

## PERIODIC CLASSIFICATION OF ELEMENTS

*Periodic table is an arrangement of elements with similar properties placed together. The periodic table evolved largely as a result of experimental observations.*

### Earlier Attempt to Classify Elements.

(1) **Dobereiner's law of triads** (1829) : It was the classification of elements into groups of three elements each with similar properties such that the atomic weight of the middle element was the arithmetic mean of the other two e.g. Ca, Sr, Ba ; Cl, Br, I etc.

(2) Telluric screw or Helix was proposed by Chancourtois in 1862.

(3) **Newlands law of octaves** (1864) : It was an arrangement of elements in order of increasing atomic weights in which it was observed that every eighth element had properties similar to those of the first just like the eighth note of an octave of music.

(4) **Mendeleef's period law** (1869) : The first significant classification (arrangement of known elements in a systematic way) was given by Mendeleeff (a Russian chemist) in 1869 in the form of periodic table, commonly known as Mendeleeff's periodic table. His periodic table was based on periodic law, "**The physical and chemical properties of elements are periodic functions of their atomic weights.**"

In Mendeleef's periodic table elements are arranged in order of their increasing atomic weights in such a way that elements with similar properties are placed in the same group. It consists of seven horizontal rows called periods. These are numbered from 1 to 7.

Mendeleef's original table consists of 8 vertical columns called groups. These are numbered as I, II III..... VIII. However, 9<sup>th</sup> vertical column called Zero group was added with the discovery of inert gases. Except for group VIII and zero, each group is further divided into two sub-groups designated as A and B. Group VIII consists of 9 elements arranged in three sets each containing three elements.

### Modern Periodic Law and Modern Mandeleeff's Periodic Table .

The recent work has established that the fundamental property of an atom is atomic number and not atomic weight. Therefore, atomic number is taken as the basis of the classification of the elements. The modern periodic law may be stated as : "**The properties of elements are periodic functions of their atomic number.**" (Moseley). When atomic number is taken as the basis for classification of elements, many anomalies of Mendeleef's table disappear, such as the,

(1) **Position of hydrogen** : Dual behaviour of hydrogen is explained on the fact that it has one electron in its outermost orbit. When it loses its electron it gives  $H^+$  and behaves like alkali metals and when it gains an electron it gives  $H^-$  and behaves like halogens. Thus, it resembles with both the alkali metals and the halogens.

(2) **Dissimilar elements placed together** : The lengths of periods are determined by the arrangement of electrons in different orbits. The period ends on the completion of last orbits (last members always being the inert gas). Different periods contain 2, 8, 18 or 32 elements. Now out of the two elements which every long period adds to the group, one resembles the typical elements while the other does not. This gives rise to formation of subgroups. This explains the inclusion of dissimilar elements in the same group but different subgroups.

(3) **Position of rare earth elements** : The electronic arrangement of rare earths can be written as 2, 8, 18, (18 + x), 9, 2 where x varies from 0 to 13, i.e., from Lanthanum to Lutecium. The number of electrons in valency shell, in case of all the elements remains the same although the atomic number increases. Since they possess the

## PERIODIC CLASSIFICATION OF ELEMENTS

same number of valency electrons, the chemical behaviour is also similar. This justifies their positions in the same group and in the same place of the periodic table.

(4) **Anomalous pairs of elements** : Now the basis of classification is atomic number, therefore, this anomaly disappears as the elements occupy their normal position in the new periodic table.

(5) **Position of isotopes** : Since the isotopes of same element possess same atomic number they should occupy one and the same position in the periodic table.

(6) **Position of VIII group elements** : In long periods 18 elements are to be distributed among 8 groups; 1 to 7 groups get 2 elements each and zero group accommodates inert elements, the rest three elements are placed at one place in a new group, known as VIII group. This lack of space justifies the induction of VIII group in the periodic table.

(7) **Transuranic elements** : These elements form a series known as *actinide series*, it begins from actinium and ends at lawrencium (89–103). Discovery of elements 104, 105 and 112 has recently been reported. This series has been placed outside the periodic table. The electronic configuration of these elements can be written as  $2, 8, 18, 32, (18 + x), 9, 2$ , where  $x$  varies from zero (for actinium) to 14 (for lawrencium). The number of valency electrons remains the same for all these elements although atomic number increases. Therefore, their chemical behaviour is similar. This justifies their position outside the periodic table at one place.

### Extended or Long Form of Periodic Table .

**Modern periodic table** is also called long form of the periodic table or Bohr's table. In this table, the elements are arranged in order of their increasing atomic number. It consists of 4 blocks ( $s$ ,  $p$ ,  $d$  and  $f$ ), 18 groups numbered from 1 to 18 and 7 periods numbered from 1 to 7.

**Blocks** : The periodic table is divided into four main blocks ( $s$ ,  $p$ ,  $d$  and  $f$ ) depending upon the subshell to which the valence electron enters into.

(1) Elements of group 1 and 2 constitute  $s$ -Block.

(2) Elements of group 13, 14, 15, 16, 17, 18 constitute  $p$ -Block

(3) Elements of group 3, 4, 5, 6, 7, 8, 9, 10, 11, 12 constitute  $d$ -Block

(4) The  $f$ -Block elements comprise two horizontal rows placed at the bottom of the periodic table to avoid its unnecessary expansion.

Elements of  $s$  and  $p$ -blocks are called normal or representative elements, those of  $d$ -block are called transition elements while the  $f$ -block elements are called inner transition elements.

# PERIODIC CLASSIFICATION OF ELEMENTS

## Periodic Table

Metal  
 Metalloid  
 Nonmetal

(s-Block) Main-Group Elements ( $ns^{1-2}$ )		(d-Block) Transition Elements [ $(n-1)d^{1-10}ns^{1-2}$ ]										(p-Block) Main-Group Elements ( $ns^2np^{1-6}$ )					
1 IA Modern Group No. Old Group No.												18 VIIIA					
1	2											13	14	15	16	17	18
1	2											13	14	15	16	17	18
3	4											5	6	7	8	9	10
11	12											13	14	15	16	17	18
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54
55	56	57	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86
87	88	89	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118
		(f-Block) Inner-Transition Elements [ $(n-2)f^{1-14}(n-1)d^{0-1}ns^2$ ]															
* Lanthanides (4f-series) ( $4f^{1-14}5d^{0-1}46s^2$ )		58	59	60	61	62	63	64	65	66	67	68	69	70	71		
** Actinides (5f-series) ( $5f^{1-14}6d^{0-1}7s^2$ )		90	91	92	93	94	95	96	97	98	99	100	101	102	103		

Note : Only IUPAC names are given for elements with Atomic Number more than 103. Identity of elements Atomic Numbers 113, 115, 117 is yet to be established.

**Groups :** The 18 vertical columns are called groups. The elements belonging to a particular group is known as a family and is usually named after the first number. Apart from this some of the groups are given typical names as exemplified beneath ,

- (1) Elements of group 1 are called Alkali-Metals.
- (2) Elements of group 2 are called Alkaline Earths.
- (3) Elements of group 3 are called Pnicogens.
- (4) Elements of group 16 are called Chalcogens.
- (5) Elements of group 17 are called Halogens.
- (6) Elements of group 18 are called Noble Gases or Aerogens.

All the other groups are named after the first member of each group.

**Periods :** The horizontal rows are called periods. There are Seven Periods in the long form of the periodic table.

- (1) 1st period ( ${}_1H \rightarrow {}_2He$ ) contains 2 elements. It is the shortest period.
- (2) 2nd period ( ${}_3Li \rightarrow {}_{10}Ne$ ) and 3rd period ( ${}_{11}Na \rightarrow {}_{18}Ar$ ) contains 8 elements each. These are short periods.
- (3) 4th period ( ${}_{19}K \rightarrow {}_{36}Kr$ ) and 5th period ( ${}_{37}Rb \rightarrow {}_{54}Xe$ ) contains 18 elements each. These are long periods.
- (4) 6th period ( ${}_{55}Cs \rightarrow {}_{86}Ra$ ) consists of 32 elements and is the longest period.

## PERIODIC CLASSIFICATION OF ELEMENTS

(5) 7th period starting with  ${}_{87}\text{Fr}$  is incomplete and consists of 19 elements.

### Periodicity in Properties.

**"The repetition of similar electronic configuration after a definite period is the cause of periodicity of the properties of elements."**

It can be explained with the help of electronic arrangement of elements. According to the modern views, the valency of an element is indicated by the number of electrons present in the outermost orbit. The chemical properties of elements are dependent on valency electrons. Variation in electronic arrangement leads to the variation in properties. After a definite interval, recurrence of similar electronic arrangement takes place when the number of valency electrons is the same. Thus, there is a regular gradation and repetition in the properties of elements. For example,

Alkali metals		Halogens	
$\text{Li}^3$	2, 1	$\text{F}^9$	2, 7
$\text{Na}^{11}$	2, 8, 1	$\text{Cl}^{17}$	2, 8, 7
$\text{K}^{19}$	2, 8, 8, 1	$\text{Br}^{35}$	2, 8, 18, 7
$\text{Rb}^{37}$	2, 8, 18, 8, 1	$\text{I}^{53}$	2, 8, 18, 18, 7
$\text{Cs}^{55}$	2, 8, 18, 18, 8, 1	$\text{At}^{85}$	2, 8, 18, 32, 18, 7

Therefore, in group IA all elements possess one valency electron and they have a tendency to lose this electron. They are all monovalent and electropositive having similar chemical properties. Same is the case with halogens. They had seven electrons in their outermost orbit and, have a tendency to gain one electron. Therefore, they are all monovalent and electronegative and resemble each other in chemical properties. Thus, it is observed that the same electronic arrangement of outermost orbit is repeated after regular intervals and that accounts for the periodicity of the properties of the elements.

Periodic properties are directly or indirectly related to their electronic configuration and show a regular gradation on moving from left to right in a period or from top the bottom in a group. Some period or from top to bottom in a group. Some important periodic properties are : oxidation number, shielding effect, atomic radii, ionization energy, electron affinity, electronegativity, valency, density, m.pt. and b.pt.

### The Screening Effect or Shielding Effect.

A valence-electron in a multi-electron atom is attracted by the nucleus, and repelled by the electrons of inner-shells. The combined effect of this attractive and repulsive force acting on the valence-electron experiences less attraction from the nucleus. This is called **shielding** or **screening effect**. The magnitude of the screening effect depends upon the number of inner electrons, i.e., higher the number of inner electrons, greater shall be the value of screening effect. The screening effect constant is represented by the symbol ' $\sigma$ ' is determined by the **Slater's rules**.

**The magnitude of screening constant in the case of s- and p- block elements increases in a period as well as in a group as the atomic number increases.**

### Effective Nuclear Charge.

Due to screening effect the valency electron experiences less attraction towards nucleus. This brings decrease in the nuclear charge ( $Z$ ) actually present on the nucleus. The reduced nuclear charge is termed **effective nuclear charge** and is represented by  $Z^*$ . It is related to actual nuclear charge ( $Z$ ) by the following formula,

$$Z^* = (Z - \sigma) \text{ where } \sigma \text{ is screening constant.}$$

## PERIODIC CLASSIFICATION OF ELEMENTS

It is observed that **magnitude of effective nuclear charge increases in a period when we move from left to right.**

**In a subgroup of normal elements the magnitude of effective nuclear charge remains almost the same.**

### Atomic, Ionic and Van der Waals' Radii.

**The radius of an atom is the distance between the centre of its nucleus and electrons in the last orbit.** However, according to quantum mechanics, there is no certainty about the exact position of electrons at any time. Theoretically, an electron, at one time, may be very close to the nucleus while at other time it may be far away from the nucleus. In spite of these limitations we need to have some operational definition of the term atomic radius. There are three operational concepts of atomic radius.

- (1) If the bonding is covalent, the radius is called a *covalent radius*.
- (2) If the two atoms are not bonded by a chemical bond (as in noble gases) the radius is called *van der Waal's radius*.
- (3) If the bonding is ionic, the radius is called *ionic radius*.

(1) **Covalent radius** : **It is half of the distance between the nuclei of two like atoms bonded together by a single bond.** Thus covalent radius of carbon in a compound having C – C single bond can be determined by dividing the bond length by 2, i.e.,

$$r_c = \frac{C-C}{2} \therefore C-C = 2r_c \quad \text{or} \quad r_c + r_c$$

where,  $r_c$  is the single bond covalent radii (SBCR) of carbon. However, if atoms forming the covalent bond are different i.e., one is more electronegative than the other then the atomic radius is determined by the relation,  $A-B = r_A + r_B - 0.009(\chi_A - \chi_B)$ , where  $\chi_A$  and  $\chi_B$  are electronegativities of the atoms A and B respectively. This relation was given by **Stevenson** in 1941.

In a given period, **atomic radius generally decreases from left to right** and thus in any period, alkali metal is the largest and halogen is the smallest atom. For example, in second period elements the covalent radii decrease from Li to F.

${}_3\text{Li}$	${}_4\text{Be}$	${}_5\text{B}$	${}_6\text{C}$	${}_7\text{N}$	${}_8\text{O}$	${}_9\text{F}$	${}_{10}\text{Ne}$
1.23	0.89	0.80	0.77	0.74	0.74	0.72	1.6

The decrease in size along a period is due to the effect of successive increasing nuclear charge without addition of a new shell, i.e., in each element of a given period a new electron is added in the same principal quantum number. For example, in the second period the nuclear charge increases from + 3 in Li to + 9 in F. The increased nuclear charge attracts the electrons more strongly to the nucleus and thus decreases the size of the atom. In case of noble gases, the atomic radii are only the van der Waal's radii which are naturally higher than the covalent radii of other elements.

In a given group, **Atomic radius generally increases as one moves from top to bottom**, e.g., in group 1 atomic size increases steadily from lithium to cesium, i.e.  $r_{\text{Cs}} > r_{\text{Rb}} > r_{\text{K}} > r_{\text{Na}} > r_{\text{Li}}$

## PERIODIC CLASSIFICATION OF ELEMENTS

The increase in size on descending a group is due to addition of extra shell (i.e., the number of principal quantum number increases) which outweighs the effect of increased nuclear charge. Remember that He and Fr are smallest and largest atom respectively.

(2) **Ionic radius** : It is the effective distance from the nucleus of an ion upto which it has its influence on its electron cloud.

A cation (formed by the removal of one or more electrons from an atom) is always much smaller than the corresponding atom. Further, more the number of electrons removed smaller will be the size of the resulting positive ion. For example,  $r_{Fe} > r_{Fe^{2+}} > r_{Fe^{3+}}$ . This is due to following two factors

$$1.26 \quad 0.76 \quad 0.64$$

(i) A cation formed by the loss of electrons may result in the complete disappearance of the outer shell and since the remaining inner shells do not extend so far in space, the cation is much smaller than the metal atom. For example, Sodium atom (Na)  $\rightarrow$  Sodium ion (Na<sup>+</sup>)



(ii) Whenever a cation is formed, the ratio of nuclear charge to the number of electrons (Z/e ratio) is increased with the result the effective nuclear charge is increased and the electrons are pulled towards the nucleus. Consequently, the cation becomes smaller. An anion (formed by gain of one or more electrons to the atom) is always larger than the corresponding atom. For example, Atomic radius of I = 1.23 ; Ionic radii of I<sup>-</sup> = 2.16

This is again due to following two factors : (a) Since in the formation of an anion, one or more electrons are added, the electron cloud expands and the ionic size increases. (b) In the formation of anion, the effective nuclear charge decreases with the result the electrons get away from the nucleus and thus the anion becomes larger than the corresponding atom.

In any particular group, **the ions of elements increase in size on moving from top to bottom.**

In case of isoelectronic ions (ions having same number of electrons but different nuclear charge); the greater the nuclear charge, the greater is the attraction for electrons and smaller is ionic radius. Hence size of such ions decreases from top to bottom as shown in the given table,

**Variation of Radii of Iso-electronic Ions (Atom)**

Ion / Atom	At. number (Nuclear charge)	No. of electrons in the ion	Z/e ratio	Ionic (atomic) radii
C <sup>4-</sup>	6	10	0.6	2.60
N <sup>3-</sup>	7	10	0.7	1.71
O <sup>2-</sup>	8	10	0.8	1.40
F <sup>-</sup>	9	10	0.9	1.36
Ne	10	10	1.0	1.12
Na <sup>+</sup>	11	10	1.1	0.95
Mg <sup>2+</sup>	12	10	1.2	0.65
Al <sup>3+</sup>	13	10	1.3	0.50
Si <sup>4+</sup>	14	10	1.4	0.41
P <sup>5+</sup>	15	10	1.5	0.34
S <sup>6+</sup>	16	10	1.6	0.29
Cl <sup>7+</sup>	17	10	1.7	0.26

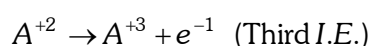
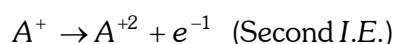
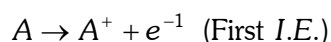
## PERIODIC CLASSIFICATION OF ELEMENTS

(3) **Van der Waal's radius** : *It is one-half of the distance between the nuclei of two adjacent atoms belonging to two neighbouring molecules of an element in the solid state.*

The covalent radius is always smaller than the corresponding van der Waal's radius. This is because of the fact that in the formation of a chemical bond, the two atoms have to come closer to each other. This also explains *why covalent bonds are much stronger than the van der Waal's forces*. It is important to note that since the noble gases ordinarily do not form any covalent bond, in crystals of noble gases, no chemical forces are operating between the atoms. Hence the van der Waal's forces are the only attractive forces in these cases. In other words, **the van der Waal's radii constitute the atomic radii of noble gases** and since van der Waal's radii are larger than covalent radii, **atomic radii of noble gases are largest in their respective periods** (anomaly).

### Ionisation Potential or Ionisation Energy .

The electrons in an atom are attracted by the nucleus. When an electron is to be removed then work is done against this nuclear attraction. In other words energy is required to remove an electron from an atom. To understand the details of chemical behaviour of an element we must have an indication of the energy with which an atom binds its electrons. This is obtained by the measurement of ionisation potential or ionisation energy. It may be defined as **the energy required to remove an electron from the outermost orbit of an isolated gaseous atom in its ground state**. It is expressed in electron volts (eV) or kilo calories per gram atom. In an atom, the energy required to remove first electron from a gaseous atom is called first ionisation energy. The energy required to remove one electron from a unipositive ion to form a bipositive ion is called second ionisation energy. Second ionisation energy is higher than the first. The reason is that in unipositive ion left after the removal of one electron from the atom, the electrons are more firmly bound to the nucleus than in the atom. Hence more energy is needed to remove the second electron.



Similarly, third ionisation energy is even more than second ionisation energy.

#### (1) Variation of ionisation energy in periodic table

(i) **Ionisation energy decreases in a group as the atomic number increases**. It is based on the fact that as we move down a group, the size of atom increases, and the outer electrons become farther away from the nucleus thus reducing the force of attraction and hence ionisation energy decreases.

Li	Na	K	Rb	Cs
5.4 eV	1. eV	4.3 eV	4.2 eV	3.9 eV

(ii) **Ionisation energy increases along a period with increase in atomic number**. This is due to the size of atom since it decreases along a period and outer electrons are most strongly attracted by the nucleus and hence more energy is required to remove the electron.

Li	Be	B	C	N	O	F	Ne
5.4 eV	9.3 eV	8.3 eV	11.3 eV	14.6 eV	13.6 eV	17.0 eV	21.6 eV

## PERIODIC CLASSIFICATION OF ELEMENTS

(iii) The ionisation energies of inert gases are greater than that of their immediate neighbour. It is due to their complete octet  $ns^2p^6$  configuration which is highly stable. Therefore, it is very difficult to remove an electron from the outermost orbit of an inert gas.

### (2) Factors affecting the value of ionisation energy

(i) **Size of atom** : With an increase in atomic size, the ionisation potential is reduced, since the distance of the outermost electron from the nucleus increases and hence the force of attraction decreases.

(ii) **The charge on the nucleus** : With an increase in the nuclear charge, there is an increase in force of attraction of nucleus for electrons making the removal of the electrons more difficult. Thus an increase in nuclear charge increases the ionisation potential.

(iii) **The shielding or screening effect of inner shells** : The valence electrons in a multi-electron atom are pulled by the nucleus but are repelled by the electrons of the inner shells. The valence electrons, therefore, do not experience the total pull of the nucleus. Instead the total pull of the nucleus is reduced by the electrons in inner shells. This effect of reducing the force of attraction of nucleus by the inner shells is called *screening effect*. This effect is exhibited maximum by  $s^2p^6$  (the most stable) shell. Therefore, the ionisation energy of K is much less than Cu, however, both have one electron in their fourth shell.



The ionisation energy of K is 4.33 eV while that of Cu is 7.72 eV. This is due to a large screening effect of  $s^2p^6$ , penultimate orbit in K while  $s^2p^6d^{10}$ , penultimate orbit in Cu which exhibit little screening effect.

(iv) **Type of electrons involved** : Ionisation energy also depends upon the type, i.e., s, p, d or f, electrons which are to be removed, s –electrons are closer to the nucleus and are more tightly held as compared to p, d or f electrons. Hence, ionisation energy decreases in the order of  $s > p > d > f$  orbitals.

(v) **Completely filled or half filled sub-shells** : According to Hund's rule, completely filled or half filled orbitals are more stable. Therefore, it is comparatively difficult to remove the electrons from these shells. The ionisation energy of Be (9.3 eV) is more than B (8.3 eV) because Be has  $2s^2$  configuration of the outermost orbit which is fully filled. Similarly, nitrogen (14.6 eV) has more ionisation energy than oxygen (13.6 eV) because nitrogen has outermost shell configuration as  $2s^2p^3$  in which p shell is half filled and is more stable. Similarly, ionisation energy of Mg is more than Al and that of P is more than S.

### (3) Relative ionisation energies

IE<sub>1</sub> and IE<sub>2</sub> of the 2<sup>nd</sup> period elements

IE<sub>1</sub> : Li < B < Be < C < O < N < F < Ne

IE<sub>2</sub> : Be < C < B < N < F < O < Ne < Li

IE<sub>1</sub> of elements with very high values

Cl < H < O < Kr < N < Ar < F < Ne < He

IE<sub>1</sub> and IE<sub>2</sub> of the 3<sup>rd</sup> period elements

IE<sub>1</sub> : Na < Al < Mg < Si < S < P < Cl < Ar

IE<sub>2</sub> : Mg < Si < Al < P < S < Cl < Ar < Na

### (4) Importance of ionisation energy

(i) Lower is the ionisation potential of an element, more would be its reducing power and also reactivity.

(ii) It gives rough estimate about the basic character of the elements.

(iii) The relative values of ionisation potential and electron affinity of two elements are related to the nature of bond formed during their combination.



## PERIODIC CLASSIFICATION OF ELEMENTS

(iv) The ionisation potentials provide an indication about the number of valence electron(s) in an atom; the abnormally high value indicates that the electron removed is other than the valence electron.

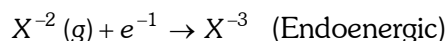
**For example**,  $IE_1$ ,  $IE_2$  and  $IE_3$  values are 5.39, 75.62 and 122.42 eV. Since the values shows sudden jump, it indicates that the number of valence electron in its atom is one. Similarly, values of  $IE_1$ ,  $IE_2$  and  $IE_3$  as 9.32, 18.21 and 153.85 eV indicate that the number of valence electrons in its atom is two.

### Electron Affinity .

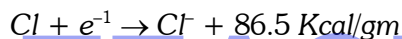
Those atoms whose nuclear forces are not completely screened by electronic shells, offer attraction for electrons. Such atoms capture electrons if these are available with in their effective fields to neutralise the electrostatic forces of the nucleus. Energy is always liberated whenever there is a force of attraction offered by an atom or ion, and this energy is called electron affinity. This may be defined as, "**the energy released when an extra electron is added to a neutral gaseous atom**".

This is first electron affinity. Similarly, second electron affinity will be the energy released (absorbed) when a second electron is added.  $X(g) + e^{-1} \rightarrow X^{-}(g) + E_1$  (Exoenergetic) ;  $X^{-}(g) + e^{-1} \rightarrow X^{-2}(g) + E_2$

But the third electron affinity corresponds to energy absorbed instead of energy evolved in the process.



For example, chlorine atom readily accepts one electron and 86.5 Kcal/gm energy is released.



Thus, higher the energy released in the process of taking up an extra electron, the higher will be the electron affinity. Higher the value of electron affinity of an atom, the more is its tendency to change into anion. It is very difficult to determine the electron affinity experimentally. The values have been calculated on the basis of thermodynamic concepts. It is expressed in electron volts. The values of inert gases are assumed to be zero because they have stable  $ns^2p^6$  configuration and unable to accept any electron. The values for alkali metals are between zero and one.

#### Electron Affinity of Elements (For one electron only at 25° C)

Li	Be	B	C	N	O	F	Ne
0.54	0	0.3	1.13	0.20	1.48	3.62	0
Na	Mg	Al	Si	P	S	Cl	Ar
0.74	0	0.4	1.9	0.80	2.07	3.79	0

The electron affinities of Be, Mg and zero since they have complete  $ns^2$  configuration which can not accommodate extra electron. Similarly, the values for N and P are very low because they also have completely half-filled  $p$  orbitals ( $ns^2p^3$ ) and are more stable.

#### (1) Factors affecting the value of electron affinity

(i) **Atomic size** : The value of electron affinity decreases with the increase in the size of atom since the nuclear attraction decreases down a group as the atomic number increases. Its value increases as we move along a period since the size of atoms decreases along a period. The lower value of  $F$  than  $Cl$  is due to the very small size of  $F$  in which negative charge is highly concentrated and repels the incoming electron thereby reducing the force of attraction of the nucleus towards the adding electron and hence decreasing the electron affinity. Thus, chlorine has a highest value of electron affinity.

(ii) **Nuclear charge** : The value of electron affinity increases with increasing nuclear charge. Thus, its value increases with increase in nuclear charge along a period.

## PERIODIC CLASSIFICATION OF ELEMENTS

(iii) **Screening or shielding effect** : The value of electron affinity increases with the decrease in shielding effect of inner electrons. Besides, the value of electron affinity also depends to some extent upon the type of orbital in which electron is added. The value is greater when electron enters 's' orbital and decreases successively for *p*, *d* and *f* orbitals.

(2) **Importance of electron affinity** : Certain properties of the elements are predicted on the basis of values of electron affinity.

(i) The elements having high values of electron affinity are capable of accepting electron easily. They form anions and electrovalent compounds. These elements are electronegative in nature.

(ii) The elements having high values of electron affinity act as strong oxidising agents, for example, *F, Cl, Br, O, S*, etc.

On the basis of the general trend of ionisation potential and electron affinity, the following properties can be predicted,

(a) Metallic nature decreases in a period while nonmetallic nature increases. Metallic nature increases in a group while non-metallic nature decreases. The arrow ( $\downarrow$ ) represents a group and ( $\rightarrow$ ) represents a period.



(b) Reducing nature decreases in a period while oxidising nature increases. The reducing nature increases in a group while oxidising nature decreases.



(c) Stability of metal increases while activity of the metal decreases in a period and in a group stability decreases while activity increases.



This trend is observed especially in IA, IIA and IIIA elements.

## PERIODIC CLASSIFICATION OF ELEMENTS

(d) The basic nature of the oxides decreases in a period while acidic nature increases. In a group, basic nature increases while acidic nature decreases.



### Electronegativity

**The tendency of an atom in a compound to attract a pair of bonded electrons towards itself is known as electronegativity of the atom.** It is important to note that electron affinity and electronegativity both measure the electrons attracting power but the former refers to an isolated gaseous atom while the latter to an atom in a compound. Thus electron affinity is attraction for a single electron while electronegativity is for a pair of bonded electrons. Further electron affinity is energy while electronegativity is a tendency.

#### (1) Factors affecting the value of electronegativity

(i) The size of the atom.

(ii) Electronic configuration. Small atoms attract electrons more than the larger one and are therefore more electronegative. Secondly, atoms with *nearly* filled shell of electrons, will tend to have higher electronegativity than those sparsely occupied ones.

#### (2) Variation of electronegativity in the periodic table

(i) In a period, electronegativity increases from left to right. This is due to decrease in size and increase in nuclear charge. Thus the alkali metals possess the lowest value, while the halogens have the highest. Inert gases have zero electronegativity.

(ii) In a group, electronegativity decreases from top to bottom. This is due to increase in atomic size.

If an element exhibits various oxidation state, the atom in the higher oxidation state will be more negative due to greater attraction for the electron, e.g., Sn II (1.30) and Sn IV (1.90).

(3) Electronegativity may be expressed on the following three scales

(i) **Mulliken's scale** : Mulliken regarded electronegativity as the average value of ionization potential and electron affinity of an atom.

$$\text{Electronegativity} = \frac{\text{Ionization potential} + \text{Electron affinity}}{2}$$

(ii) **Allred-Rochow scale** : Allred and Rochow defined electronegativity as the electrostatic force exerted by the nucleus on the valence electrons. Thus  $\chi = \frac{0.359 Z}{r^2} + 0.744$  where  $Z$  is the effective nuclear charge and  $r$  is the covalent radius of the atom in Å.

(iii) **Pauling scale** : Pauling scale of electronegativity is the most widely used. It is based on excess bond energies. He determined electronegativity difference between the two atoms and then by assigning arbitrary values to few elements (e.g. 4.00 to fluorine, 2.5 to carbon and 2.1 to hydrogen), he calculated the electronegativity of the other elements.  $\chi_A - \chi_B = 0.208 \sqrt{\Delta E}$  where  $\chi_A$  and  $\chi_B$  are electronegativities of the atoms A and B respectively,

## PERIODIC CLASSIFICATION OF ELEMENTS

the factor 0.208 arises from the conversion of kcal to electron volt (1 eV = 23.0 kcal/mole), while  $\Delta E = \text{Actual bond energy} - \sqrt{(E_{A-A} \times E_{B-B})}$

Pauling and Mulliken values of electronegativities are related as below  $\chi$  (Pauling) = 0.34  $\chi$  (Mulliken) – 0.2

**(4) Importance of electronegativity :** The following predictions can be made from value of electronegativity,

(i) Nature of the bond between two atoms can be predicted from the electronegativity difference of the two atoms.

(a) The difference  $X_A - X_B = 0$ , i.e.,  $X_A = X_B$  the bond is purely covalent.

(b) The difference  $X_A - X_B$  is small, i.e.,  $X_A > X_B$ , the bond is polar covalent.

(c) The difference  $X_A - X_B$  is 1.7, the bond is 50% covalent and 50% ionic.

(d) The difference  $X_A - X_B$  is very high, the bond is more ionic and less covalent. The molecule will be represented in such case as  $BA (B^+ A^-)$ .

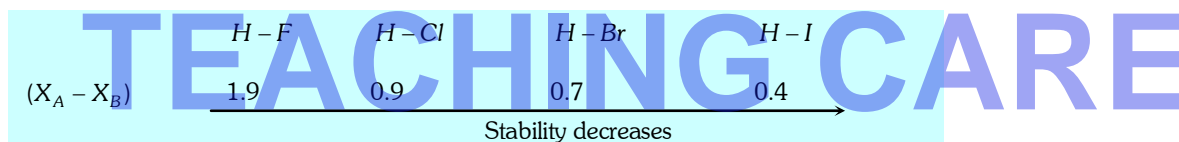
Percentage ionic character may be calculated as,

$$\text{Percentage of ionic character} = 16 |X_A - X_B| + 3.5(X_A - X_B)^2$$

where  $X_A$  and  $X_B$  represents electronegativity of bonded atoms A and B.

This relation was given by A.L. Allred (1961).

(ii) Greater the value of difference ( $X_A - X_B$ ) more stable will be the bond.



Stability of compounds in which  $X_A - X_B$  is very small are unstable in nature,  $SiH_4(0.3)$ ,  $NCl_3(0.0)$ ,  $PH_3(0)$ ,  $AsH_3(0.1)$  are unstable.

(iii) ( $X_O - X_A$ ) difference predicts the nature of the oxides formed by the element A.  $X_O$  is the electronegativity of oxygen.

$X_O - X_A$  is large, the oxide shows basic nature, (e.g.,  $Na_2O$ ).

$X_O - X_A$  is small, the oxide shows acidic nature, (e.g.,  $SO_2$ ).

(iv) Ionic compounds having percentage ionic character less than 20% were found coloured, e.g.,

AgCl	AgBr	AgI	$Ag_2S$
22%	18%	11%	8%
White	Light yellow	Dark yellow	Black

Lesser the percentage ionic character, darker will be the colour.

### Some Other Periodic Properties .

**(1) Atomic volume :** It is defined as the volume occupied by one gram atom of an element. Mathematically,

$$\text{Atomic volume} = \frac{\text{Gram atomic weight}}{\text{Density in solid state}}$$

## PERIODIC CLASSIFICATION OF ELEMENTS

Units of atomic volume are c.c./mole. Atomic volume signifies the volume occupied by one mole (Avogadro number) of atoms of the given element in solid state. Lower atomic volume generally leads to higher density, increased hardness and brittleness, higher melting and boiling points, less malleability and ductility.

(i) while descending a group, the atomic volume generally increases which is due to increase in the number of shells though the valence electrons in a given group remains constant.

(ii) While going left to right across a period the atomic volume first decreases to a minimum and then increases. Francium has the highest atomic volume and boron has lowest atomic volume.

**(2) Density :** The density of the elements in solid state varies periodically with their atomic numbers. At first, the density increases gradually in a period and becomes maximum somewhere for the central members and then starts decreasing afterwards gradually.

**(3) Melting and boiling points :** The melting points of the elements exhibit some periodicity with rise of atomic number. It is observed that elements with low values of atomic volumes have high melting points while elements with high values of atomic volumes have low melting points. In general, melting points of elements in any periodic at first increase and become maximum somewhere in the centre and thereafter begins to decrease.

Tungsten has the maximum melting point ( $3410^{\circ}\text{C}$ ) amongst metals and carbon has the maximum melting point ( $3727^{\circ}\text{C}$ ) amongst non-metals. Helium has the minimum melting point ( $-270^{\circ}\text{C}$ ). The metals, Cs, Ga and Hg are known in liquid state at  $30^{\circ}\text{C}$ .

The boiling points of the elements also show similar trends, however, the regularities are not so striking as noted in the case of melting points.

**(4) Oxidation state (Oxidation number, O.N.) :** *Oxidation number of an element in a compound is the total number of electrons it appears to have gained or lost (negative and positive oxidation states respectively) during the formation of that particular compound.*

*Trend of oxidation states in various groups*

(1) Group 1 ( $ns^1$ ) and group II ( $ns^2$ ) elements attain the inert gas configuration by the loss of outer s electrons. The group 1 and 2 elements have oxidation states of I and II respectively.

(2) Groups 13 elements ( $ns^2p^1$ ) can exhibit oxidation states of I (by the loss of the  $np^1$  electron) and III (by the loss of  $np^1 + ns^2$  electrons). The stability of the lowest state (I) increases while that of higher state (III) decreases with increase in atomic number. Thus B, Al and Ga show only III oxidation state. In shows both mono and trivalent states while in Tl monovalent state is more stable.

(3) Group 14 elements ( $ns^2p^2$ ) show oxidation states of II (by the loss of  $np^2$  electrons) and IV (by the loss of  $ns^2p^2$  electrons). The stability of II state increases while that of IV decreases with the increase in atomic number. Certain elements of this group (C, Si and Ge) also show -IV state in which elements attain inert gas configuration ( $ns^2p^6$ ) by acquiring four electrons. This state can exist only with the highly electropositive elements in carbides, silicides and germanides which are covalent.

(4) Group 15 elements ( $ns^2p^3$ ) show oxidation state of -III (by the gain of three electrons), III (by the loss of  $np^3$  electrons) and V (by the loss of  $np^3 + ns^2$  electrons). The stability of -III and V states decreases while that of III state increases with increasing atomic number. Nitrogen is unique in having a large number of oxidation states, including a fractional one (e.g.  $-\frac{1}{3}$  in  $\text{NH}_3$ ).

## PERIODIC CLASSIFICATION OF ELEMENTS

(5) Group 16 elements ( $ns^2p^4$ ) show mainly – II oxidation state which can be easily achieved by the gain of two electrons short of the next inert gas configuration. Hence the elements of 16 group are electronegative. The stability of – II state decreases down the group. Other important oxidation states of these elements are II, IV and VI (II oxidation state is not very stable). The different oxidation states may be explained as below,

M	$ns^2 p_x^2 p_y^1 p_z^1$
M [–II]	$ns^2 p_x^2 p_y^2 p_z^2$
M [II]	$ns^2 p_x^2$
M [IV]	$ns^2$
M [VI]	No electron in the outermost shell of the atom.

(6) Group 17 elements ( $ns^2p^5$ ) show mainly –I oxidation state and hence the elements are extremely high electronegative. Fluorine is the most electronegative and cannot give a positive oxidation state. Other members can show the oxidation states of I, III, V and VII; the stability of these states decreases in the order : V > VII > III > I. Moreover, chlorine shows oxidation states of IV (in  $\text{ClO}_2$ ) and VI (in  $\text{ClO}_3$ ).

(7) Group zero elements ( $ns^2p^6$ ) are stable. However, after 1962 compounds of inert gases with F and O (most reactive elements) have been characterised. In these compounds inert gases show oxidation states of IV, VI, II and VIII (in order of decreasing stability).

(8) **Oxidation states in transition elements** : The general electronic configuration  $(n-1) d^x ns^2$  of the transition elements suggests,

- II (achieved by the loss of  $ns^2$  electrons) as the lowest common oxidation state, and
- $2 + x$  [achieved by the loss of  $ns^2 + (n-1) d^x$  electrons] as the maximum oxidation state of these elements.

(a) In the 3d series, the Ti (II) is unstable and strongly reducing. The stability of II state increases (with a decrease in reducing character) with the addition of electrons in  $(n-1) d$  orbital. In 4d. and 5d series, II state is unstable except for Pt (II) and Pd (II).

(b) In the 3d series, the highest oxidation state increases from III in Sc to VII in Mn. Beyond Mn ( $d^5$  in the ground state), electron pairing commences in the  $d$  orbitals and the highest oxidation state for the subsequent members does not exceed VI. In the 4d and 5d series, the higher states are more stable and less oxidising than those in the  $d$  series. Thus Nb (V), Ta (V), Mo (VI), W (VI), Tc (VII) and Re (VII) are almost non-oxidising. In general, the stability of the higher states is in the order,  $3d \ll 4d < 5d$

**(5) Oxidising and Reducing Power** : Tendency to lose electrons and reducing power are directly related to each other; while tendency to gain electrons and oxidising power are directly related to each other.

(i) In a group, the reducing character generally increases. Thus among alkali metals (except francium), cesium is the most powerful reducing element (in absence of water).

(ii) The reducing character decreases and oxidising character increases along the period from left to right. Thus alkali metals are strong reducing agents while halogens are oxidising agents among halogens, fluorine is the most powerful oxidising agent; the oxidising property decreases from F to I and actually iodine shows reducing properties.

## PERIODIC CLASSIFICATION OF ELEMENTS

(iii) Inert gases are neither oxidising nor reducing agents. (iv) Generally, metals are reducing agents and non-metals are oxidising agents.

**(6) Paramagnetism, Diamagnetism, and Ferromagnetism :** Magnetic properties of matter depend on the properties of the individual atoms. A substance (atom, ion or compound) capable of being attracted into a magnetic field is known as paramagnetic. The paramagnetic substances have a net magnetic moment which in turn is due to the presence of unpaired electron(s) in atoms, ions or molecules. Since most of the transition metal ions have unpaired  $d$ -electrons, they show paramagnetic behaviour. The exceptions are  $Sc^{3+}$ ,  $Ti^{4+}$ ,  $Zn^{2+}$ ,  $Cu^{+}$ , etc. which do not contain any unpaired electron and hence are diamagnetic.

On the other hand, **a substance which is repelled by a magnetic field is known as diamagnetic.** Such substances do not have any net magnetic moment because they do not have any unpaired electron. Electrons determine the magnetic properties of matter in two ways,

(i) Each electron can be treated as a small sphere of negative charge spinning on its axis. The spinning of charge produces magnetic moment.

(ii) An electron travelling in closed path around a nucleus will also produce magnetic moment just as does electric current travelling in a loop of wire.

The observed magnetic moment is therefore the sum of the two moments: the spin moment and the orbital moment. It is expressed in units called Bohr Magnetons (BM). In terms of  $n$  (number of unpaired electron), magnetic moment is given by the formula,  $\mu = \sqrt{n(n+2)}$

Thus when  $n = 1$   $\mu = \sqrt{1 \times 3} = 1.73 \text{ BM}$

$$n = 2 \quad \mu = \sqrt{2 \times 4} = 2.83 \text{ BM}$$

$$n = 3 \quad \mu = 3.87 \text{ BM}$$

$$n = 4 \quad \mu = 4.90 \text{ BM}$$

$$n = 5 \quad \mu = 5.92 \text{ BM}$$

Thus greater the number of unpaired electrons in a substance, the greater is the magnetic moment of the substance. The value of magnetic moment has been used to calculate the number of unpaired electrons in an ion. In some cases, even the structure of the molecule or complex is indicated by its magnetic moment.

**Paramagnetism** is generally measured by a simple device known as Guoy's balance which involves weighing the species in presence of a magnetic field. Diamagnetic substances show a decrease in weight whereas paramagnetic substances show increase in weight. The larger the number of unpaired electrons in a substance, the greater is the increase in its weight in a magnetic field.

**Ferromagnetism** is a special property observed in some substances in the solid state (not in solution). Such substances are strongly attracted to magnetic field and may retain the magnetic properties for some time even after the removal of the field. The most common example is of Fe followed by Co and Ni.

### (7) Hydration and hydration energy

(i) Hydration energy is the enthalpy change that accompanies the dissolving of 1 mol of gaseous ions in water.

(ii) Size of ions and its charge determines extent of hydration. Greater the charge smaller the size of the ion, greater the attraction for the lone pair of O of  $H_2O$ , hence greater the extent of hydration energy.

## PERIODIC CLASSIFICATION OF ELEMENTS

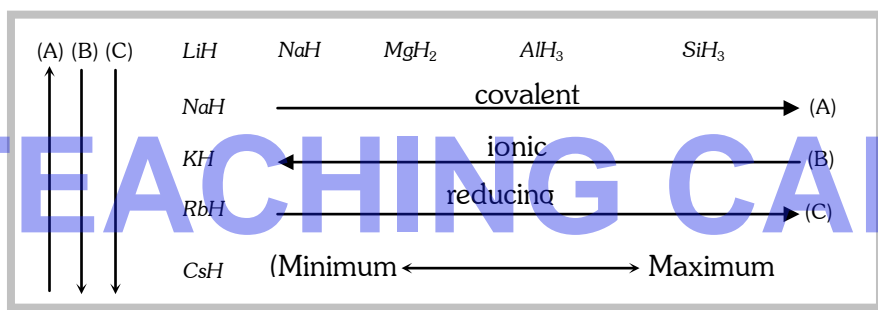
- (a) Size of the hydration ion increases.
- (b) Ionic mobility decreases i.e. heavier (hydrated) ions moves slower.

### (8) Acid-base-character of oxides

- (i) On moving across a period, the basic character of the oxides gradually changes first into amphoteric and finally into acidic character.
- (ii) On moving down a group, reverse behaviour is observed i.e., from more acidic to more basic.
- (iii) Stability of oxides decreases across a period.

### (9) Hydrides

- (i) Hydrogen combines with a number of other elements including metals and non-metals to form compounds called hydrides (with  $H^-$ ).
- (ii) Covalent nature of hydrides increases across a period and decreases down the group.
- (iii) Ionic hydride are better reducing agents than covalent hydride and reducing nature of hydride decreases across a period and increases down the group.
- (iv) Covalent and ionic hydrides are classified as follows,



### Diagonal Relationship.

Certain elements of 2<sup>nd</sup> period show similarity with their diagonal elements in the 3<sup>rd</sup> period as shown below :

	Group 1	Group 2	Group 13	Group 14
2 <sup>nd</sup> period	<i>Li</i>	<i>Be</i>	<i>B</i>	<i>C</i>
3 <sup>rd</sup> period	<i>Na</i>	<i>Mg</i>	<i>Al</i>	<i>Si</i>

Thus, *Li* resembles *Mg*, *Be* resembles *Al* and *B* resembles *Si*. This is called diagonal relationship and is due to the reason that these pairs of element have almost identical ionic radii and polarizing power (i.e. charge/size ratio). Element of second period are known as bridge elements.

**Anomalous behaviour of the first elements of a group :** The first element of a group differs considerably from its congeners (i.e. the rest of the element of its group). This is due to (i) small size (ii) high electronegativity and (iii) non availability of d-orbitals for bonding. Anomalous behaviour is observed among the second row elements (i.e. *Li* to *F*).