	5	6	Gı 7	roup 8	9	10	11	12	Al • 1.25	Si • 1.17	P • 1.10	S • 1.04	CI 0.99	Ar • 1.91*
4	K 2.03	Ca • 1.74	Sc • 1.44	Ti • 1.32	V • 1.22	Cr • 1.17	Mn • 1.17	Fe • 1.17	Co • 1.16	Ni • 1.15	Cu • 1.17	Zn • 1.25	Ga • 1.25	Ge • 1.22	As • 1.21	Se • 1.14	Br • 1.14	Kr • 2.00*
5	Rb • 2.16	Sr • 1.91	Y • 1.62	Zr • 1.45	Nb • 1.34	Mo • 1.29	Tc •	Ru • 1.24	Rh • 1.25	Pd • 1.28	Ag • 1.34	Cd • 1.41	In • 1.50	Sn • 1.40	Sb • 1.41	Te • 1.37	1 • 1.33	Xe • 2.20*
6	Cs • 2.35	Ba • 1.98	La • 1.69	Hf • 1.44	Ta • 1.34	W • 1.30	Re • 1.28	Os • 1.26	Ir • 1.26	Pt • 1.29	Au • 1.34	Hg • 1.44	TI • 1.55	Pb • 1.46	Bi. 1.52	Ро	At	Rn
7	Fr	Ra	Ac									•	•					

#### ISOELECTRONIC SERIES

A series of atoms, ions and molecules in which each species contains same number of electrons but different nuclear charge is called isoelectronic series.

	N³-	O <sup>2</sup> -	F	Ne	Na <sup>+</sup>	Mg <sup>2+</sup>
Number of e	10	10	10	10	10	10
Number of p	7	8	9	10	11	12

- (a) Number of electrons is same.
- (b) Number of protons is increasing.
- (c) So the effective nuclear charge is increasing and atomic size is decreasing. In an isoelectronic series atomic size decreases with the increase of charge.

Some of the examples of isoelectronic series are as under.

$$S^{2-}$$
,  $Cl^{-}$ ,  $K^{+}$ ,  $Ca^{2+}$ ,  $Sc^{3+}$   $SO_{9}$ ,  $NO_{3}^{-}$ ,  $CO_{3}^{2-}$   $N_{9}$ ,  $CO$ ,  $CN^{-}$   $NH_{3}$ ,  $H_{3}O^{+}$ 

# IONISATION POTENTIAL OR IONISATION ENERGY OR IONISATION ENTHALPY

Minimum energy required to remove most loosly held outer most shell e<sup>-</sup> in ground state from an isolated gaseous atom is known as ionisation potential.

(Isolated  $\rightarrow$  Without any bonding with other atom)

### 1. Successive Ionisation Energy

(a) For an atom M, successive ionisation energies are as follows -

 $I^{st}$  Ionisation Potential  $\leq II^{nd}$  Ionisation Potential  $\leq III^{rd}$  Ionisation Potential

- (b) Electron can not be removed from solid state of an atom, it has to convert in gaseous form, Energy required for conversion from solid state to gaseous state is called Sublimation energy.
- (c) Ionisation Potential is always an endothermic process ( $\Delta$  H = +ve)
- (d) It is measured in eV/atom (electron volt/atom) or Kcal/mole or KJ/mole

#### 2. Factors affecting ionisation potential

(a) Atomic size: Larger the atomic size, smaller is the Ionisation Potential It is due to that the size of atom increases the outermost electrons e<sup>-</sup> farther away from the nucleus and nucleus loses the attraction on that electrons and hence can be easily removed.

Ionisation Potential 
$$\propto \frac{1}{\text{Atomic size}}$$

(b) Effective nuclear charge ( $Z_{\rm eff}$ ): Ionisation potential increases with the increase in nuclear charge between outermost electrons and nucleus.

(c)	Screening effect: Higher is the screening effect on the outer most electrons causes less attraction from
	the nucleus and can be easily removed, which is leading to the lower value of Ionisation Potential
	Ionisation Potential $\propto \frac{1}{\text{Screening effect}}$
(d)	Penetration power of sub shells :
(i)	Order of attraction of subshells towards nucleus (Penetration power) is -
	s > p > d > f
(ii)	As subshell is more closer to nucleus so more energy will be required to remove $e^-$ in comparision to p,d & f. Ex. Be B
	$1s^2$ , $2s^2$ $1s^2$ , $2s^2$ $2p^1$
	Ionisation Potential Be > B
	After loosing one $e^-$ , $B$ attains electronic configuration of $Be$ , so $II^{nd}$ ionisation potential of $B$ is more than
	Be. $II^{nd}$ Ionisation Potential of B > Be
(e)	Stability of half filled and fully filled orbitals:
(i)	Half filled $p^3$ , $d^5$ , $f^7$ or fully filled $s^2$ , $p^6$ , $d^{10}$ , $f^{14}$ are more stable than others so it requires more energy.
Ex.	N O
	$1s^2,\ 2s^2\ 2p^3 \qquad 1s^2,\ 2s^2\ 2p^4 \qquad I^{st}\ \ \mbox{Ionisation Potential}\ \ \mbox{order is}\ \ O\ \ \mbox{$<$$$N$}$ Because of half filled p-orbitals in N, its ionisation energy (stability) is higher than O.
	$I^{st}$ ionisation potential order Na < Al < Mg
(ii)	Because s-orbital in Mg is completely filled and its penetration power is also higher than p-orbital (Al).
	$II^{nd}$ ionisation potential order $Mg^+ < Al^+ < Na^+$
	(2,8,1) $(2,8,2)$ $(2,8)$
Peri	odic variation of ionisation energy
(a)	Variation in period among the representative elements: Ionisation energies generally increases along the period because in moving left to right in a period the effective nuclear charge per outermost electron increases while the corresponding principal quantum number remain same.
(b)	Variation in a group among the representative elements: The ionisation energy generally decreases in moving from top to bottom because the size increases due to the increase of the principal quantum number. On the other hand the effective nuclear charge Zeff for the outermost electron remains almost the same along the group.
Exc	eption
(a)	Ionisation Potential of Al $<$ Ionisation Potential of Ga (While Ionisation Potential decreases down 577 kj mol <sup>-1</sup> 579 kj mol <sup>-1</sup> the group it is due to Transition contraction)
(b)	Ionisation Potential of Hf>Ionisation Potential of $Zr$ (While Ionisation Potential should decreases down 760 kj mol $^{-1}$ 5d 674 kj mol $^{-1}$ 4d the group. It is due to lanthanide contraction )
(c)	In a period atomic size decreases and zeff increases so removal of electron becomes difficult and ionisation potential increases. But N, Be, P, Mg, show high ionisation energy than corresponding of next element. Li Be B C N O F Ne
	atomic size decreases, zeff increases, Ionisation Potential increases.
	Order of ionisation potential $Li \le B \le Be \le C \le O \le N \le F \le Ne$

### Application of ionisation potential

(a) Metalli c and non metallic character

Metallic → Ionisation Potential Low (Na, K, Rb etc.)

non metallic → Ionisation Potential High (F, Cl, Br etc.)

Ionisation Potential 
$$\propto \frac{1}{\text{Metallic property}}$$

(b) Reducing character

Re ducing character 
$$\propto \frac{1}{\text{Ionisation Potential}}$$

- (i) IA group has minimum ionisation potential so they are strong reducing agents in gaseous state ( Li < Na < K < Rb < Cs)
- (ii) IA group In Aqueous state

reducing character Li > K  $\stackrel{\sim}{\_}$  Rb > Cs > Na

As the degree of hydration is more in Li due to high charge density.

- (iii) VIIA group has maximum ionisation potential so they are strong oxidising agents (F > Cl > Br > I)
- (c) Stability of oxidation states :
- (i) If the difference between two successive ionisation potential  $\geq 16eV$  then lower oxidation state is stable.

Difference of ionisation potential > 16 eV So Na<sup>+</sup> is more stable.

(ii) If the difference between two successive ionisation potential  $\leq 11$  then higher oxidation state is stable.

Difference of ionisation potential < 11 eV So  $Mg^{+2}$  is more stable.

 $\left\{ \begin{array}{ll} Al^{\mbox{\tiny +}} \mbox{ is stable only in gaseous state} \\ \\ Al^{\mbox{\tiny +}3} \mbox{ is stable in liquid and solid state.} \end{array} \right.$ 

Ionization energy in KJ mol<sup>-1</sup>

Group Period	1	2											13	14	15	16	17	18
1	Н																Н	Не
	1311																1311	2372
2	Li	Be											В	С	N	o o	F	Ne
	520	899											801	1086	1403	1314	1681	2080
3	Na	Mg				-	Gr	oup					Al	Si	P	S	Cl	Ar
	496	737	3	4	5	6	7	8 8	9	10	11	12	577	786	1012	999	1255	1521
4	К	Ca	Sc	Ti	V	Сг	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
	419	590	631	656	650	652	717	762	758	736	745	906	579	760	947	941	1142	1351
5	Rb	Sr	Y	Zr	Nb	Мо	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	ı	Xe
	403	549	616	674	664	685	703	711	720	804	731	876	558	708	834	869	1191	1170
6	Cs	Ba	La	Hf	Та	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
	376	503	541	760	760	770	759	840	900	870	889	1007	589	715	703	813	912	1037
7	Fr	Ra	Ac															

#### ELECTRON AFFINITY

- (a) The amount of energy released when an electron is added to the outermost shell of one mole of an isolated gaseous atom in its lower energy state.
- (b) The positive value of the electron affinity indicates that the process, i.e.  $X_{(g)} + e^- \rightarrow X_{(g)}^-$ , is exothermic and the negative value indicates the process to be an endothermic one. Thus the convention accepted in defining the electron affinity apparently contradicts the established convention in the thermodynamics.

Thus, 
$$F_{(g)} + e^- \rightarrow F_{(g)}^-$$
,  $\Delta H = -328 \text{ kJ mol}^{-1}$ , and  $EA = 328 \text{ kJ mol}^{-1}$  and  $N_{(g)} + e^- \rightarrow N_{(g)}^-$ ,  $\Delta H = +31 \text{ kJ mol}^{-1}$ , and  $EA = -31 \text{ kJ mol}^{-1}$ 

(c) Electron affinity just defined is actually first electron affinity since it corresponds to the addition of one electron only. In the process of adding further electron, the second electron will be added to gaseous anion against the electrostatic repulsion between the electron being added and the gaseous anion. Energy instead of being released is supplied for the addition of an electron to an anion.

$$A_{\scriptscriptstyle (\!g\!)} \,+\, e^{\scriptscriptstyle -} \,\to\, A_{\scriptscriptstyle (\!g\!)}^{\,-} \,+\, E_1 \qquad ; \qquad \qquad A_{\scriptscriptstyle (\!g\!)}^{\,-} \,+\, e^{\scriptscriptstyle -} \,+\, \text{Energy supplied} \,\to\, A_{\scriptscriptstyle (\!g\!)}^{\,\,2-}$$

## Factors affecting electron affinity

(A)	Atomic size	Electron Affinity $\propto \frac{1}{\text{Atomic size}}$
(B)	Screening effect	Electron Affinity $\propto \frac{1}{\text{Screening effect}}$
(C)	Effective nuclear charge $(Z_{\mbox{\tiny eff}})$	Electron Affinity ∝ Zeff

### (d) Stability of completely filled or half filled orbitals

Electron affinity of filled or half filled orbital is very less or zero.

- Ex. (i) Elements (He, Ne, Ar, ....), Electron Affinity = Zero ( $\Delta$ egH = + ve)
  - (ii) Elements (Be, Mg, Ca, ....), Electron Affinity =  $\frac{\sim}{2}$  Zero ( $\Delta$ egH = + ve)
  - (iii) Elements (N, P, As, ....), Electron Affinity = Very less

### Periodic variation of electron affinity

(a) In a period: The effective nuclear charge increases and the size decreases with the increase of atomic number in a period. This is why, the electron affinity in general increases in a period. In fact, it reaches the climax for the Group VII A (i.e. halogens) elements.

Electron affinities (kJ mol<sup>-1</sup>)

IA	IIA	IIIA	IVA	VA	VIA	VIIA	Noble gas
Li	Ве	В	С	N	О	F	Ne
59.8	-60	27	122	-31	141	328	-90
Na	Mg	Al	Si	Р	S	Cl	Ar
53	-60	44	134	72	200	349	0
		Ga	Ge	As	Se	Br	
		29	120	77	195	324	

(b) In a group: For the representative elements, in moving down in a group generally the electron affinity falls down with the increases of atomic number because the effective nuclear charge Zeff at periphery per electron remain almost same but the size gradually increases due to addition of new shell.

#### Exceptions

- (a) Electron affinity values of nitrogen and phosphorous (VA) are lesser than the electron affinity values of carbon and silicon respectively. It is due to the comparatively stable half filled configuration (np³) of nitrogen and phosphorus and the tendency to acquire the stable np³ configuration by the gain of one electron in carbon and silicon (np²).
- (b) The theoretical value of the electron affinity of zero group i.e. inert gas elements is zero due to stable  $s^2p^6$  configuration.
- (c) F < Cl, O < S, N < P, B < Al. Here it is interesting to note that the electron affinity sequence is in the opposite order as is expected from the size sequence. To explain the observed sequence of electron affinity, we are to consider the other factors. Though the electrostatic attractive pull towards the nucleus favours the 2nd period elements more compared to the corresponding 3rd period elements, the added electron creates an unfavourable effect, i.e. electron-electron repulsion, which is more for the 2nd period elements because of their smaller sizes. This repulsive force is not so large in the 3rd period elements because of their larger size.

#### **ELECTRONEGATIVITY** (EN)

- (a) The tendency of an atom to attract shared electrons towards itself is called electronegativity.
- (b) Electronegativity and Electron affinity both have tendency to attract electrons but electron affinity is for isolated atoms. Where as electronegativity is for bonded atoms.
- (c) A polar covalent or ionic bond of A B may be broken as
  - (i)  $A B \longrightarrow A^-: + B^+$  (Electronegativity A > Electronegativity B)
- or (ii)  $A B \longrightarrow A^+ + :B^-$  (Electronegativity A < Electronegativity B) depending on their tendency to attract bonded electron.
- (d) There is no unit of electronegativity because it is a relative value
- (e) Electronegativity is property of a bonded atom not an isolated gaseous atom so no energy will be liberated or absorbed.

### Difference between electronegavity and Electron Affinity

Electronegativity	Electron Affinity
Tendency of an atom in a molecule to attract the bonded electrons	Energy released when an electron is added to neutral isolated gaseous atom
Relative value of an atom	Absolute value of an atom
It regularly changed in a period or group	It does not changes regularly
It has no unit	It is measured in eV/atom or KJ mol <sup>-1</sup> or K cal mole <sup>-1</sup>

Note: Small atoms are normally having more electronegativity than larger atoms.

#### Pauling's Scale

Pauling related the resonance energy ( $\Delta_{AB}$ ) of a molecule AB with the electronegativities of the atoms A and B. If  $x_A$  and  $x_B$  are the electronegativities of atoms A and B respectively then

$$0.208 \sqrt{\Delta_{AB}} = x_A - x_B \text{ if } x_A > x_B$$
  
or  $\Delta_{AB} = 23.06 (x_A - x_B)^2$ 

 $\Delta_{AB} = E_{AB(experimental)} - E_{AB(theoritical)}$  where  $E_{A-B}$  is the energy of A-B bond.

$$E_{AB(theoritical)} = \sqrt{(E_{A-A} \times E_{B-B})}$$

In a purely covalent molecule, AB, the experimental and theoritical values of bond energy A-B are equal,

So 
$$\Delta_{AB} = 0$$
  
or  $0 = 23.06 (x_A - x_B)^2$   
or  $x_A = x_B$ 

In an ionic molecule AB,  $\boldsymbol{E}_{AB(experimental)}$  is more than  $\boldsymbol{E}_{AB(theoritical)}$ 

Pauling assumed the electronegativity value of fluorine 4 and calculated the electronegativity values of other elements from this value.

							Н
							2.1
L	i	Be	В	С	N	0	F
1.	0	1.5	2.0	2.5	3.0	3.5	4.0
N	a	Mg	Al	Si	Р	S	а
0.	9	1.2	1.5	1.8	2.1	2.5	3.0
k	ζ.	Ca	Ga	Ge	As	Se	Br
0.	8	1.0	1.6	1.8	2.0	2.4	2.8
R	5	Sr	In	Sn	Sb	Te	I
0.	8	1.0	1.7	1.8	1.9	2.1	2.5
С	s	Ba	П	Pb	Bi	Ро	
O.	7	0.9	1.8	1.8	1.9	2.0	
P	r	Ra					
Ο.	7	0.9					

In Pauling's scale, elements having almost same electronegativity are-

$$C = S = I = 2.5$$
  
 $N = CI = 3.0$   
 $P = H = 2.1$   
 $Cs = Fr = 0.7$   
 $Be = AI = 1.5$ 

#### Mulliken's Electronegativity

According to Mulliken, the electronegativity of an element is the average value of its ionisation potential and electron affinity.

or electro-negativity = 
$$\frac{\text{Electron affinity + Ionisation potential}}{2}$$

When both are expressed in electron volt

Alred Rochow's Electronegativity: The electronegativity of an element is the electrostatic force of attraction between the electron present on the circumference of outermost shell of this atoms and the atomic nucleus. If the distance between the circumference of outermost shell & the neucleus is r and the effective nuclear charge  $Z_{\rm eff}$  then –

Electron-negativity = 
$$\frac{Z_{eff} e^2}{r^2} = \frac{0.359 \, Z_{eff}}{r^2} + 0.744$$
  $\Rightarrow$   $Z_{eff} = Z - \sigma$ 

Z = The actual number of charge present in the nucleus i.e. number of protons and  $\sigma$  = Shielding constant.

### Factors Affecting electronegativity

(A)	Atomic size	(B)	Effective nuclear charge (Z <sub>eff</sub> )
	Electronegativity $\propto \frac{1}{\text{Atomic size}}$		Electronegativity ∝ Zeff
(C)	Hybridisation state of an atom		Oxidation state
	Electronegativity $\propto$ % s character in hybridised atom $sp > sp^2 > sp^3$		Electronegativity $\propto$ oxidation state $Mn^{+2} < Mn^{+4} < Mn^{+7}$
	s character 50% 33% 25%		$O^{-2} < O^{-1} < O < O^{+1} < O^{+2}$
	Electronegativity3.25 2.75 2.5		Fe $<$ Fe $^{+2}$ $<$ Fe $^{+3}$

**Note:** • s-orbital is nearer to nucleus so by increasing s-character in hybridisation state, Electronegativity also increases.

 Electronegativity does not depends on filled or half filled orbitals, because it is a tendency to attract bonded electron, not to gain or loss electron from out side.

#### Periodic Variation

- (a) In a period: In moving from left to right in a period, the size gradually contracts and the effective nuclear charge increases. This is why, the electronegativity gradually increases with the increase of atomic number in a period up to the group VIIA elements.
- (b) In a group: In the representative elements, in moving down in a group, the size increase while Zeff per electron at the periphery remains almost constant. This is why, the electronegativity generally falls in a group with the increase of atomic number.

#### Exceptions

(a) In '0' group - Electronegativity is always zero, because inert gas do not form molecule.

(b) Electronegativity of Cs and Fr are equal, it is because from  $_{55}$ Cs to  $_{87}$ Fr only one shell increases but nuclear charge (No. of proton) increases by +32.

Note: So effect of nuclear charge balanced the effect of increase in number of shell.

#### Electronegativity of F > Cl but Electron affinity of Cl > F

- (c) In group of IIB elements (Zn, Cd, Hg) value of electronegativity increases down the group, because of lanthanide contraction
- (d) In IIIA group, value of electronegativity increases down the group, because of transition contraction Electronegativity of Ga > Electronegativity of Al

### Application of electronegativity

(a) Metallic and non metallic nature

Low electronegativity  $\longrightarrow$  Metals

High electronegativity → Non Metals

Metallic character increases down the group but decreases along a period.

(b) Bond length

$$\Delta EN \propto \frac{1}{Bond \ length}$$
 Here  $\Delta EN = difference$  in electronegativities of bonded atoms

Note: HF has minimum bond length as expected because of much difference in the electronegativities of H and F.

(c) Acidic strength of hydrides

$$NH_3 \le H_2O \le HF$$

In a perticular period acidic strength of hydride is depends on electronegativity of M in M – H bond. Higher the electronegativity of M greater the acidic strength of hydride.

- (d) Nature of bonds:
- (i) According to Hanny & Smith formula

Ionic % = 
$$16 (X_A - X_B) + 3.5 (X_A - X_B)^2$$

Here  $X_{\Delta}$  = Electronegativity of A

 $X_{R}$  = Electronegativity of B

If  $X_A - X_B \ge 2.1$  Ionic % > 50% i.e. Ionic bond

If  $\rm X_{A}^{}$  –  $\rm X_{B}^{} \leq~2.1$   $\,$  Ionic % < 50% i.e. covalent bond

(ii) According to Gallis

$$X_A - X_B \ge 1.7$$
 Ionic  $X_A - X_B \le 1.7$  Covalen

If  $X_A = X_B$ ; then A - B will be non polar.

Ex. H-H, F-F

If  $X_A > X_B$  and difference of electronegativities is small then

 $A^{\delta \! -} \ \, -\!\!\!\!\! - B^{\delta \! +} \ \,$  bond will be polar covalent

- (e) Nature of hydroxides
- (i) As per Gallis, In AOH if electronegativity of A is more than 1.7 (Non metal) then it is acidic in nature.
- (ii) If electronegativity of 'A' is less than 1.7 (metal) then AOH will be basic in nature

Ex. NaOH CIOH  $X_A$  0.9 3.0

Nature Basic Acidic

- (iii) If  $X_A X_0 \ge X_0 X_H$  then AO bond will be more polar and will break up as  $A \longrightarrow OH \longrightarrow A^+ + OH^-$  It shows basic nature

#### Ex. In NaOH

$$\rm X_{_{\rm O}}$$
 –  $\rm X_{_{\rm Na}}$  (2.6) >  $\rm X_{_{\rm O}}$  –  $\rm X_{_{\rm H}}$  (1.4) — So hydroxide is basic

In ClOH

$$X_{O} - X_{CI}$$
 (0.5) <  $X_{O} - X_{H}$  (1.4) So hydroxide is acidic

- (f) Nature of oxides: Consider an oxide AO
  - If  $X_A X_O > 2.3$  Basic oxide

If  $X_A - X_O = 2.3$  Amphoteric oxide

If  $X_A - X_O < 2.3$  Acidic oxide

- (i) Along a period acidic nature of oxide increases.
- (ii) Down the group basic nature of oxide increases

ie. when in periodic table the distance between the element and oxygen increases, basic character increases.

acidic character decreases

Note: BeO,  $Al_2O_3$ , ZnO, SnO, PbO,  $SnO_2$ ,  $PbO_2$ ,  $Sb_2O_3$  etc. are amphoteric oxides.

CO, H<sub>2</sub>O, NO, N<sub>2</sub>O etc. are neutral oxides.

Acidic strength of oxide and oxyacid  $\propto$  Electronegativity

$$B_2O_3$$
  $CO_2$   $N_2O_5$ 

EN increase, acidic nature increasse.

Acidic properties increases with increasing oxidation state of an element when centrel atom is same. Ex.

(i) 
$$Sb_2O_5 > Sb_2O_3$$

(ii) 
$$HClO_4 > HClO_3 > HClO_2 > HClO$$

(iii) 
$$HNO_3 > HNO_2$$

(iv)  $SO_3 > SO_2$ 

$$(v) \qquad N_{o}O_{s} > N_{o}O_{s}$$

(vi)  $H_2SO_4 > H_2SO_3$ 

(g) Hydrolysis products of AX

Where A = Other element and X = Halogen

- (i) If electronegativity of X > Electronegativity of A then on hydrolysis product will be HX.
- Ex. (BCl<sub>2</sub>), Electronegativity of Cl > Electronegativity of B

$$PCl_3 + 3HOH \longrightarrow 3HCl + H_3PO_3$$

$$PCl_3$$
.  $Cl_2 + H_2O \longrightarrow 2HCl + POCl_3$ 

$$POCl_3 + 3HOH \longrightarrow 3HCl + H_3PO_4$$

- (ii) If electronegativity of  $X \le$  electronegativity of A then on hydrolysis product will be HOX (hypohalous acid)
- **Ex.**  $\operatorname{Cl}_2\operatorname{O}$   $\operatorname{O}^{\mathbb{S}^+}$  Here electronegativity of  $\operatorname{O} > \operatorname{Cl}$

So On hydrolysis -

$$O^{\delta} \begin{array}{cccc} O^{\delta^{+}} & HO^{-} + H^{\uparrow} \\ & + & & \longrightarrow 2HOCl + H_{2}O \\ O^{\delta^{+}} & HO^{-} + H^{\uparrow} \end{array}$$

(h) Nomenclature of inorganic compounds

Prefix — less electronegative element

Suffix — More electronegative element

Ex. Cl<sub>2</sub>O(Right) OCl<sub>2</sub>(Wrong)

In Dichloroxide the electronegativity of Cl is less than 'O' i.e. why Cl is in prefix position.

OF<sub>2</sub> Oxygen difluoride

ICl Iodine chloride

NH<sub>3</sub> Exception (Here H is less electronegative but it is suffix)

#### **DENSITY**

- (a) In a group volume of an atom increases along with atomic weight but atomic weight increases more than atomic volume, So density increases in a group.
- (b) Factors affecting density are
  - (i) Inner shell configuration (ii) Atomic weight (iii) Packing capacity (iv) Chemical bond

#### Periodic variation

- (a) In period density first increases till maximum and then decreases. (s-block to d-block increases, d-block to p-block decreases)
- (b) In group from top to bottom density increases regularly

Ex. In VIIA group -F and Cl are gases (Low density) Br is liquid (density 3.19 g/cm<sup>-3</sup>)

From s-block to p-block packing capacity and strength of bond increases.

I is solid (density 4.94 g/cm<sup>-3</sup>)

#### Exceptions

The density of sodium and magnesium is greater than K and Ca respectively. This can be explained by (a) inner shell configuration.

In K, 3d<sup>0</sup> orbital is vacant, 3<sup>rd</sup> orbit has the capacity to hold 18e<sup>-</sup> but it has only 8e<sup>-</sup>. Due to empty orbitals atomic volumes increases and so density decreases

- (b) Li is the lightest metal known.
- (c) Highest density of solid metal Ir (22.63 gm/cc) and Os (22.6 gm/cc) and liquid metal Hq(13.6 gm/cc)

### Order of density of elements

Li < K < Na < Rb < Cs	Sc < Y < La	Hg < Au < Os < Ir	Cr < Fe < Cu
Ca < Mg < Be < Sr < Ba	Ti < Zr << Hf	Sc < Zn < Fe < Hg	Fe < Cu < Pb
He < Ar < Kr < Rn	Zn < Cd < Hg		Fe < Hg < Au

#### BOILING POINTS AND MELTING POINTS

- It is a property of aggregate of atoms and not of a single atom. (a) i.e. why it is a molecular propertry.
- (b) Melting point of a solid depend on -
  - (i) Structure of solid
- (ii) Chemical bond
- (iii) Bond energy
- (c) Structure of solid made up of (i) atomic solid (ii) molecular solid (iii) metallic solid.

Order of decreasing melting point is: Atomic solid > Metallic solid > Molecular solid

- (d) Chemical bond among particles in solid. Order of bond strength is -
  - Covalent bond > Metallic bond > Vander waal bond
- Bond energy Covalent solids like diamond, SiO, etc have only covalent bonds between atoms so their (e) bond energy is higher than molecular or metallic solids.

#### Periodic variation

In period from left to right boiling point and melting point first increases then decreases.

Alkali metals - Crystal structure BCC (low boiling point & melting point)

Transition metals - .................. FCC (High boiling point & melting point)

Inert gases ...... Lowest boiling point & melting point (Vander waal force) Transition elements ...... Highest melting point

W(Tungston) maximum melting point (3410 C)
Hg(Mercury) lowest melting point (-38 C)

Metals

Non metals Carbon (In the form of diamond) Highest melting point (3727 C) Helium Lowest melting point (-270 C)

### In Group

(a) In s-block elements boiling point & melting point decreases down the group.

Li, Na (solid) 
$$\rightarrow$$
 Cs, Fr (liquid)

It is due to weak cohesive energy of metalic bond in IA.

- (b) In **d-block** elements boiling point & melting point increases down the group (due to lanthanide contraction, zeff increases and hence bond energy increases)
- (c) In p-block elements
- (i) From IIIA IVA group boiling point & melting point decreases down the group and from VA to '0' group, boiling point & melting point increases down the group. (Atomic or molecular weigh  $\infty$  vander waal force)
- (ii) boiling point and melting point of monoatomic molecules are lesser than diatomic molecules.

  '0' group < Halogens
- (iii) Atomic solid non metals like B, C and Si has higher boiling point and melting point due to strong covalent bond.
- (iv) Boiling point & melting point of molecular solids are less because of weaker vander waal force among molecules  $\mathbf{Ex.}\ \mathrm{I_9}$ .

#### Order of melting point

Li > Na > K > Cs	C > Si > Ge	He < Ne < Ar < Rn
Be > Ca > Sr > Ba > Mg	C > B > Si	Zn > Cd > Hg
$F_2 \le Cl_2 \le Br_2 \le I_2$	B > Al > Ga	Cu > Au > Ag