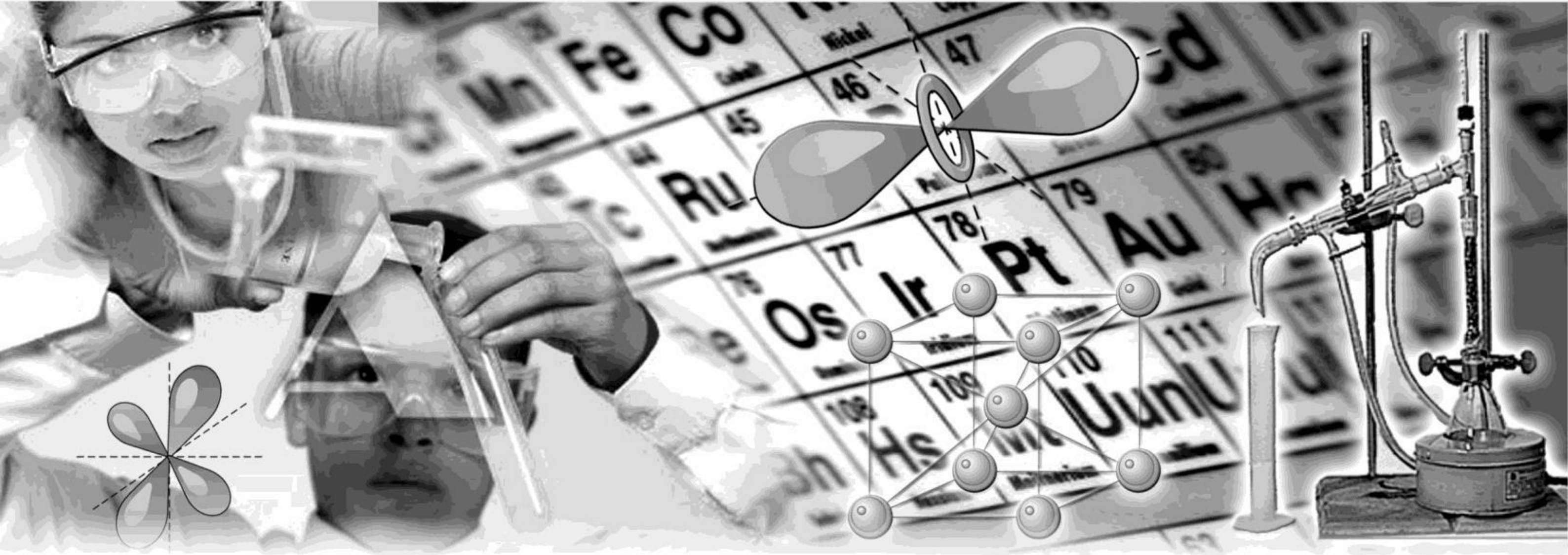


Chapter

15

Chemical Periodicity

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** (1862)**:** It was proposed by Chancourtois.

(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 node of an octave of music.

(4) **Mendeleef's period law** (1869) : The first significant classification was given by Mendeleeff 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, 9th 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.

(5) **Modern Periodic Law :** 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 was given by **Moseley, it may be stated as** : ''The properties of elements are periodic functions of their atomic number''.

When atomic number is taken as the basis for classification of elements, many anomalies of Mendeleef's table disappear, such as the,

(i) ***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.

(ii) ***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.

(iii) ***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 remain the same although the atomic number increases. Since they possess the 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.

(iv) ***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.

(v) ***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.

(vi) ***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.

(vii) ***Transuranic elements*** : These elements form a series known as **actinide series**, it begins from actinium and ends at lawrencium (89–103). 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.

Classification of element on the basis of electronic configuration

According to Bohr the element have been grouped into four types

(1) **Inert gases :** These atom have been full fill outer most s and p subshell and having the configuration ns^2np^6 (Exception helium having $1s^2$) due to stable configuration these element do not show chemical activity under normal condition and thus termed as inert gases. Under special conditions, the higher members do form some compounds with other elements and hence, the name has been changed to **Noble gases**. Six element He, Ne, Ar, Kr, Xe and Rn belongs to this group.

(2) **Representative or normal elements :** Element in which atom have all shells complete except outermost shell which is incomplete. The number of electrons in the outermost shell varies from 1 to 7 *i.e.* the configuration of the outermost shell varies from ns^1 to ns^2np^5. These consist of some metals, all non metals and metalloid. These are the elements which are found in nature in abundance and active in nature. On account of this, these elements are called representative elements. All the three types of valencies are observed in the case of these elements. These elements have one of the following configuration in their outermost shell.

$$\underset{1}{ns^1}\quad \underset{2}{ns^2}\quad \underset{2}{ns^2np^1}\quad \underset{4}{ns^2np^2}\quad \underset{5}{ns^2np^3}\quad \underset{6}{ns^2np^4}\quad \underset{7}{ns^2np^5}$$

The number of electrons present in the outermost shell signify the group to which these element belong.

(3) **Transition elements :** In the atoms of these elements the outermost shell and the penultimate shell (Next to the outermost) are incomplete. These elements have the general configuration $(n-1)d^{1-9}\ ns^{0 \text{ or } 1 \text{ or } 2}$ either in the ground state or in excited state. These elements are present in IV^{th}, V^{th}, VI^{th} and VII^{th} period of periodic table and called transition elements. There are four transition series every series consists 9 elements each.

(4) **Inner transition elements :** Atoms of these elements have three outermost shell incomplete. The general configuration is $(n-2)f^{1-14}(n-1)d^{0 \text{ or } 1}ns^2$. There are two series of elements.

(i) Lanthanides or rare earths from $Ce(58)$ to $Lu(71)$.

(ii) Actinides from $Th(90)$ to $Lr(103)$

Each series consists of 14 elements *i.e.* in the lanthanides, $4f$ is gradually filled up while in actinides, $5f$ is gradually filled up.

The properties of these elements are similar to transition elements. The members of actinide series are radioactive and majority of them are not found in nature. The elements from atomic number of 93 onwards are called transuranic elements and have been discovered artificial means.

In this classification the element, Zn, Cd and Hg have not been included in any of the four groups of elements. The elements Lu and Lr of the inner transition group have $(n-2)f$ shell complete consisting 14 electron hence their inclusion in this group is not justified.

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**.

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 examplified beneath,

(1) Elements of group 1 are called **Alkali-Metals**.

(2) Elements of group 2 are called **Alkaline Earths**.

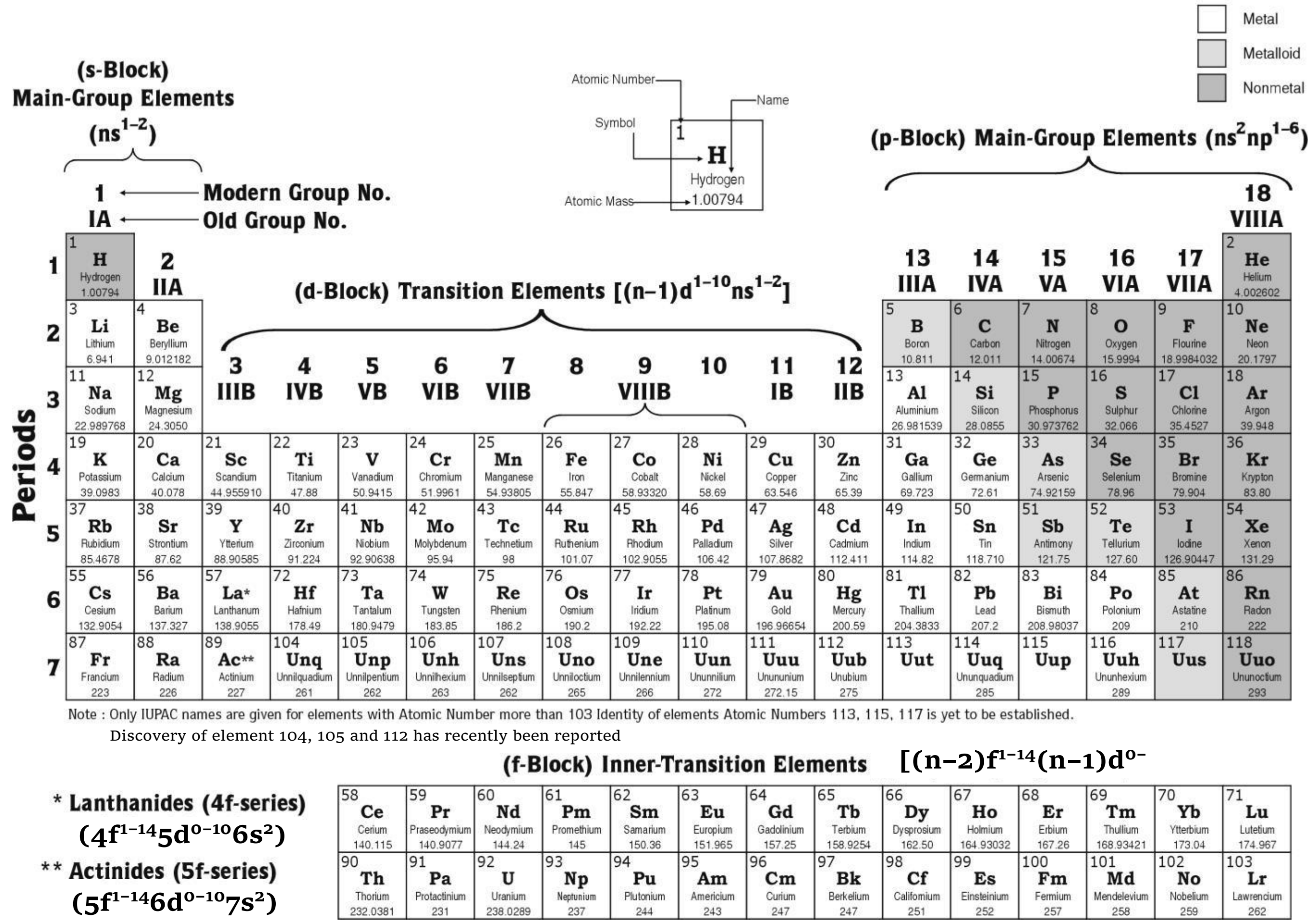
(3) Elements of group 3 are called **Pnicogens**.

(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**.

Periodic Table



Periods	1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8	9 VIIIB	10	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
1	1 **H** Hydrogen 1.00794																	2 **He** Helium 4.002602
2	3 **Li** Lithium 6.941	4 **Be** Beryllium 9.012182											5 **B** Boron 10.811	6 **C** Carbon 12.011	7 **N** Nitrogen 14.00674	8 **O** Oxygen 15.9994	9 **F** Flourine 18.9984032	10 **Ne** Neon 20.1797
3	11 **Na** Sodium 22.989768	12 **Mg** Magnesium 24.3050											13 **Al** Aluminium 26.981539	14 **Si** Silicon 28.0855	15 **P** Phosphorus 30.973762	16 **S** Sulphur 32.066	17 **Cl** Chlorine 35.4527	18 **Ar** Argon 39.948
4	19 **K** Potassium 39.0983	20 **Ca** Calcium 40.078	21 **Sc** Scandium 44.955910	22 **Ti** Titanium 47.88	23 **V** Vanadium 50.9415	24 **Cr** Chromium 51.9961	25 **Mn** Manganese 54.93805	26 **Fe** Iron 55.847	27 **Co** Cobalt 58.93320	28 **Ni** Nickel 58.69	29 **Cu** Copper 63.546	30 **Zn** Zinc 65.39	31 **Ga** Gallium 69.723	32 **Ge** Germanium 72.61	33 **As** Arsenic 74.92159	34 **Se** Selenium 78.96	35 **Br** Bromine 79.904	36 **Kr** Krypton 83.80
5	37 **Rb** Rubidium 85.4678	38 **Sr** Strontium 87.62	39 **Y** Ytterium 88.90585	40 **Zr** Zirconium 91.224	41 **Nb** Niobium 92.90638	42 **Mo** Molybdenum 95.94	43 **Tc** Technetium 98	44 **Ru** Ruthenium 101.07	45 **Rh** Rhodium 102.9055	46 **Pd** Palladium 106.42	47 **Ag** Silver 107.8682	48 **Cd** Cadmium 112.411	49 **In** Indium 114.82	50 **Sn** Tin 118.710	51 **Sb** Antimony 121.75	52 **Te** Tellurium 127.60	53 **I** Iodine 126.90447	54 **Xe** Xenon 131.29
6	55 **Cs** Cesium 132.9054	56 **Ba** Barium 137.327	57 **La*** Lanthanum 138.9055	72 **Hf** Hafnium 178.49	73 **Ta** Tantalum 180.9479	74 **W** Tungsten 183.85	75 **Re** Rhenium 186.2	76 **Os** Osmium 190.2	77 **Ir** Iridium 192.22	78 **Pt** Platinum 195.08	79 **Au** Gold 196.96654	80 **Hg** Mercury 200.59	81 **Tl** Thallium 204.3833	82 **Pb** Lead 207.2	83 **Bi** Bismuth 208.98037	84 **Po** Polonium 209	85 **At** Astatine 210	86 **Rn** Radon 222
7	87 **Fr** Francium 223	88 **Ra** Radium 226	89 **Ac**** Actinium 227	104 **Unq** Unnilquadium 261	105 **Unp** Unnilpentium 262	106 **Unh** Unnilhexium 263	107 **Uns** Unnilseptium 262	108 **Uno** Unniloctium 265	109 **Une** Unnilennium 266	110 **Uun** Ununnilium 272	111 **Uuu** Unununium 272.15	112 **Uub** Unubium 275	113 **Uut**	114 **Uuq** Ununquadium 285	115 **Uup**	116 **Uuh** Ununhexium 289	117 **Uus**	118 **Uuo** Ununoctium 293

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.

Discovery of element 104, 105 and 112 has recently been reported

(f-Block) Inner-Transition Elements [$(n-2)f^{1-14}(n-1)d^{0-}$

* Lanthanides (4f-series) ($4f^{1-14}5d^{0-10}6s^2$)	58 **Ce** Cerium 140.115	59 **Pr** Praseodymium 140.9077	60 **Nd** Neodymium 144.24	61 **Pm** Promethium 145	62 **Sm** Samarium 150.36	63 **Eu** Europium 151.965	64 **Gd** Gadolinium 157.25	65 **Tb** Terbium 158.9254	66 **Dy** Dysprosium 162.50	67 **Ho** Holmium 164.93032	68 **Er** Erbium 167.26	69 **Tm** Thullium 168.93421	70 **Yb** Ytterbium 173.04	71 **Lu** Lutetium 174.967
** Actinides (5f-series) ($5f^{1-14}6d^{0-10}7s^2$)	90 **Th** Thorium 232.0381	91 **Pa** Protactinium 231	92 **U** Uranium 238.0289	93 **Np** Neptunium 237	94 **Pu** Plutonium 244	95 **Am** Americium 243	96 **Cm** Curium 247	97 **Bk** Berkelium 247	98 **Cf** Californium 251	99 **Es** Einsteinium 252	100 **Fm** Fermium 257	101 **Md** Mendelevium 258	102 **No** Nobelium 259	103 **Lr** Lawrencium 262

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) Ist 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.

(5) 7th period starting with $_{87}Fr$ 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.

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 to 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, electro-negativity, 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 'σ' 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,

$Z^* = (Z - \sigma)$ where σ is screening constant.

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.

Covalent, Ionic and Vander waal's 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 bonding is ionic, the radius is called *ionic radius.*

(3) If the two atoms are not bonded by a chemical bond (as in noble gases) the radius is called *vander Waal's 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.,*

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

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 χ_A and χ_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*.

$_3Li$	$_4Be$	$_5B$	$_6C$	$_7N$	$_8O$	$_9F$	$_{10}Ne$
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 vander 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.* $r_{Cs} > r_{Rb} > r_K > r_{Na} > r_{Li}$

The increase in size on descending a group is due to addition of extra shell 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 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, $\underset{1.26}{r_{Fe}} > \underset{0.76}{r_{Fe^{2+}}} > \underset{0.64}{r_{Fe^{3+}}}$.

This is due to following two factors

(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,

$$\underset{(2,\,8,\,1)}{\text{Sodium atom } (Na)} \rightarrow \underset{(2,\,8)}{\text{Sodium ion } (Na^+)}$$

(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 is always larger than the corresponding atom. For example, Atomic radius of *I* = 1.23 ; Ionic radii of I^- = 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. Which is as follows

$$\underrightarrow{C^{-4} > N^{-3} > O^{-2} > F^{-1} > Ne > Na^{+} > Mg^{+2} > Al^{+3} > Si^{+4} > P^{+5} > S^{+6} > Cl^{+7}}$$

Size of ions (in decreasing order)

(3) **Vander 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 vander 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 vander 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 vander Waal's forces are the only attractive forces in these cases. In other words, *the vander Waal's radii constitute the* *atomic radii of noble gases* and since vander 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.

$$A \rightarrow A^{+} + e^{-1} \quad \text{(First } I.E.\text{)}$$

$$A^{+} \rightarrow A^{+2} + e^{-1} \quad \text{(Second } I.E.\text{)}$$

$$A^{+2} \rightarrow A^{+3} + e^{-1} \quad \text{(Third } I.E.\text{)}$$

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*

(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.

$$K^{19} = 1s^2, 2s^2p^6, 3s^2p^6, 4s^1$$

$$Cu^{29} = 1s^2, 2s^2p^6, 3s^2p^6d^{10}, 4s^1$$

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_1 and IE_2 of the 2nd period elements

  $IE_1 : Li < B < Be < C < O < N < F < Ne$

  $IE_2 : Be < C < B < N < F < O < Ne < Li$

- IE_1 and IE_2 of the 3rd period elements

  $IE_1 : Na < Al < Mg < Si < S < P < Cl < Ar$

  $IE_2 : Mg < Si < Al < P < S < Cl < Ar < Na$

- IE_1 of elements with very high values

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

(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.

(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*".

When first electron is added in a neutral atom then some energy is released that is called first electron affinity but in case of second electron affinity energy will be absorbed due to electronic repulsion. Example as

(a) $O_{(g)} + e^- \rightarrow O^-_{(g)} + E_1 (\Delta H = -ve, \text{Exoenergic})$

(b) $O^-_{(g)} + e^- \rightarrow O^{-2} + E_2 \ (\Delta H = +ve, \text{Endoenergic})$

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.

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.

(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.

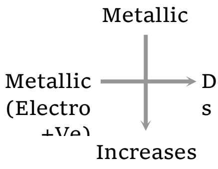
(2) **Importance of electron affinity :** Certain properties of the elements are predicted on the basis of values of electron affinity.

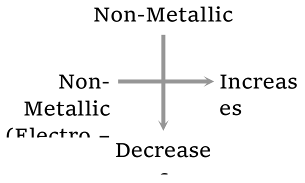
(i) The elements having high value high values of electron affinity are capable of accepting electron easily. They form anions and electrovalent compounds. These elements are electronegative in nature.

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

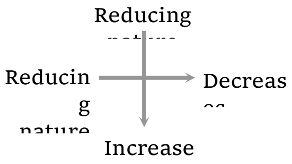
On the basis of the general trend of ionisation potential and electron affinity, the following properties can be predicted,

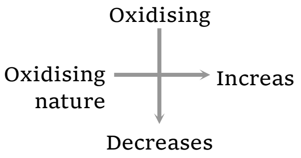
(a) Metallic nature decreases in a period while nonmetallic nature increases. Metallic nature increases in a group while non-metallic nature decreases. The arrow (↓) represents a group and (→) represents a period.



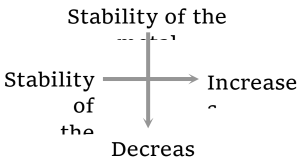


(b) Reducing nature decreases in a period while oxidising nature increases. The reducing nature increases in a group while oxidising nature decreases.



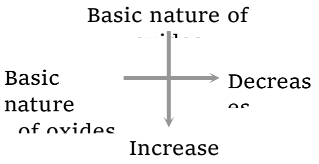


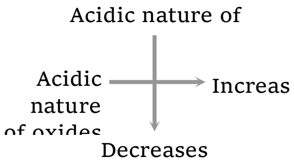
(c) Stability of metal increases while activity of the metal decreases in a period and in a group stability decreases while activity increases.



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

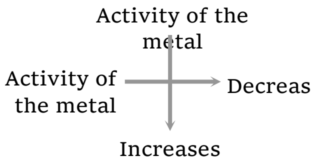
(d) The basic nature of the oxides decreases in a period while acidic nature increases. In a group, basic nature increases while acidic nature decrases.





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.

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

(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 χ_A and χ_B are electronegativities of the atoms A and B respectively, the factor 0.208 arises from the conversion of kcal to electron volt (1 eV = 23.0 kcal/mole),

while $\Delta E =$ Actual bond energy $-\sqrt{(E_{A-A} \times E_{B-B})}$

Pauling and Mulliken values of electronegativities are related as below χ (Pauling) = 0.34χ (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 eelctronegativity 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,

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. Allerd (1961).

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

	$H-F$	$H-Cl$	$H-Br$	$H-I$
$(X_A - X_B)$	1.9	0.9	0.7	0.4

$$\xrightarrow{\hspace{8cm}}$$

Stability decreases

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,

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

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 decreases.

Tungsten has the maximum melting point (3410°C) amongst metals and carbon has the maximum melting point (3727°C) amongst non-metals. Helium has the minimum melting point (–270°C). The metals, Cs, Ga and Hg are known in liquid state at 30°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.*

Note : For detail see chapter redox reaction.

(5) **Magnetic properties :** 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,

- Each electron can be treated as a small sphere of negative charge spinning on its axis. The spinning of charge produces magnetic moment.
- 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, $\mu = \sqrt{n(n+2)}$

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.

Ferromagnetism is a special property observed in some substances in the solid state. 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*.

(6) **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.

(a) Size of the hydration ion increases.

(b) Ionic mobility decreases *i.e.* heavier (hydrated) ions moves slower.

(7) **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.

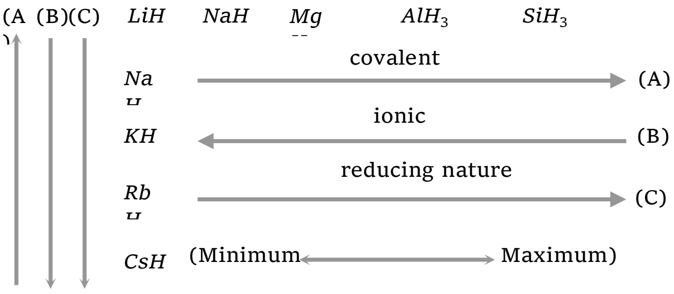
(iii) Stability of oxides decreases across a period.

(8) **Hydrides**

(i) Hydrogen combines with a number of other elements including metals and non-metals to form compounds called hydrides.

(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 2nd period show similarity with their diagonal elements in the 3rd period as shown below :

Group 1 Group 2 Group 13 Group 14

2nd perio *Li* *Be* *B*
C

3rd period *Na* *Mg* *Al* *Si*

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*).