CHAPTER-1

PERIODICITY

Basics of Periodic Table:

Periodic table represents the arrangement of all of the known elements according to their properties so that similar elements fall within the same vertical column and dissimilar elements are arranged in horizontal rows with slow gradation in properties.

"The properties of elements are periodic functions of their atomic numbers". If elements are arranged in increasing order of their atomic numbers, there is repetition of properties after 2, 8, 18 and 32 elements in 1st, 2nd , 3rd and 4th period respectively. The numbers 2, 8, 18 and 32 are also referred as magic numbers.

The periodicity is repetition of elements with similar properties after certain regular intervals when the elements are arranged in order of increasing atomic numbers.

The periodic repetition of properties is due to the recurrence of similar valence shell electronic configurations after regular intervals.

1.1 Mendeleev's Periodic Law : According to Mendeleev's periodic law

"*The physical and chemical properties of the elements are a periodic function of their atomic weight.*"
He arranged the elements in increasing order of atomic weights into groups and periods.

Drawbacks of Mendeleev's Periodic Table **:**

Anomaly was found in three pairs of elements -
(i) Tellurium (Te) and Iodine (I)
(ii) Argon (Ar) and Potassium (K)
(iii) Nickel(Ni) and Cobalt (Co)
which were not in accordance of their chemical behaviours.

1.2 Moseley's Law: Long form (modern) Periodic Table:

On the basis of X-ray diffraction, Mosely proposed that
"*The physical and chemical properties of elements are a periodic function of their atomic number or their electronic configuration*".

Characteristic features of Long form of Periodic Table **:**

(1) The modern periodic table is divided into two main categories known as -
(a) Vertical Column- groups (18)
(b) Horizontal rows - periods (7)

(2) Elements of the same group have same valence shell configurations.

(3) Elements of group IA to VII A (1,2,13,14,15,16,17) are known as ***representative elements*** (main group elements) and of group IB to VIII B (3.................12) are known as ***transition elements***.

(4) Elements of group-18 (also known as zero group) are noble gases.

(5) In periods , the number of valence shell remains the same, however the number of electrons increases from left to right.

s-block ← → | d-block ← → | p-block ← →

Period \ Group	1 IA	2 IIA		3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8 VIII	9 VIII	10 VIII	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 Zero
1	1 H 1.008																		2 He 4.0026
2	3 Li 6.94	4 Be 9.0122												5 B 10.81	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.998	10 Ne 20.180
3	11 Na 22.990	12 Mg 24.305												13 Al 26.982	14 Si 28.085	15 P 30.974	16 S 32.06	17 Cl 35.45	18 Ar 39.948
4	19 K 39.098	20 Ca 40.078		21 Sc 44.956	22 Ti 47.867	23 V 50.942	24 Cr 51.996	25 Mn 54.938	26 Fe 55.845	27 Co 58.933	28 Ni 58.693	29 Cu 63.546	30 Zn 65.38	31 Ga 69.723	32 Ge 72.63	33 As 74.922	34 Se 78.96	35 Br 79.904	36 Kr 83.798
5	37 Rb 85.468	38 Sr 87.62		39 Y 88.906	40 Zr 91.224	41 Nb 92.906	42 Mo 95.96	43 Tc [97.91]	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.90	54 Xe 131.29
6	55 Cs 132.91	56 Ba 137.33	*	71 Lu 174.97	72 Hf 178.49	73 Ta 180.95	74 W 183.84	75 Re 186.21	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po [208.98]	85 At [209.99]	86 Rn [222.02]
7	87 Fr [223.02]	88 Ra [226.03]	**	103 Lr [262.11]	104 Rf [265.12]	105 Db [268.13]	106 Sg [271.13]	107 Bh [270]	108 Hs [277.15]	109 Mt [276.15]	110 Ds [281.16]	111 Rg [280.16]	112 Cn [285.17]	113 Uut [284.18]	114 Fl [289.19]	115 Uup [288.19]	116 Lv [293]	117 Uus [294]	118 Uuo [294]
*Lanthanoids			*	57 La 138.91	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm [144.91]	62 Sm 150.36	63 Eu 151.96	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.05		
**Actinoids			**	89 Ac [227.03]	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np [237.05]	94 Pu [244.06]	95 Am [243.06]	96 Cm [247.07]	97 Bk [247.07]	98 Cf [251.08]	99 Es [252.08]	100 Fm [257.10]	101 Md [258.10]	102 No [259.10]		

1.3. Classification of elements based on electronic configuration: All the electrons in an atom into specific shells or orbitals (s, p, d, f) is known as the element's electronic configuration. The elements can be arranged in the long form of the periodic table based on the electronic configuration and classified as s, p, d and f block elements. The s-block and p-block elements are called representative elements. The d-block elements are called transition elements and f-block elements are called inner transition elements.

1. s-block elements: If the last electron enters into s-orbital, the elements are called as s-block elements.

- The general valence (outermost) shell electronic configuration is ns^{1-2} (where *n* represents the outermost shell). It contains elements of group 1 and 2. 1 are called alkali metals and 2 are called alkaline earth metals.
- They are all reactive elements
- Except Beryllium, all other compounds of this block are predominantly ionic.

2. p-block elements: If the last electron enters into the p-orbital, the elements are called p-block elements.

- Electronic configuration is $ns^2\ np^{1-6}$.
- They are placed in group number IIIA to VIII A (13 to 18).
- He (ns^2) is excluded from p-block in terms of electronic configuration and it is better to consider it as s-block element. But according to its chemical behaviour it is justified to place it in the group 0, that is group 18.
- Most of these, elements are non-metals, some are metalloids and a few other are heavy elements which exhibit metallic character.
- The non-metallic character increases as we move from left to right across a period and metallic character increases as we go down the group.

3. d-block elements (Transition elements): If the last electron enters into d-orbital, the elements are called as d-block elements (except Thorium)

- Electronic configuration is $ns^{0-2}(n-1)d^{1-10}$

  or, $ns^{1-2}(n-1)d^{1-10}$ (except for palladium)
- d-block contains three complete, row of ten elements in each. The fourth row is incomplete the three rows are called first, second and third transition element series. They involve the filling of $3d$, $4d$ and $5d$ orbitals respectively.
- The d-block contains elements of group 3 to 12 of the periodic table.

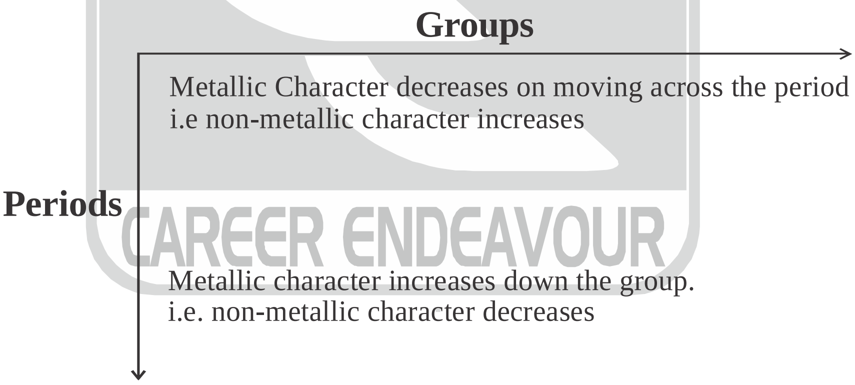
4. f-block elements: (Inner transition elements): If the last electron of the elements enters into f-orbital, they are considered as f-block elements.

- Electronic configuration is $ns^2(n-1)d^{0-1}(n-2)f^{1-14}$
- They consist of two series of elements placed at the bottom of the periodic table. The elements of first series follow lanthanum (La) and are called Lanthanoids. The elements of second series follow actinium (Ac) and are called actinoids.

1.4 Periodic trends in properties of elements

(i) Metallic and Non-Metallic Character :

- The tendency of an element to lose electrons and form the ions is called electropositive character or metallic character.
  e.g. alkali metal are the most electropositive elements
- The tendency of an element to accept electrons to form an anion is called electronegative character or non-metallic character.
  e.g. chlorine, oxygen, nitrogen etc.



Problem-1: Arrange the following elements in the increasing order of their metallic character.
Si, Be, Mg, Na, P

Soln. P < Si < Be < Mg < Na

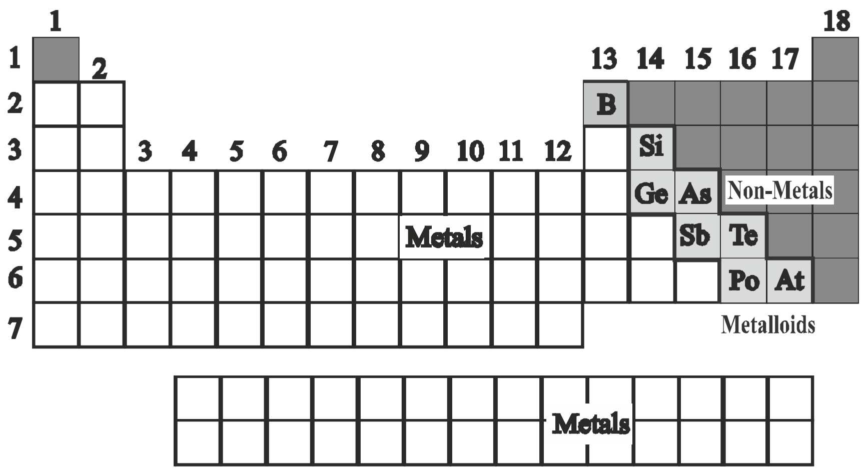
Note

Metals are usually solids at room temperature having high melting point and boiling point mercury is an exception (liquid metal) and Ga and Fr also have very low melting points (303K and 302K respectively).

(ii) *Metalloids / semi-metals* :

There are no sharp line dividing metals from non-metals. A zig-zag line separates metals from non-metals as shown in figure. The borderline elements such as silicon, germanium, arsenic, antimony and tellurium exhibit characteristic properties of metals as well as non-metals. These elements are called semimetals or metalloids.

e.g. Si, As, Sb, Ge, Te



Position of metals, non-metals and metalloids in the periodic table.

Metals have the tendency to form cations by loss of electrons and this property make the elements as electro positive elements or metals.

$$M(g) \longrightarrow M^{+}(g) + e^{-}$$

- The tendency of an element to lose electron is closely connected to the (IE) of the element.
- Smaller the (IE) of an element, the greater will be its tendency to lose electrons and thus greater will be its metallic character.
- Greater the metallic character, greater the reducing nature.

* (IE) increases moving along a period left to right and decreases down the group, hence metallic and reducing nature decrease along the period and increase down the group.

Nuclear charge $\xrightarrow{\text{increases left to right in period}}$

Shielding $\xrightarrow{\text{increases left to right in period}}$

But the nuclear charge wins so :

Tendencey to form the ions $\xleftarrow{\text{decreases left to right in period}}$

Reducing power $\xleftarrow{\text{decreases left to right in period}}$

Metallic nature $\xleftarrow{\text{decreases left to right in period}}$

Problem-2: Tendency to lose electrons shows reducing property of the element. Arrange the following in order of reducing property.

(a) Na,K,Rb (b) Na, Mg, Al (c) F^-, Cl^-, Br^-, I^- (d) Mg, Ca, Sr

Soln. (a) $Na < K < Rb$ (b) $Na > Mg > Al$

(c) $F^- < Cl^- < Br^- < I^-$ (d) $Mg < Ca < Sr$

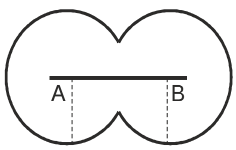
(iii) Size of atoms and ions

(a) Atomic Radii :

The distance from centre of the nucleus to the outermost shell is called radius of an atom, it depends on following factors:

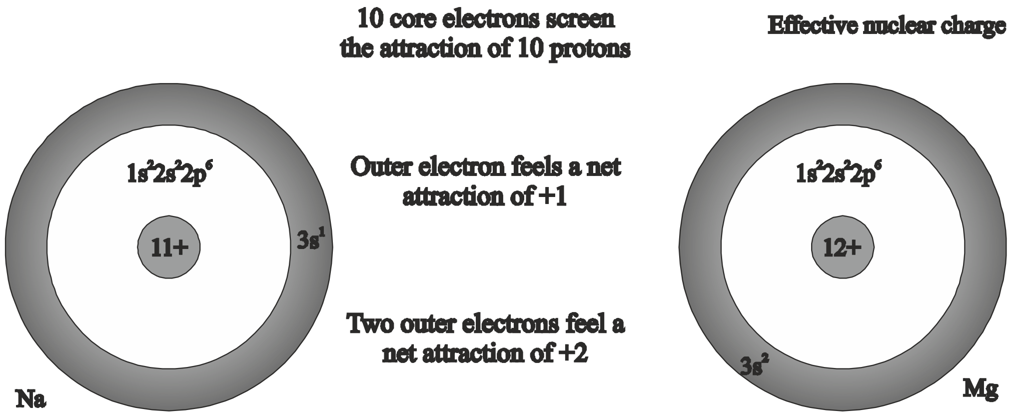
(i) Principal Quantum number (n)

(ii) Effective Nuclear Charge



$\frac{1}{2}AB$ = covalent radius

Effective nuclear charge (ENC) or Z*:



• The effective nuclear charge is the positive charge that an electron experience from the nucleus.
• It is the nuclear attractive force experienced by the electron when it is shielded by innerlying electrons.
• It is the nuclear charge reduced by shielding or screening from any intervening electrons.
• 2p electron is shielded more than or 2s electron as it penetrates the 1s orbital less than 2s orbital.
• As a result we have the energy sequence.

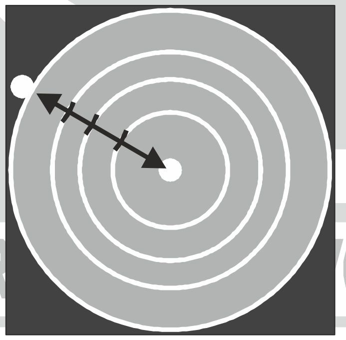
$2s < 2p$

$3s < 3p < 3d$

$4s < 4p < 4d < 4f$

As we move to atoms of elements of higher atomic number, the energy difference between orbitals of same value of n decreases.

Screening Effect:



The decrease in the nuclear force of attraction on the valence electrons or outermost electrons due to repulsive forces of inner lying electrons is called **screening effect.**

The electrons of inner shell repel the electrons of outermost shells. The electrons of outermost shell are thus shielded or screened from the nucleus by inner electrons.

As a result of screening effect the outermost electrons do not experience the complete nuclear charge. The radial distribution of electron densities indicates that 2s and 2p orbitals of H-atom have substantial values at the distance of 1s orbital also, the 2s and 2p orbitals penetrate the 1s orbtial.

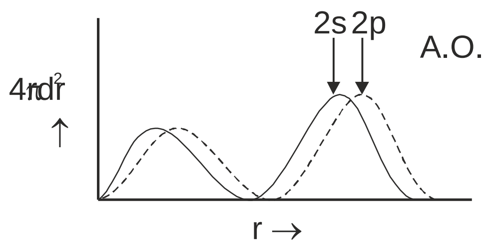


Figure: Probability distribution of electron density

- Accurate calculations indicate the penetration effect of 2s orbital is greater than 2p orbital.
- Penetration of 2s > 2p.
- So, when an electron is filled in 2s or 2p atomic orbital it experiences
  - (a) the attractive nuclear charge
  - (b) the repulsive forces due to innerlying electrons.
- Electrons of ns, np group contribute nearly 35% each to screening constant.
- (n–1) electrons contribute 85%
- (n–2) electrons contribute 100% to screening.

Empirical Rules for estimating ENC – "Slater Rules":

The actual nuclear charge experienced by the electrons in different orbitals is estimated by Slater Rules. These rules are based upon experimental data for electron promotion energies and ionization energies. The ENC (Z^*) acting on a given electron is obtained by substracting the screening or shielding constant 'S', 'S' is estimated as follows

(1) Write the E.C. in the following order and groupings

(1s), (2s, 2p), (3s, 3p) (3d), (4s 4p), (4d) (4f), (5s, 5p) etc.

(2) Electron in any group higher in this sequence than the electron under consideration contributes nothing to 's'.

(3) Then for an electron in an 'ns' or 'np' orbital.

(a) All other electrons in the (ns, np) group contribute s = 0.35 each.

(b) All electrons in the (n–1) shell contribute s = 0.85 each.

(c) All electrons in (n–2) or lower shells contribute s = 1.00 each.

(4) For an electron in an 'nd' or 'nf' orbital, all electrons in the same group contribute s = 0.35 each.

Those in groups lying lower in the sequence than (nd) or (nf) contributes s = 1.00 each.

e.g. 'K' = $(1s^2)\ (2s^2p^6)\ (3s^2p^6)\ (4s^1)$

The ENC experienced by '4s' electron is $Z^* = Z - S = 19 - (0.85 \times 8) + (1.00 \times 10) = 2.20$

If we consider the E.C. of K as $\left(1s^2\right)\left(1s^2p^6\right)\left(3s^2p^6\right)\left(3d^1\right)$ then Z^* would be $Z^* = 19 - (1.00 \times 18) = 1.00$

Thus the electron in the 4s orbital is under the influence of the greater effective nuclear charge and hence in the ground state this orbital is occupied.

Atomic size decreases from left to right in a period $L \rightarrow R\left(\text{Atomic Size}\downarrow\right)$

Atomic size increases from top to down in a group.