

CHAPTER - 03

CLASSIFICATION OF ELEMENTS AND PERIODICITY IN PROPERTIES

History and significance of periodic classification

1800 - Only 31 elements were discovered

1865 - No. of elements discovered become 63

There arises significance of classification. Because it is difficult to study chemistry of each elements individually. So elements with similar properties are grouped together.

1. DOREREINER'S LAW OF TRIADS (1829)

He grouped 3 elements in a group known as triads, where atomic weight of middle element is the arithmetic mean of other two (approximately).

Triads	Li	Na	K	Arithmetic mean
Atomic mass	7	23	39	$\frac{7 + 39}{2} = 23$
Triads	Cl	Br	I	Arithmetic mean
Atomic mass	35.5	80	127	$\frac{35.5 + 127}{2} = 81.25$
Triads	Ca	Sr	Ba	Arithmetic mean
Atomic mass	40	87.5	137	$\frac{40 + 137}{2} = 88.5$

Demerits : It is valid only for a few elements.

2. TELLURIC HELIX MODEL (1862 BY A.E.B. CHANCOURTOIS)

- Telluric helix model was proposed by Chancourtois (French geologist)
- He took a vertical cylinder and drew sixteen equidistant lines on its surface perpendicular to the axis of cylinder. Then arranged elements in helix at an 45° angle in the increasing order of atomic mass. He observed that elements whose atomic weights differ from each other by 16 shows similar properties.

Demerits : It is a complex model. So didn't get well attention.

3. NEWLANDS LAW OF OCTAVES (1865)

When the elements were arranged in the increasing order of atomic weight, the properties of every eighth element were similar to those of first one like the eighth note of a musical scale.

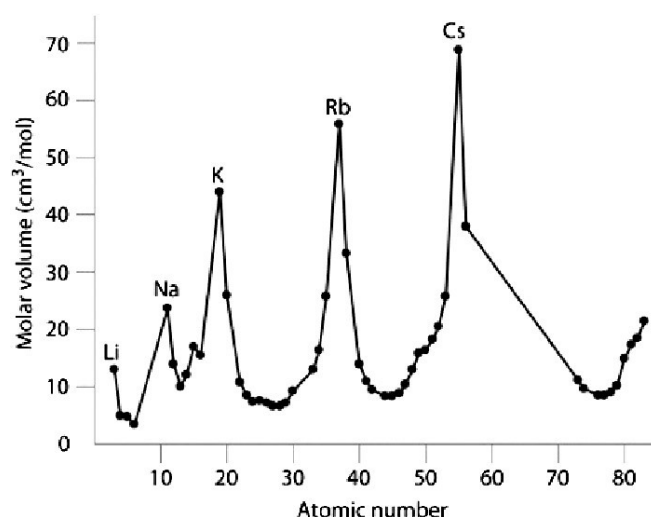
Li	Be	B	C	N	O	F
Na	Mg	Al	Si	P	S	Cl
K	Ca					

Newlands was awarded Davy medal for his contribution

Demerits :

1. It is only applicable to lighter elements upto calcium
2. With the discovery of Noble gases, the properties of eighth element were no longer similar to those of first one.

4. LOTHAR MEYER ARRANGEMENT (1869)



He plotted a graph between the atomic volume and atomic weight of the elements and observed that the element with the similar properties occupied similar positions on the curve.

- Strongly electropositive metal [Li, Na, K, Rb and Cs) occupies peak of the curve.
- Alkaline earth metals occupy [Be, Mg, Ca, Sr, Ba] occupy descending position of the curve.
- Halogens [F, Cl, Br, I] occupy the ascending position of the curve.

On the basis of observations, he proposed that physical properties are the function of atomic weights.

Mendeleev's Periodic Table and Periodic Law (1869)

He took 63 cards and wrote down all the physical and chemical properties of 63 elements [Only 63 elements were discovered at that time). The elements with similar properties were arranged in same vertical column and he observed that elements got arranged in the increasing order of atomic weights.

Mendeleev's Periodic Law

Physical and chemical properties of elements are a periodic function of their atomic weights.

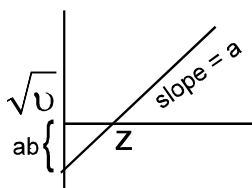
- Correction of doubtful atomic weights.

Demerits of Mendeleev's Periodic Table

- Anomalous position of hydrogen : Hydrogen shows resemblance with both alkali metals and halogens.
- He violated his own periodic law. Eg: In the case of Te and I, even though atomic weights of Te is greater than I, I is placed after Te.
- Some dissimilar elements are grouped together while some different elements are placed in different groups.
- Position of Lanthanoids and Actinoids.

Atomic Number and Modern Periodic Law (1913)

In 1913, Moseley measured the frequencies of X-rays emitted by a metal when bombarded with high speed electrons. He discovered that the square root of the frequency (ν) of the prominent X-rays by a metal is proportional to the atomic number and not to the atomic weight.



$$\text{ie, } \sqrt{\nu} = a(z - b)$$

$$\sqrt{\nu} = az - ab$$

$$Y = mX + c$$

CHARACTERISTICS OF MENDELEEV'S PERIODIC TABLE [MODIFIED]

1. Mendeleev's periodic table was modified due to the discovery of new elements.
2. Some elements are arranged in vacant spaces left by Mendeleev.
3. Noble gases were discovered in 1900, and they were accommodated in a new group called zero group.
4. Later lanthanides and actinoids were discovered and arranged in bottom of periodic table.
5. Nine vertical columns called groups and consist of seven horizontal rows known as series [Now it is periods].

Merits of Mendeleev's periodic table

1. Systematic study of the elements.
2. Prediction of new elements : -Mendeleev leave some gaps in periodic table and suggested that some elements will be discovered in future. For eg: He predicted the properties of Gallium [Eka Aluminium] and Germanium [Eka silicon] which were unknown at that time. Later these elements were discovered and their properties were found to be similar to those predicted by Mendeleev.

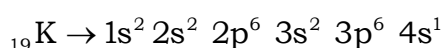
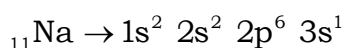
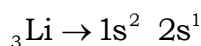
MODERN PERIODIC LAW

It states that physical and chemical properties of the elements are a periodic functions of their atomic numbers.

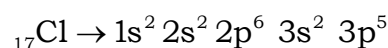
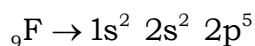
CAUSE OF PERIODICITY

The cause of periodicity in properties is the repetition of similar outer electronic configuration after certain regular intervals.

For Example



General electronic configuration = ns^1
where $n = 2 - 7$



General electronic configuration = $ns^2 np^5$

The repetition of electronic configuration of alkali metals and halogens only after certain intervals. These regular intervals are 2, 8, 18, 18, 32, 32 are known as magic numbers.

PRESENT FORM/LONG FORM/BOHR'S TABLE

- Vertical columns are known as Groups
- Horizontal rows are known as Periods
- 18 Groups and 7 Periods

In First period	→	2 elements
In Second period	→	8 elements
In Third period	→	8 elements
In Fourth period	→	18 elements
In Fifth period	→	18 elements
In Sixth period	→	32 elements
In Seventh period	→	32 elements

14 elements of 6th period are called Lanthanoid and 14 elements of 7th period are called actinoids are placed in separate panels at the bottom.

IUPAC NOMENCLATURE OF ELEMENTS WITH ATOMIC NUMBERS > 100

Both American and Soviet Scientists claimed credit for discovering element 104. American's named it as Rutherfordium whereas Soviets named it as Kurchatovium (Ku) which leads to controversy. In order to avoid these difficulties, IUPAC suggests a rational system for nomenclature of elements with atomic number greater than 100.

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

Z	Recommended Name	Symbol	Official name	Symbol
101	Unnilunium	Unu	Mendelevium	Md
102	Unnilbium	Unb	Nobelium	No
103	Unniltrium	Unt	Lawrencium	Lr
104	Unnilquadium	Unq	Rutherfordium	Rf
105	Unnilpentium	Unp	Dubnium	Db
106	Unnilhexium	Unh	Seaborgium	Sg
107	Unnilseptium	Uns	Bohrium	Bh
108	Unniloctium	Uno	Hassium	Hs
109	Unnilennium	Une	Mtnerium	Mt
110	Ununnilium	Uun	Darmstadtium	Ds
111	Unununium	Uuu	Roentgenium	Rg
112	Ununbium	uub	Copernicium	Cn
113	Ununtrium	uut	Nihonium	Nh
114	Ununquadium	uuq	Flerovium	Fl
115	Ununpentium	uup	Moscovium	Mc
116	Ununhexium	uuh	Livermorium	Lv
117	Ununseptium	uus	Tennessine	Ts
118	Ununoctium	uuo	Oganesson	Og

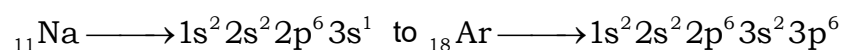
ELECTRONIC CONFIGURATION OF ELEMENTS IN PERIODS

First period [K shell] : It has only one orbital. So it can accommodate 2 electrons. These are hydrogen ($1s^1$) and Helium ($1s^2$)

Second period [L shell] : This shell has 4 orbitals, which can accommodate 8 electrons. \therefore 2nd period contains 8 elements.

It starts with ${}_3\text{Li}[1s^2 2s^1]$ and ends with ${}_{10}\text{Ne} \rightarrow 1s^2 2s^2 2p^6$

Third period [M shell] : This shell has 9 orbitals [one 3s, three 3p, and five 3d orbitals. But 3d-orbitals have higher energy than 4s orbital. So 3d orbitals fill only after the filling of 4s-orbital. So third period contains 8 elements. [One 3s, three sp] and contains 8 elements. It starts from



Fourth period [N-shell] : $\therefore n = 4$; starts with ${}_{19}\text{K} \rightarrow [\text{Ar}]4s^1$

- After filling 4s, the filling of five 3d orbital begins.
- These arises first transition series [3d-transition series]. $[{}_{21}\text{Sc} - {}_{30}\text{Zn}]$
- After filling 3d, then 4s.
- \therefore No. of orbitals = $1 + 5 + 3 = 9$
- So it can accomodate 18 electrons.
- Then 4th period contain 18 elements. $[{}_{19}\text{K} - {}_{36}\text{Kr}]$

Fifth period $[\therefore n = 5]$

- It also contain 9 orbitals. [One 5s, five 4d and three 5p]
- So 18 elements $[{}_{37}\text{Rb} - {}_{54}\text{Xe}]$
- Second transition series $[{}_{39}\text{Y} - {}_{48}\text{Cd}]$

Sixth period : There are 16 orbitals present. (One 6s, Seven 4f, Five 5d, and three 6p)

- \therefore 6th period contains 32 elements. $[{}_{55}\text{Cs} - {}_{86}\text{Rn}]$
- 14 elements after ${}_{57}\text{La}$, ie ${}_{58}\text{Ce} - {}_{71}\text{Lu}$ are placed in bottom of periodic table. Known as Lanthanoids or first inner transition series.
- After ${}_{71}\text{Lu}$ $[{}_{72}\text{Hf} - {}_{80}\text{Hg}]$, electron enters to 5d orbitals. Hence it is 5d transition series.

Seventh period : [n = 7]

- 16 orbitals present [one 7s, seven 5f, five 6d, 8 three 7p]
- So it also contain 32 elements. $[{}_{87}\text{Fr} - {}_{118}\text{Og}]$.
- 14 elements after ${}_{89}\text{Ac}$ ie ${}_{90}\text{Th} - {}_{103}\text{Lr}$ are placed in bottom of periodic table. known as
- Actinoids or second inner transition series.
- After ${}_{103}\text{Lr}$, electron enters to 6d orbitals. Hence it is 6d transition series.

Periodic Properties

Trends in Physical Properties

There are numerous physical properties of elements such as melting and boiling points, heats of fusion and vaporization, energy of atomization, etc. Which show periodic variations. However, we shall discuss the periodic trends with respect to atomic and ionic radii, ionization enthalpy, electron gain enthalpy and electronegativity.

The properties which are directly or indirectly related to their electronic configuration and show gradual change when we move from left to right in a period or from top to bottom in a group are called periodic properties.

Atomic Radius

One practical approach to estimate the size of an atom of a non-metallic element is to measure the distance between two atoms when they are bound together by a single bond in a covalent molecule and from this value, the "Covalent Radius" of the element can be calculated. For example, the bond distance in the chlorine molecule (Cl_2) is 198 pm and half this distance (99 pm), is taken as the atomic radius of chlorine. For metals, we define the term "Metallic Radius" which is taken as half the internuclear distance separating the metal cores in the metallic crystal. For example, the distance between two adjacent copper atoms in solid copper is 256 pm; hence the metallic radius of copper is assigned a value of 128 pm. we use the term Atomic Radius to refer to both covalent or metallic radius depending on whether the element is a non-metal or a metal. Atomic radii can be measured by X-ray or other spectroscopic methods

Covalent radius

It is the distance from the centre of the nucleus to the outermost shell of electrons. Covalent radius for an atom A in a molecule A_2

$$r_A = r_A + r_A / 2 = d_{A-A} / 2$$

For heteroatomic molecule AB, (Stevenson-Shoemakers formula)

$$d_{A-B} = r_A + r_B - 0.09(\chi_A - \chi_B)$$

where, χ_A and χ_B are electronegativities of A and B.

In general, the atomic size decreases on moving from left to right in a period due to increase in effective nuclear charge and increases on moving from top to bottom in a group due to addition of new shells.

van der Waals' Radius

It is defined as one-half of the distance between the nuclei of two non – bonded isolated atoms or two adjacent atoms belonging to two neighbouring molecules of an element in the solid state.

Metallic Radius

It is define as one-half of the distance between the centres of nuclei of the two adjacent atoms in the metallic crystal.

The decreasing order of atomic radii is : $\text{Li}(152) > \text{Be}(111) > \text{B}(88) > \text{C}(77) > \text{N}(74) > \text{O}(66) > \text{F}(64)$

Ionic Radius

An atom can be changed to a cation by removal of electrons and to an anion by gain of electrons. A cation is always smaller than the parent atom because during its formation effective nuclear charge increases and sometimes a shell may also decrease. On the other hand, the size of an atom is always larger than the parent atom because during its formation effective nuclear charge decreases.

In case of isoelectronic ions, higher the nuclear charge. Smaller is the size.

$$\text{eg., } \text{Al}^{3+} < \text{Mg}^{2+} < \text{Na}^{+} < \text{F}^{-} < \text{O}^{2-} < \text{N}^{3-}$$

(As the Z/e value increases ionic radii decreases for isoelectronic species). Where Z-atomic number e-charge.

The order of radii is covalent radius < metallic radius < van der Waals' radius

ATOMIC RADII OF CERTAIN ELEMENTS

Atomic Radii/pm Across the Periods

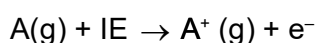
Atom (Period II)	Li	Be	B	C	N	O	F
Atomic radius	152	111	88	77	74	66	64
Atom (Period III)	Na	Mg	Al	Si	P	S	Cl
Atomic radius	186	160	143	117	110	104	99

Atomic Radii/pm Down a Family

Atom (Group I)	Atomic Radius	Atom (Group 17)	Atomic Radius
Li	152	F	64
Na	186	Cl	99
K	231	Br	114
Rb	244	I	133
Cs	262	At	140

Ionisation Enthalpy (IE)

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



Various factors with which IE varies are :

- Atomic size: varies inversely
- Screening effect: when shielding increases, I.E. decreases
- Nuclear charge: varies directly

Generally left to right in periods ionisation enthalpy increases; down the group, it decreases.

IE values of inert gases are exceptionally higher due to stable configuration.

Successive ionisation enthalpies

$$IE_3 > IE_2 > IE_1$$

IE₁ of N is greater than that of oxygen due to stable half – filled 2p-orbitals.

Among transition elements of 3d-series, ²⁴Cr and ²⁹Cu have higher IE₂ due to half-filled and fully-filled stable d-orbitals

1. Ionisation enthalpy of beryllium is greater than Boron

It is known that full filled orbital's are most stable and after than half filled atomic orbital's are most stable. In the above case,

(i) Be has most stable full filled configuration

Be = $1s^2, 2s^2$. While in B one unpaired electron is present. B = $1s^2, 2s^2, 2p^1$

So, in order to remove electron from Be we have to supply very high amount of energy because it has full filled electronic configuration but in B one unpaired electron is present so it is easy to remove electron from B.

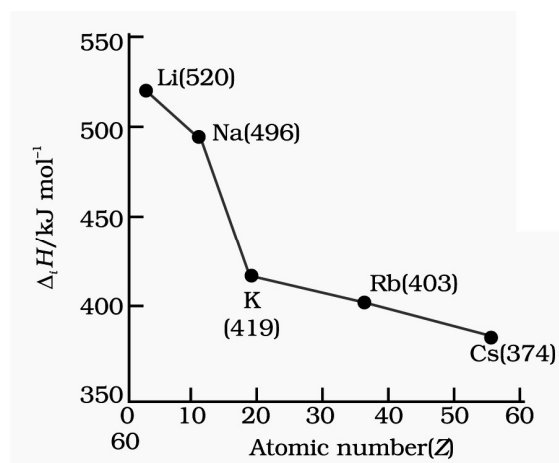
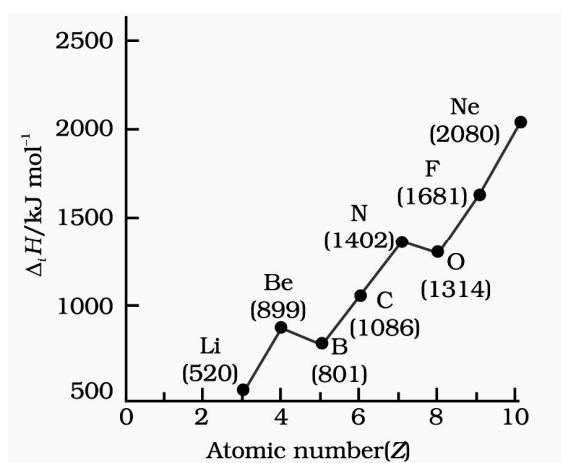
That's why ionisation enthalpy of Be is more than B

(ii) Similarly, in the case of Nitrogen and Oxygen nitrogen has half filled electronic configuration

N = $1s^2, 2s^2, 2p^3$ while in oxygen one more electron is present than nitrogen O = $1s^2, 2s^2, 2p^4$.

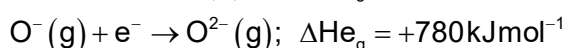
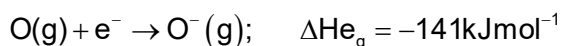
So it is easy to remove electron from oxygen but in nitrogen we have to supply a high amount of energy in order to remove the electron. That is why ionisation enthalpy of N is more than O.

IONISATION ENTHALPY VALUES



Electron Gain Enthalpy (EGE or ΔH_{eg})

It is the amount of energy released when an electron is added in an isolated gaseous atom. First electron gain enthalpy is negative while the other successive electron gain enthalpy will be positive due to repulsion between the electrons already present in the anion and the electron being added.



Various factors with which electron gain enthalpy varies are

(i) Atomic size: Atomic size increases, value of ΔH_{eg}^H decreases

(ii) Nuclear charge: varies directly

Along a period, electron gain enthalpy becomes more and more negative while on moving down the group, it becomes less negative.

➤ Noble gases have positive electron gain enthalpies.

➤ Halogen have maximum value of ΔH_{eg} with in a period due to smallest atomic size.

- F and O atom have small size and high charge density, therefore have lower electron gain enthalpy, than Cl and S respectively: $\text{Cl} > \text{F}$; $\text{S} > \text{O}$.
- Elements having half-filled and fully-filled orbitals exhibit more stability. Therefore, electron gain enthalpy will be low for such elements.
- Electron gain enthalpy can be measured by Born-Haber cycle and elements with high ΔH_{eg} are good oxidising agent.

Nitrogen has positive electron gain enthalpy ($\Delta_{\text{eg}}H = +31 \text{ KJ/mol}$)

The Main Concept Behind these Statements is the Extra Stability of half filled p orbitals.

Nitrogen has a electronic configuration of $1s^2, 2s^2, 2p^3$. As the p orbital is half filled, it has an extra stability than other elements next to it. Due to this, to add electron to nitrogen energy is required, hence it has a positive value of electron gain enthalpy.

ELECTRON GAIN ENTHALPY VALUES

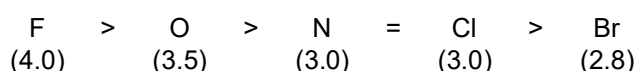
Electron Gain Enthalpies* / (kJ mol^{-1}) of Some Main Group Elements

Group 1	$\Delta_{\text{eg}}H$	Group 16	$\Delta_{\text{eg}}H$	Group 17	$\Delta_{\text{eg}}H$	Group 0	$\Delta_{\text{eg}}H$
H	- 73					He	+ 48
Li	- 60	O	- 141	F	- 328	Ne	+ 116
Na	- 53	S	- 200	Cl	- 349	Ar	+ 96
K	- 48	Se	- 195	Br	- 325	Kr	+ 96
Rb	- 47	Te	- 190	I	- 295	Xe	+ 77
Cs	- 46	Po	- 174	At	- 270	Rn	+ 68

Electronegativity (EN)

It is defined as the tendency of an atom to attract the shared electron pair towards itself in a covalent bond. Various factors with which electronegativity varies are :

- Atomic size: varies inversely
 - Charge on the ion: varies directly, e.g., $\text{Li} < \text{Li}^+$, $\text{Fe}^{2+} < \text{Fe}^{3+}$
 - Hybridisation : As the % of S character increases electronegativity increases
- Electronegativity of carbon atom = $\text{C}_2\text{H}_6 < \text{C}_2\text{H}_4 < \text{C}_2\text{H}_2$
 - In periods as we move from left to right electronegativity increases, while in the groups electronegativity decreases down the group.
 - For noble gases, its value is taken as zero.
 - Electronegativity helps to predict the polarity of bonds and dipole moment of molecules.
 - Electronegativity order of some elements (on Pauling scale) is



Electronegativity Values (on Pauling scale) Across the Periods

Atom (Period II)	Li	Be	B	C	N	O	F
Electronegativity	1.0	1.5	2.0	2.5	3.0	3.5	4.0
Atom (Period III)	Na	Mg	Al	Si	P	S	Cl
Electronegativity	0.9	1.2	1.5	1.8	2.1	2.5	3.0

Electronegativity Values (on Pauling scale) Down a Family

Atom (Group I)	Electronegativity Value	Atom (Group 17)	Electronegativity Value
Li	1.0	F	4.0
Na	0.9	Cl	3.0
K	0.8	Br	2.8
Rb	0.8	I	2.5
Cs	0.7	At	2.2

Valency

- It is defined as the combining capacity of the element. The valency of an element is related to the electronic configuration of its atom and usually determined by electrons present in the valence shell.
- On moving along a period from left to right, valency increases from 1 to 4 and then decreases to zero (for noble gases) while on moving down a group the valency remains the same.
- Transition metals exhibit variable valency because they can use electron (from outer as well as penultimate shell).

Chemical Reactivity

- The atomic and ionic radii, as we know, generally decrease in a period from left to right. As a consequence, the ionization enthalpies generally increase and electron gain enthalpies become more negative across a period.
- In other words, the ionization enthalpy of the extreme left element in a period is the least and the electron gain enthalpy of the element on the extreme right is the highest negative (note : noble gases having completely filled shells have rather positive electron gain enthalpy values).
- This results into high chemical reactivity at the two extremes and the lowest in the centre. Thus, the maximum chemical reactivity at the extreme left (among alkali metals) is exhibited by the loss of an electron leading to the formation of a cation and at the extreme right (among halogens) shown by the gain of an electron forming an anion.
- Hence alkali metals are best reducing agents and halogens are best oxidising agents.
- On moving across the group, metallic character decreases (Non-metallic character increases).
- In general, oxides formed by elements in extremely left of the periodic table is basic (Na_2O , CaO etc) But oxides of elements in extreme right are acidic (eg: N_2O_5 , Cl_2O_7)
- Oxides of elements in the centre are amphoteric (Al_2O_3 , ZnO , As_2O_3) or neutral (CO , N_2O)
- Amphoteric oxide behave as both acid and base, whereas neutral have no acidic or basic properties.
- Among transition metals (3d series), the change in atomic radii is much smaller as compared to those of representative elements across the period. The change in atomic radii is still smaller among inner-transition metals (4f series). The ionization enthalpies are intermediate between those of s- and

p-blocks. As a consequence, they are less electropositive than group 1 and 2 metals.

- In a group, the increase in atomic and ionic radii with increase in atomic number generally results in a gradual decrease in ionization enthalpies and a regular decrease (with exception in some third period elements) in electron gain enthalpies in the case of main group elements.
- Reactivity of metal increases with decrease in IE, electronegativity and increase in atomic size as well as electropositive character.
- Reactivity of non-metals increases with increase in electronegativity as well as electron gain enthalpy and decrease in atomic radii.

Melting and Boiling Points

- On moving down the group, the melting point and boiling point for metallic elements go on decreasing due to the decreasing forces of attraction. However, for non-metals, melting point and boiling point generally increase down the group.
[Along a period from left to right, melting point and boiling point increases and reaches a maximum value in the middle of the period and then start decreasing].
- Tungsten (W) has highest m.p. (3683K) among metals, carbon (diamond) has the highest m.p., (4000 K) among non-metals.
- Li metal has minimum density while iridium (Ir) metal has maximum density.

Electropositivity or Metallic Character

- The tendency of an atom of the element to lose valence electrons and form positive ion is called electropositivity.
- Greater the electropositive character, greater is the metallic character.
- Electropositive character decreases on moving across the period and increases on moving down the group.
- Alkali metals are the most electropositive and halogens are the least electropositive element in their respective period.
- Basic nature of oxides of metallic character, i.e., it also decreases along a period and increases down the group.

Diagonal Relationship

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

	Group 1	Group 2	Group 13	Group 14
2nd period	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 elements have almost identical ionic radii and polarizing power (i.e., charge/size ratio). Elements of third period, i.e., Mg, Al and Si are known as bridge elements.

Anomalous Properties of Second Period Elements

- The first element of each of the groups 1 (lithium) and 2 (beryllium) and groups 13-17 (boron to fluorine) differs in many respects from the other members of their respective group. (They are known as head elements).
- For example, lithium unlike other alkali metal ls, and beryllium unlike other alkaline earth metals, form compounds with pronounced covalent character; the other members of these groups predominantly

form ionic compounds. In fact the behaviour of lithium and beryllium is more similar with the second element of the following group i.e., magnesium and aluminium, respectively.

- This sort of similarity is commonly referred to as diagonal relationship in the periodic properties.
- The anomalous behaviour is attributed to their
 - * small size
 - * Large charge/ radius ratio
 - * High electronegativity of the elements.
- Consequence

In addition, the first member of group has only four valence orbitals (2s and 2p) available for bonding, whereas the second member of the groups have nine valence orbitals (3s, 3p, 3d). As a consequence of this, the maximum covalency of the first member of each group is 4 (eg., boron can only form $[\text{BF}_4]^-$ whereas the other members of the groups can expand their valence shell to accommodate more than four pairs of electrons eg., aluminium forms $[\text{AlF}_6]^{3-}$).
- Furthermore, the first member of p-block elements displays greater ability to form $p\pi - p\pi$ multiple bonds to itself (e.g., $\text{C}=\text{C}$, $\text{C}\equiv\text{C}$, $\text{N}=\text{N}$, $\text{N}\equiv\text{N}$) and to other second period elements (eg: $\text{C}=\text{O}$, $\text{C}=\text{N}$, $\text{C}\equiv\text{N}$, $\text{N}=\text{O}$) compared to subsequent members of the same group.