

# Periodic Properties

The term periodicity it indicate that the elements with similar properties reappear at certain regular intervals of atomic numbers in Periodic table

## Periodic Table of the Elements



1	IA 1A	2	IIA 2A	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	VIIIA 8A						
1	H Hydrogen 1.008	2	Be Beryllium 9.012	3	Li Lithium 6.941	4	Be Beryllium 9.012	5	VB 5B	6	VIB 6B	7	VIIIB 7B	8	VIII 8	9	IB 1B	10	IIB 2B	2	He Helium 4.003				
11	Na Sodium 22.990	12	Mg Magnesium 24.305	3	3B	4	IVB 4B	5	VB 5B	6	VIB 6B	7	VIIIB 7B	8	VIII 8	9	IB 1B	10	IIB 2B	19	K Potassium 39.098				
19	K Potassium 39.098	20	Ca Calcium 40.078	21	Sc Scandium 44.961	22	Ti Titanium 47.867	23	V Vanadium 50.942	24	Cr Chromium 51.996	25	Mn Manganese 54.938	26	Fe Iron 55.845	27	Co Cobalt 58.933	28	Ni Nickel 58.693	29	Cu Copper 63.548	30	Zn Zinc 65.38	13	B Boron 10.811
37	Rb Rubidium 85.468	38	Sr Strontium 87.62	39	Y Yttrium 88.904	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	He Neon 20.180				
55	Cs Cesium 132.995	56	Ba Barium 137.328	57-71	Hf Hafnium 178.49	72	Ta Tantalum 180.948	73	74	75	76	77	78	79	80	81	82	83	84	85	He Neon 20.180				
87	Fr Francium 223.029	88	Ra Radium 226.025	89-103	Rf Rutherfordium [261]	104	Db Dubnium [262]	105	106	107	108	109	110	111	112	113	114	115	116	117	118				
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The repetition of the elements with similar properties in the order of increasing atomic number as in the Periodic Table is called periodicity of properties.

According to modern periodic table, the properties of the elements like atomic and ionic radii, ionisation energy, electron affinity, ~~polarisability~~, electronegativity, polarisation, oxidation state of ions etc., are periodic functions of their atomic number.

In this chapter 1st we discuss about effective nuclear charge which is more important concept to clear understanding of Periodic Properties.

Effective Nuclear Charge is

Effective nuclear charge is an very important topic to understand the periodic properties.

Before we discuss Effective nuclear charge we give some idea about Screening effect or Shielding effect.

## Screening effect or Shielding effect:

In a multi-electron atom, the valence-shell electrons are attracted by the nucleus and repelled by the electrons of inner shells and the valence-shell electrons.

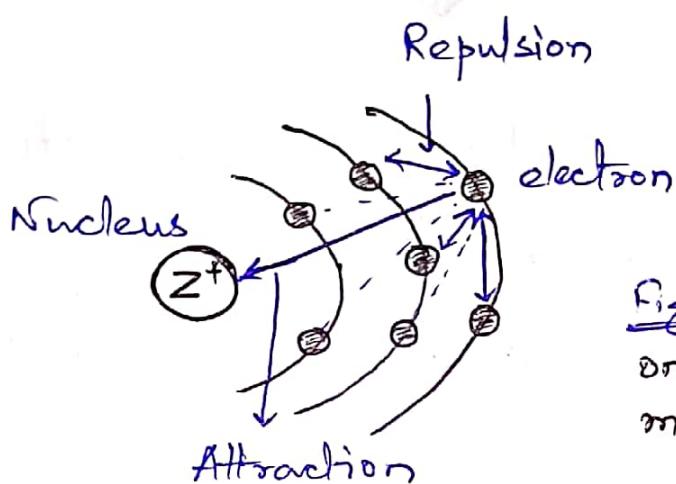


Fig:- Effect of inner-electron shells on a valence shell electron in a multi-electron atom - shielding effect

The combined effect of this attractive and repulsive force acting on the valence-electron is that the valence-electron experiences less attraction from the nucleus. This is known as screening effect.

The ~~decrease in the attractive force~~ screening effect depends upon the number of inner electrons. Greater the number of inner electrons, greater would be the screening effect.

The important factors on which the magnitude of shielding effect caused by the inner-shell electrons on the valence-shell electron depends.

- i) Greater is the number of inner-shell electrons or inner shells, greater is the magnitude of shielding effect caused by the inner electrons on the valence-shell electron.

ii) For the same shell, the s-electrons are more effective in shielding the nuclear charge than p-electrons, the p-electrons are more effective than d-electrons and d-electrons are more effective than f-electrons.

An electron present in  $n$ th orbital is more effectively screened by the electrons in the  $(n-1)$ th orbital.

Effective nuclear charge:

Due to the screening effect the valence shell's electron experiences less attractive force from nucleus. The decrease in the attractive force reduce the nuclear charge,  $Z$  represents the atomic number of the element. This decreased nuclear charge is called effective nuclear charge  $Z_{\text{eff}}/Z^*$ . It is given by the relation

$$Z_{\text{eff}} = Z - \sigma$$

$\sigma$  is called screening constant.

Effective nuclear charge,  $Z_{\text{eff}}$  is defined as the actual nuclear charge,  $Z$  minus the screening effect due to the electrons intervening between the nucleus and the outer electrons.

To calculate the value of  $Z_{\text{eff}}$ , the value of  $\sigma$  can be calculated.

$\sigma$  can be calculate by Slater's rule.

Slater's Rule's

According to these rules the value of  $\sigma$  for a given electron is estimated as follows.

i) Write the complete electronic configuration of the element. Then divide the electronic configuration into the following -

(1s), (2s, 2p), (3s, 3p), (3d), (4s, 4p), (4d), (4f), (5s, 5p)  
(5d), (5f), (6s, 6p) etc.

ii) Select the electron for which the value of  $\sigma$  is calculate. Consider one electron of the valence shell or which ~~out~~ shell electron to be determine the  $\sigma$ -value and add up the contribution of the other electrons according to the following rule.

for s and p orbital in the valence shell the contribution is

- a) Electrons with in the same group or nth shell = 0.35
- b) Electrons in other group or (n-1)th shell = 0.85
- c) Electron in the (n-2)th shell and so on = 1.00

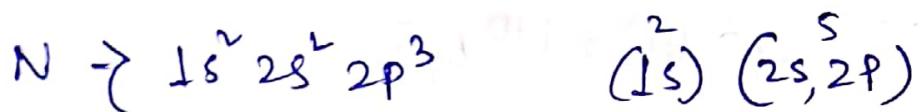
for d and f orbital in the valence shell the contribution is -

- a) Electrons with in the same shell or nth shell = 0.35
- b) Electrons in the (n-1)th shell and so on

Note:- If nth shell is 1s electron then contribution is = ~~0.35~~ 0.30

Example 1 : Calculate the effective nuclear charge experienced by a  $2p$  electron in the nitrogen atom?

The electronic configuration of N atom ( $Z=7$ )



$$Z_{\text{eff}} = Z - f$$

$$= 7 - [0.85 \times (n-1) \text{ th shell} + 0.35 \times n \text{ th shell}]$$

$$= 7 - [0.85 \times 2 + 0.35 \times 4]$$

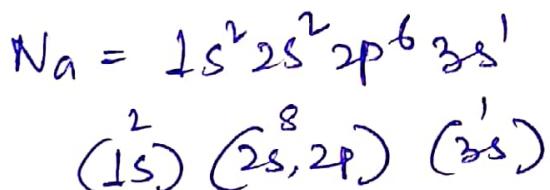
$$= 7 - [1.70 + 1.40]$$

$$= 7 - 3.10$$

$$= 3.90$$

Example 2 : Calculate the effective nuclear charge experienced by the  $3s$  electron in Sodium atom?

The electronic configuration of Na atom ( ~~$Z=11$~~ )



$$Z_{\text{eff}} = Z - f$$

$$= 11 - [1.00 \times (n-2) \text{ th shell} + 0.85 \times (n-1) \text{ th shell} + 0.35 \times n \text{ th shell}]$$

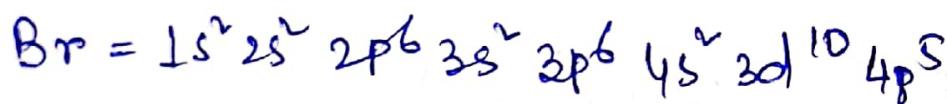
$$= 11 - [1.00 \times 2 + 0.85 \times 8 + 0.35 \times 0]$$

$$= 11 - 8.8$$

$$= 2.20$$

Example - 3 → What is the ~~the~~ shielding constant experienced by a 3d electron in the Bromine atom?

The electronic configuration of Br atom ( $Z = 35$ )

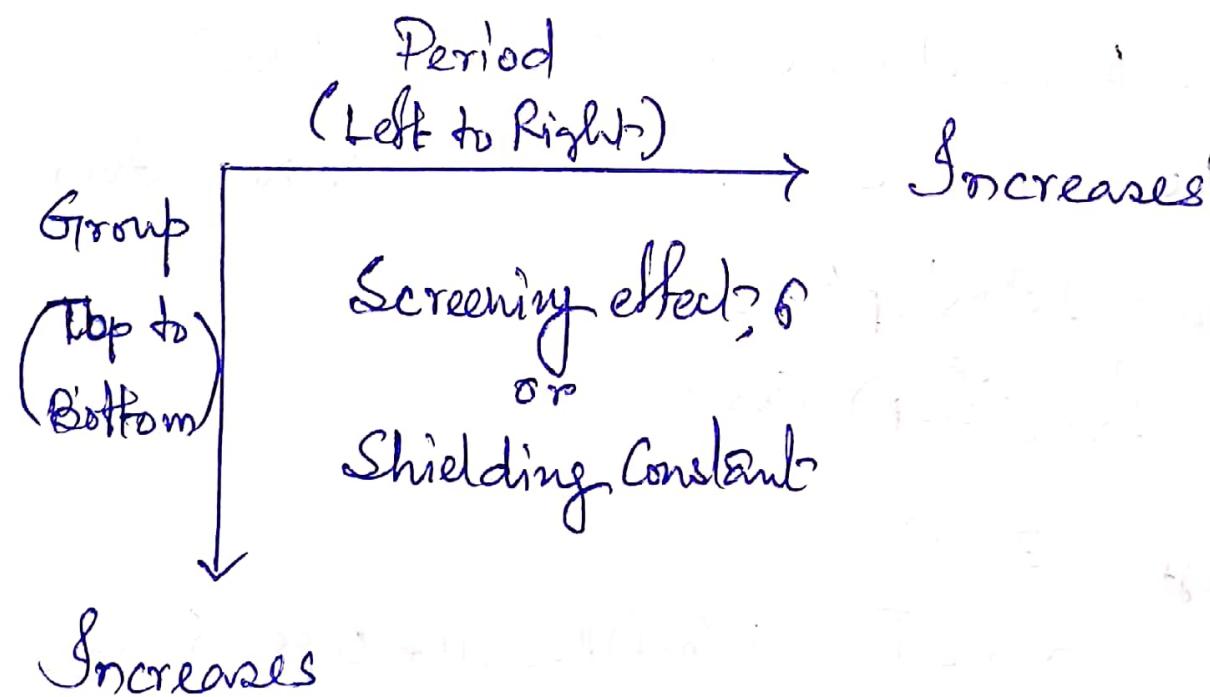


(1s) (2s, 2p) (3s, 3p) (3d) (4s, 4p)

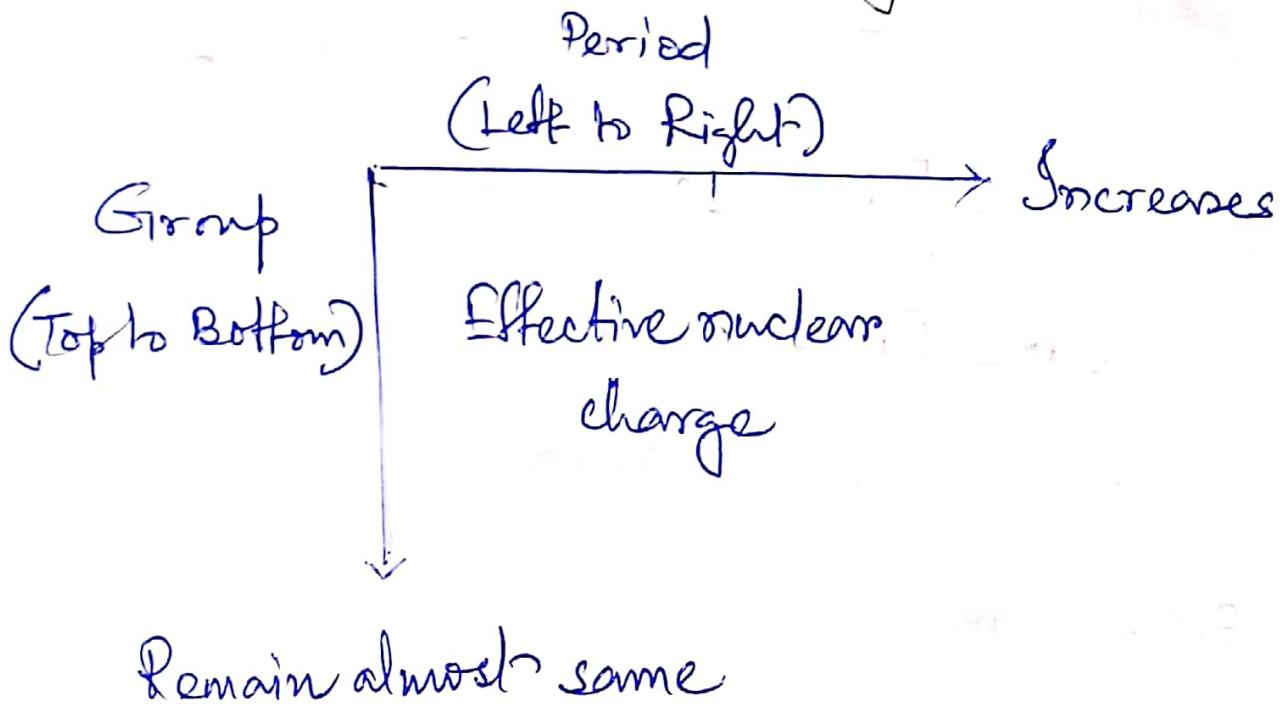
We have to calculate shielding constant at 3d electron so (4s, 4p) can be cancelled. Then experience ~~on~~ by 'd' orbital. So,

$$\begin{aligned}\sigma &= [1.00 \times (n-1)^{\text{th}} \text{ shell and so on} + 0.35 \times n^{\text{th}} \text{ shell}] \\ &= [1.00 \times 18 + 0.35 \times 9] \\ &= 21.015\end{aligned}$$

Variation of Screening effect in the Periodic Table ↴



## Variation of Effective nuclear charge in the Periodic Table



### ~~Application of Bohr's nuclear charges~~

- ②  $4s$  orbital is filled before  $3d$  orbitals explained on the basis of the concept of Effective nuclear charge:-

We know that the electronic configuration of potassium ( $Z=19$ ) is obtained by adding the extra electron to  $4s$ -orbital and not to  $3d$  orbitals, giving  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$  configuration to this atom.

Suppose the electronic configuration of potassium is  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^1$  ( $3d$  filled before  $4s$ )

Now calculate the effective nuclear charge of both the electronic configuration -

$4s$  electron

$$Z_{\text{eff}}(4s) = \frac{1s^2 2s^2 2p^6 3s^2 3p^6 4s^1}{(1s)(2s, 2p)(3s, 3p)(4s)}$$

$$\begin{aligned}
 Z_{\text{eff}} &= 19 - [1.00 \times (n-2) \text{ and so on shell electron} + 0.85 \times \\
 &\quad \text{electrons of } (n-1) \text{ shell} + 0.35 \times n^{\text{th}} \text{ shell electron}] \\
 &= 19 - [1.00 \times 10 + 0.85 \times 8 + 0.35 \times 0] \\
 &= 19 - [10 + 6.8] \\
 &= 19 - 16.8 = 2.20
 \end{aligned}$$

3d electron

$$\begin{aligned}
 Z_{\text{eff}}(3d) &= 1s^2 2s^2 2p^6 3s^2 3p^6 3d^1 \\
 &\quad (1s) (2s, 2p) (3s, 3p) (3d)
 \end{aligned}$$

$$\begin{aligned}
 Z_{\text{eff}} &= 19 - [1.00 \times \text{electrons in } (n-1) \text{ shell and so on shell} + \\
 &\quad 0.35 \times n^{\text{th}} \text{ shell electron}] \\
 &= 19 - [1.00 \times 18 + 0.35 \times 0] \\
 &\approx 19 - 18 = 1
 \end{aligned}$$

Lower value of effective nuclear charge acting on 3d electron as compared to that acting on 4s electron. That is in potassium atom 3d electron is less tightly bound to the nucleus than the 4s electron. So the additional electron in potassium atom prefers to enter 4s-orbital than 3d-orbital.

## Penetration Power:

Penetration power means the ability of an orbital to attract an electron. This process is accompanied with release of energy. The penetration effect of s-orbital is the maximum because of the closeness to the nucleus than are the p, d and f-orbital.

s-electrons spend most of their time nearer to the nucleus.

$$ns > np > nd > nf$$

penetration power  $\rightarrow$   
(Decreasing order)

The penetration power of s, p, d, f orbitals belonging to the same shell (all the orbital having same value of n).

① Variations of s, p, d and f-orbitals energies of atoms in the periodic table :-

The energy of the s, p, d, and f orbitals are related as -

$$s < p < d < f$$

This means energy increase in each and every orbital. s-orbital have the lowest energy and the highest penetration effect. But we know energy continuously increases in each block as we move down in group or left to right across the period.

The energy state of an orbital depends upon the principle quantum number, n and angular quantum number l.

As the energy of orbital have been determined by  $(n+l)$  rule which is the basis of the Aufbau Principle.

According to Aufbau principle, In the ground state of an atom the electrons occupy the lowest energy orbitals available to them. This means that the electrons enter the orbitals in the order of increasing energies. The lowest energy available orbitals being filled up first.

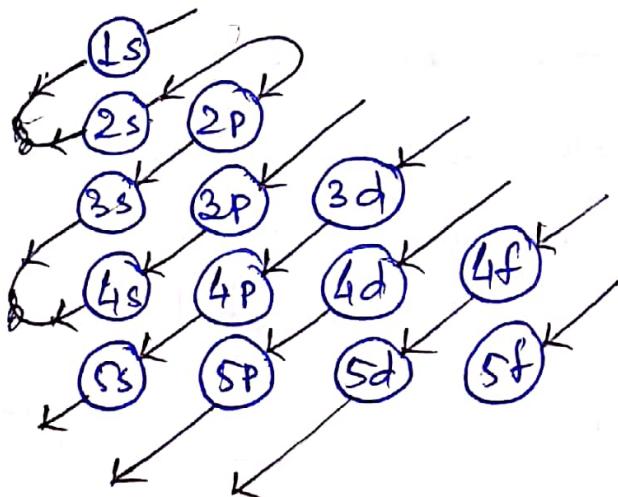
The sequence of filling the orbitals proceeds according to the following rules:

i) Orbitals are filled in order of increasing value of  $(n+l)$ .

example -  $4s$  ( $n+l = 4+0 = 4$ ) is filled before  $3d$  ( $n+l = 3+2 = 5$ ) orbital.

ii) For the orbitals having same value of  $(n+l)$  the orbital having lower value of  $n$  is filled up first.

example -  $2p$  ( $n+l = 2+1 = 3$ ) is filled before  $3s$  ( $n+l = 3+0 = 3$ ) orbital.



The order of filling orbitals.

Knowing the value of n and l

Shell

Principal Quantum Number (n)

Azimuthal Quantum Number (l) [ $l = (n-1)$ ]

K

$n = 1$

$l = 0$

( $s \Rightarrow$  Subshell)

L

$n = 2$

$l = 0$

( $s \Rightarrow$  Subshell)

$l = 1$

( $p \Rightarrow$  Subshell)

M

$n = 3$

$l = 0$

( $s \Rightarrow$  Subshell)

$l = 1$

( $p \Rightarrow$  Subshell)

$l = 2$

( $d \Rightarrow$  Subshell)

N

$n = 4$

$l = 0$

( $s \Rightarrow$  Subshell)

$l = 1$

( $p \Rightarrow$  Subshell)

$l = 2$

( $d \Rightarrow$  Subshell)

$l = 3$

( $f \Rightarrow$  Subshell)

This means that the values of l for the subshells of a shell are governed by n, when  $n=1$ , there is only one subshell, with the value  $l=0$ , when  $n=2$ , there are two subshells with the values  $l=0, 1$ , when  $n=3$ , there are three subshells with the values  $l=0, 1, 2$  when  $n=4$ , there are four subshells with the values  $l=0, 1, 2, 3$ . For every value of l, there is a

separate notation to indicate subshell.

For example  $\geq$  Quantum No  $l = 0, 1, 2, 3, 4, 5 \dots$

subshell = s, p, d, f, g, h ...

Only first four subshell, s, p, d and f are used because they are identify by spectral lines which very sharp, principal, diffuse and fundamental but subsequent subshell  $l > 3$  proceed alphabetically g, h, i, ... so on.

Every subshell have different type ability to accommodate a maximum of  $(4l + 2)$  electrons.

As for example on s-subshell ( $l=0$ ) has maximum of 2-electrons, p-subshell ( $l=1$ ) has maximum of 6-electrons, ~~d~~ and d-subshell ( $l=2$ ) has maximum of 10-electrons, f-subshell ( $l=3$ ) has maximum of 14-electrons.

## Electronic Configuration:

In describing the electron configuration by s, p, d and f subshells, one must remember that there is one orbital in s-subshell, three orbitals in p-subshell five orbitals in d-subshell and seven orbitals in f-subshell. Each orbital accommodates two electrons and a given subshell is filled before electrons are added to the next subshell.

④ Ground state electronic configuration

## Electron Configurations of the Elements

1	Hydrogen	$1s^1$	44	Ruthenium	$[Kr]4d^75s^1$
2	Helium	$1s^2$	45	Rhodium	$[Kr]4d^85s^1$
3	Lithium	$[He]2s^1$	46	Palladium	$[Kr]4d^{10}$
4	Beryllium	$[He]2s^2$	47	Silver	$[Kr]4d^{10}5s^1$
5	Boron	$[He]2s^22p^1$	48	Cadmium	$[Kr]4d^{10}5s^2$
6	Carbon	$[He]2s^22p^2$	49	Indium	$[Kr]4d^{10}5s^25p^1$
7	Nitrogen	$[He]2s^22p^3$	50	Tin	$[Kr]4d^{10}5s^25p^2$
8	Oxygen	$[He]2s^22p^4$	51	Antimony	$[Kr]4d^{10}5s^25p^3$
9	Fluorine	$[He]2s^22p^5$	52	Tellurium	$[Kr]4d^{10}5s^25p^4$
10	Neon	$[He]2s^22p^6$	53	Iodine	$[Kr]4d^{10}5s^25p^5$
11	Sodium	$[Ne]3s^1$	54	Xenon	$[Kr]4d^{10}5s^25p^6$
12	Magnesium	$[Ne]3s^2$	55	Cesium	$[Xe]6s^1$
13	Aluminum	$[Ne]3s^23p^1$	56	Barium	$[Xe]6s^2$
14	Silicon	$[Ne]3s^23p^2$	57	Lanthanum	$[Xe]5d^16s^2$
15	Phosphorus	$[Ne]3s^23p^3$	58	Cerium	$[Xe]4f^15d^16s^2$
16	Sulfur	$[Ne]3s^23p^4$	59	Praseodymium	$[Xe]4f^36s^2$
17	Chlorine	$[Ne]3s^23p^5$	60	Neodymium	$[Xe]4f^46s^2$
18	Argon	$[Ne]3s^23p^6$	61	Promethium	$[Xe]4f^56s^2$
19	Potassium	$[Ar]4s^1$	62	Samarium	$[Xe]4f^66s^2$
20	Calcium	$[Ar]4s^2$	63	Europium	$[Xe]4f^76s^2$
21	Scandium	$[Ar]3d^14s^2$	64	Gadolinium	$[Xe]4f^75d^16s^2$
22	Titanium	$[Ar]3d^24s^2$	65	Terbium	$[Xe]4f^96s^2$
23	Vanadium	$[Ar]3d^34s^2$	66	Dysprosium	$[Xe]4f^{10}6s^2$
24	Chromium	$[Ar]3d^54s^1$	67	Holmium	$[Xe]4f^{11}6s^2$
25	Manganese	$[Ar]3d^54s^2$	68	Erbium	$[Xe]4f^{12}6s^2$
26	Iron	$[Ar]3d^64s^2$	69	Thulium	$[Xe]4f^{13}6s^2$
27	Cobalt	$[Ar]3d^74s^2$	70	Ytterbium	$[Xe]4f^{14}6s^2$
28	Nickel	$[Ar]3d^84s^2$	71	Lutetium	$[Xe]4f^{14}5d^16s^2$
29	Copper	$[Ar]3d^{10}4s^1$	72	Hafnium	$[Xe]4f^{14}5d^26s^2$
30	Zinc	$[Ar]3d^{10}4s^2$	73	Tantalum	$[Xe]4f^{14}5d^36s^2$
31	Gallium	$[Ar]3d^{10}4s^24p^1$	74	Tungsten	$[Xe]4f^{14}5d^46s^2$
32	Germanium	$[Ar]3d^{10}4s^24p^2$	75	Rhenium	$[Xe]4f^{14}5d^56s^2$
33	Arsenic	$[Ar]3d^{10}4s^24p^3$	76	Osmium	$[Xe]4f^{14}5d^66s^2$
34	Selenium	$[Ar]3d^{10}4s^24p^4$	77	Iridium	$[Xe]4f^{14}5d^76s^2$
35	Bromine	$[Ar]3d^{10}4s^24p^5$	78	Platinum	$[Xe]4f^{14}5d^96s^1$
36	Krypton	$[Ar]3d^{10}4s^24p^6$	79	Gold	$[Xe]4f^{14}5d^{10}6s^1$
37	Rubidium	$[Kr]5s^1$	80	Mercury	$[Xe]4f^{14}5d^{10}6s^2$
38	Strontium	$[Kr]5s^2$	81	Thallium	$[Xe]4f^{14}5d^{10}6s^26p^1$
39	Yttrium	$[Kr]4d^15s^2$	82	Lead	$[Xe]4f^{14}5d^{10}6s^26p^2$
40	Zirconium	$[Kr]4d^25s^2$	83	Bismuth	$[Xe]4f^{14}5d^{10}6s^26p^3$
41	Niobium	$[Kr]4d^45s^1$	84	Polonium	$[Xe]4f^{14}5d^{10}6s^26p^4$
42	Molybdenum	$[Kr]4d^55s^1$	85	Astatine	$[Xe]4f^{14}5d^{10}6s^26p^5$
43	Technetium	$[Kr]4d^55s^2$	86	Radon	$[Xe]4f^{14}5d^{10}6s^26p^6$

## Electron Configurations of the Elements

87	Francium	[Rn]7s <sup>1</sup>	103	Lawrencium	[Rn]5f <sup>14</sup> 7s <sup>2</sup> 7p <sup>1</sup>
88	Radium	[Rn]7s <sup>2</sup>	104	Rutherfordium	[Rn]5f <sup>14</sup> 6d <sup>2</sup> 7s <sup>2</sup>
89	Actinium	[Rn]6d <sup>1</sup> 7s <sup>2</sup>	105	Dubnium	[Rn]5f <sup>14</sup> 6d <sup>3</sup> 7s <sup>2</sup>
90	Thorium	[Rn]6d <sup>2</sup> 7s <sup>2</sup>	106	Seaborgium	[Rn]5f <sup>14</sup> 6d <sup>4</sup> 7s <sup>2</sup>
91	Protactinium	[Rn]5f <sup>2</sup> 6d <sup>1</sup> 7s <sup>2</sup>	107	Bohrium	[Rn]5f <sup>14</sup> 6d <sup>5</sup> 7s <sup>2</sup>
92	Uranium	[Rn]5f <sup>3</sup> 6d <sup>1</sup> 7s <sup>2</sup>	108	Hassium	[Rn]5f <sup>14</sup> 6d <sup>6</sup> 7s <sup>2</sup>
93	Neptunium	[Rn]5f <sup>4</sup> 6d <sup>1</sup> 7s <sup>2</sup>	109	Meitnerium	[Rn]5f <sup>14</sup> 6d <sup>7</sup> 7s <sup>2</sup>
94	Plutonium	[Rn]5f <sup>6</sup> 7s <sup>2</sup>	110	Darmstadtium	[Rn]5f <sup>14</sup> 6d <sup>9</sup> 7s <sup>1</sup>
95	Americium	[Rn]5f <sup>7</sup> 7s <sup>2</sup>	111	Roentgenium	[Rn]5f <sup>14</sup> 6d <sup>10</sup> 7s <sup>1</sup>
96	Curium	[Rn]5f <sup>7</sup> 6d <sup>1</sup> 7s <sup>2</sup>	112	Copernium	[Rn]5f <sup>14</sup> 6d <sup>10</sup> 7s <sup>2</sup>
97	Berkelium	[Rn]5f <sup>9</sup> 7s <sup>2</sup>	113	Nihonium	[Rn]5f <sup>14</sup> 6d <sup>10</sup> 7s <sup>2</sup> 7p <sup>1</sup>
98	Californium	[Rn]5f <sup>10</sup> 7s <sup>2</sup>	114	Flerovium	[Rn]5f <sup>14</sup> 6d <sup>10</sup> 7s <sup>2</sup> 7p <sup>2</sup>
99	Einsteinium	[Rn]5f <sup>11</sup> 7s <sup>2</sup>	115	Moscovium	[Rn]5f <sup>14</sup> 6d <sup>10</sup> 7s <sup>2</sup> 7p <sup>3</sup>
100	Fermium	[Rn]5f <sup>12</sup> 7s <sup>2</sup>	116	Livermorium	[Rn]5f <sup>14</sup> 6d <sup>10</sup> 7s <sup>2</sup> 7p <sup>4</sup>
101	Mendelevium	[Rn]5f <sup>13</sup> 7s <sup>2</sup>	117	Tennessine	[Rn]5f <sup>14</sup> 6d <sup>10</sup> 7s <sup>2</sup> 7p <sup>5</sup>
102	Nobelium	[Rn]5f <sup>14</sup> 7s <sup>2</sup>	118	Oganesson	[Rn]5f <sup>14</sup> 6d <sup>10</sup> 7s <sup>2</sup> 7p <sup>6</sup>

## Atomic and Ionic sizes

The various physical properties of atoms, the atomic and ionic sizes are most important. The importance of size will become more obvious during our discussion of some other physical properties, like ionisation energy, electron affinity etc.

### Atomic radii

The absolute size of an atom is difficult to define because -

- i) Atoms are very small in size
- ii) Electrons are moving surrounding the nucleus in 3D (dimensional) motion.

The radius of an atom or ion is defined as the distance from the centre of the nucleus to the outermost shell of the atom or ion. But it is impossible to isolate an individual atom and determine its radius. So it is assumed that atoms behave as perfect hard spheres and two such sphere are just in contact each other. The distance between the centres of two atoms in molecules can be measured by X-ray and spectral studies of molecules. The radius of an atom is calculated as one half of the distance between centre of two atoms. Therefore

three different types atomic radii concepts arise.

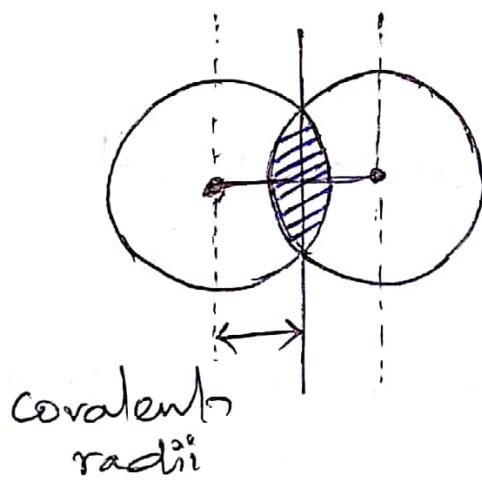
Types of atomic radii's

Covalent radii

Metallic radii

Vander Waals radii

Covalent radii's In a homonuclear diatomic molecule ( $H_2, F_2, Cl_2$ ) there is a covalent bond holding together two atoms. The internuclear distance in such molecule is called the bond length. One half of this bond length is called the covalent radii of the element.



Homonuclear diatomic molecule -

$$\text{Covalent radii} = \frac{1}{2} \times \text{internuclear distance}$$

But when two heteronuclear molecule, when electronegativity ~~of both~~ is same for both atom.

Then

$$r_{AB} = r_A + r_B$$

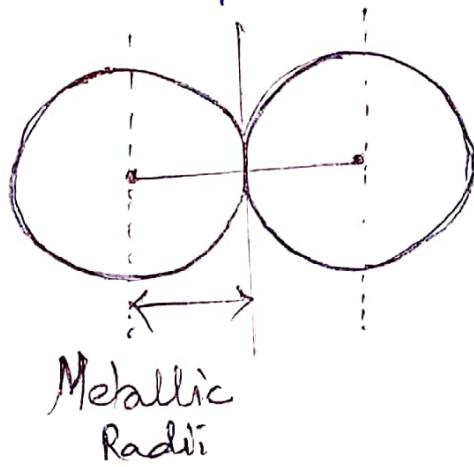
Radius of  $r_A$  can be determined by  $r_{A_2}$  and similarly  $r_B$ , can be determined by  $r_{B_2}$

Again, when two heteronuclear molecule, but electronegativity is different, then -

$$r_{AB} = r_A + r_B - 0.09(X_A - X_B)$$

$X_A$  and  $X_B$  are the electronegativity of A and B.

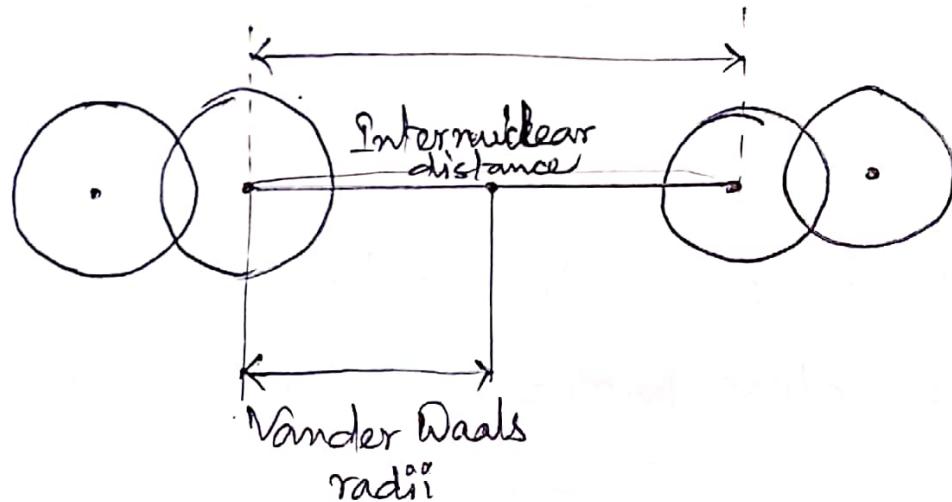
Metallic Radii: It is one half of the distance between the nuclei of two adjacent metal atoms in the metallic close packed crystal lattice.



In a covalent bond, a pair of electrons is strongly attracted by the nuclei of two atoms. In a metallic lattice, the valence electrons are mobile, therefore they are only weakly attracted by the metal ions. Thus the metallic radii always longer than its covalent radii.

Metallic radii is 10% to 15% higher than the single bond covalent radii.

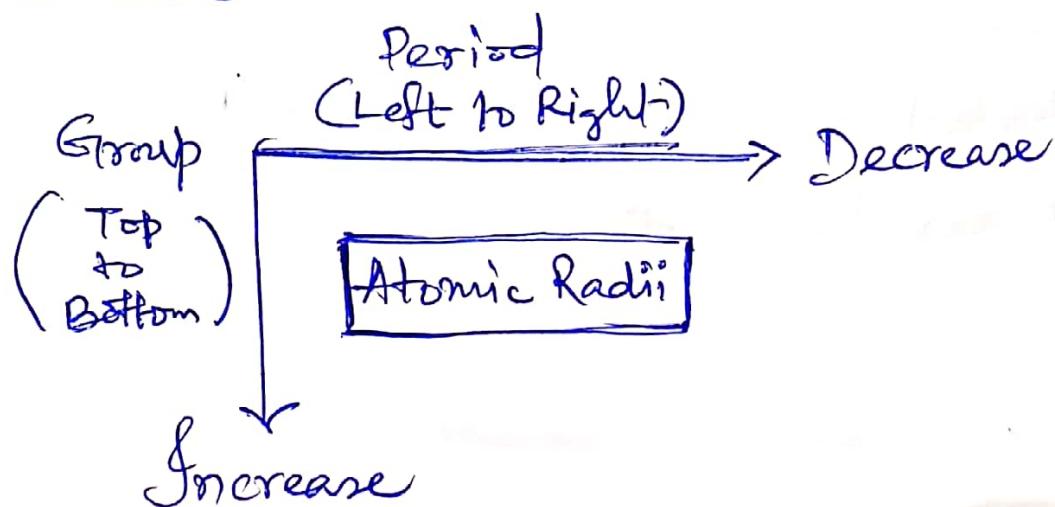
Vander Waals Radii: It is one half the distance between the nuclei of two identical non-bonded isolated atoms or two adjacent identical atoms belonging to two neighboring molecules of an element in the solid-state.



### Variation of Atomic Radii in the Periodic Table:

The periodic trends of atomic radii can be easily accounted for in terms of electronic configuration.

- i) The atomic radii decreases from left to right across a period in the periodic table. In a given period the alkali metal atom has the largest and the halogen atom the smallest atomic radius.
- ii) The atomic radii increases on descending a group in the periodic table.



## Ionic Radii

When neutral atoms gain or lose electrons, they are converted into ions and the radii are changed. The distance between the nucleus and the outermost electron in an ion is called ionic radius.

When an atom loses an electron, a positive ion (cation) is formed. The size of a cation is always smaller than a neutral atom. This can be attributed to a decrease in the number of electrons whereas the magnitude of the nuclear charge remains the same. The nuclear charge now acts on a fewer number of electrons, attracts them more tightly and hence the electron cloud shrinks in size.

When a neutral atom gains an electron, a negative ion (anion) is formed. The size of an anion is always larger than its neutral atom. In this case the same nuclear charge acts over a greater number of electrons than were present in the neutral atom. The electron cloud is now less tightly held which causes an expansion in its size.

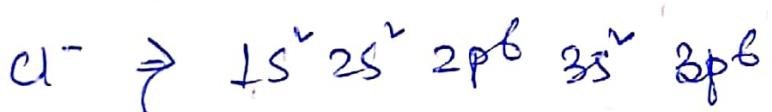
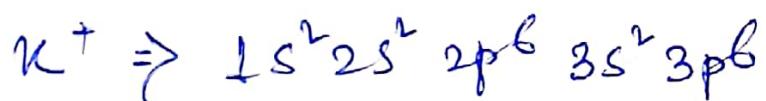
## Periodic Trends:

For an isoelectronic series (ions, which have the same number of electrons) the ionic radii decreases very significantly as the nuclear charge increases.

In a group the ionic radius increases as the atomic number increases.

Ionic radii of  $K^+$  is smaller than that of  $Cl^-$ .

Electronic configuration of  $K^+$  and  $Cl^-$  are



Thus both configurations are iso electronic, i.e. same configuration. However  $K^+$  is smaller in size compared to  $Cl^-$ . This is because  $K^+$  has a greater nuclear charge compared to  $Cl^-$ . Therefore electron cloud in  $K^+$  is pulled to a greater extent than in  $Cl^-$ . Thus  $K^+$  is smaller in size compared to  $Cl^-$ .

### Ponisation Energy

It is possible to remove one or more electrons from an atom, ion or molecule provided sufficient energy is given to the system.

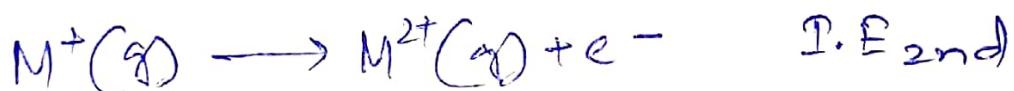
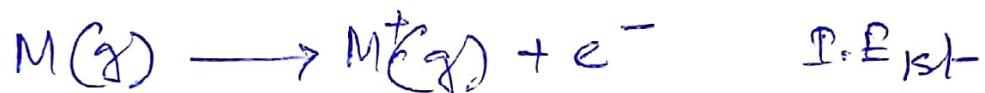
The ionisation energy of an element is defined as the ~~more~~ amount of energy needed to remove the least tightly/most loosely bound electron from a mole of isolated gaseous atom.



Ionisation energy is an endothermic process because in this process energy is absorb so  $\Delta H = (+)$ ve.

Successive Ionisation energies

After the 1st electron has been removed from a neutral atom is possible to remove second, third or even more electrons. The energies required for the removal of subsequent electrons are known as successive ionisation energies.



$$I.E_{2nd} > I.E_{2nd} > I.E_{1st}$$

It is observed that successive ionisation energies increasing progressively because increasing difficulty to remove each successive electron. This is because after removal of <sup>1st</sup> electron atoms become positively charge which the electrons are more tightly bound by the nucleus. Then the removal of 2nd electron needed much more energy again the nuclear charge remain same but electrons are less number so electrons are held more tightly by

the nucleus, so the removal of 3rd electron needed much more energy. So the successive ionisation energy goes on the requirement of energy is higher

The factors that govern ionisation energy of an element.

Ionisation energy depends upon several factors -

i) Size of the atom - As the size of the atom decreases, the outer electrons are more strongly attracted by the nucleus, so the removal of an electron is take more energy. Therefore size of the atom decreases ionisation energy increases.

$$\text{Ionisation energy} \propto \frac{1}{\text{size}}$$

ii) Charge on the nucleus - As the nuclear charge increases, the electron would be held more strongly by the nucleus. So more energy required to remove the electron from the atom. Thus the ionisation energy increases as the nuclear charge increases.

$$\text{Ionisation energy} \propto \text{Nuclear charge}$$

iii) Electronic configuration - The stable electronic configuration having arrangement of outermost shell subshell are fully filled and again half filled than these elements are more

having more stable electronic configuration. The more stable the electronic configuration the greater is the ionisation energy. That is why each noble gas has the highest ionisation energy of the element in the same period.

Variation of Ionisation energy in the Periodic table-

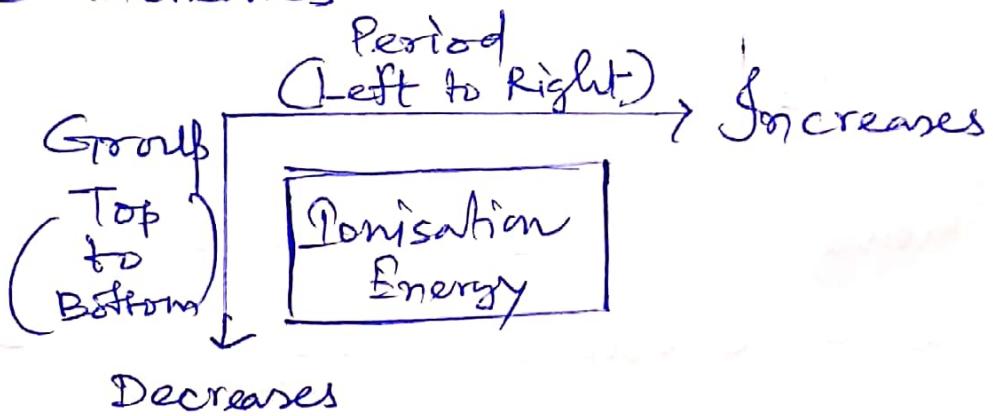
Variation along a period is In general ionisation energy increases with increasing atomic number as we move from left to right along a period. Because

- i) Nuclear charge increases from left to right.
- ii) Size of the atom decreases from left to right.

Variation along a group is The values of ionisation energy decreases in going from top to bottom.

Because

- i) There is a simultaneous increase in the number of energy levels and therefore, the atomic size increases.
- ii) In going from top to bottom in a group the nuclear charge increases.



But the variation of ionisation energy in the periodic table having such exception there are-

Ex) Example - i) Period - 2

Elements	Li	Be	B	C	N	O	F	Ne
Electronic configuration	$2s^1$	$2s^2$	$2s^2 2p^1$	$2s^2 2p^2$	$2s^2 2p^3$	$2s^2 2p^4$	$2s^2 2p^5$	$2s^2 2p^6$
-	(full shell)	(full filled)			(half filled)			(full filled)
I.E	520	900	800	1090	1400	1310	1680	2080

So the correct order is—



'Ne' is noble gas having most stable electronic configuration so that has highest I.E value again Be is more stable configuration than B so Be is higher I.E than B and same case arise on in case of N and O, N having half filled electronic configuration which is stable configuration than 'O' electronic configuration so that 'N' has higher value of I.E than O.

ii) Group - 13

The elements are - B, Al, Ga, In, Tl

We know as we down in the group the Ionisation

energy decrease. So the ~~& expected~~ order is



But in actual case the order is



The ionisation energy values as expected from the general trends do not decreases smoothly down the group. The decrease from B to Al is associated with increase in size and same as in case of Ga to In. The observed discontinuity in the ionisation energy values between Al and Ga. Here in case of

Ga (Gallium) atom is preceded by ten elements of 1st transition series. This makes the atomic radius of 'Ga' much smaller than expected. Again discontinuity shows in between In and Tl. Tl is nearer to the lanthanide series so it observe lanthanide contraction which is effect in size the size of Tl. So that's the reasons behind behind the Ga and Tl having higher ionisation energy.

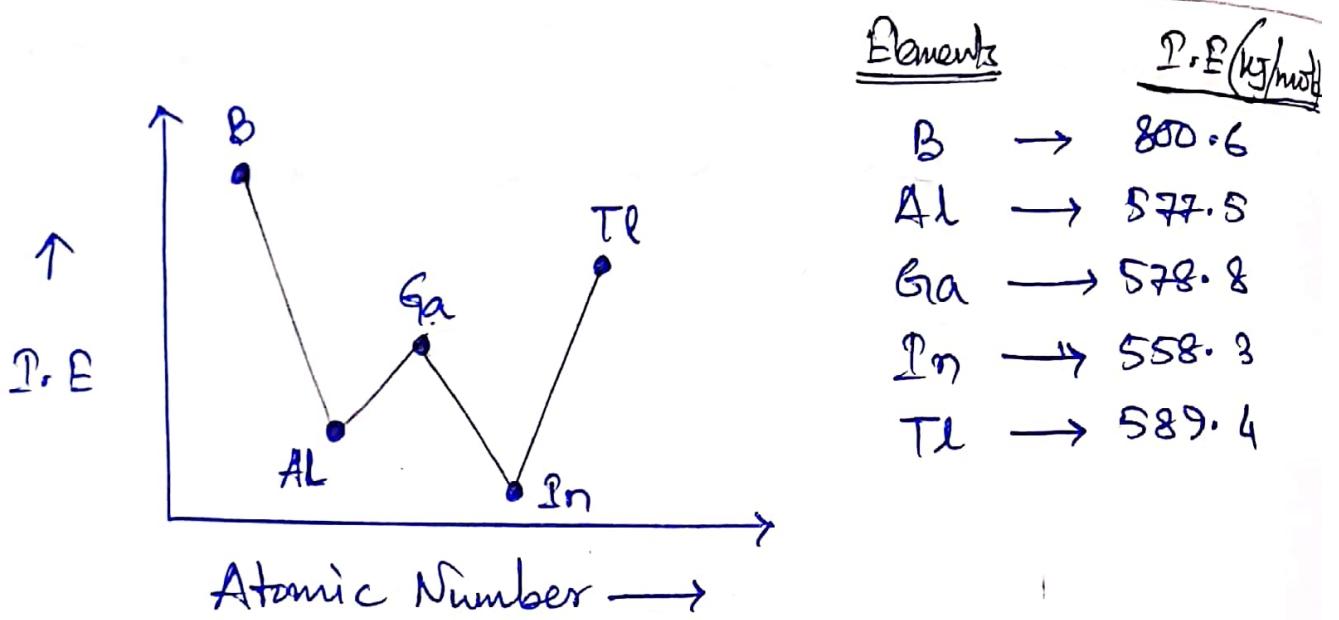


Fig: Variation of I.E in Group-13 elements

Example: How much energy needed to convert 1.5 g of potassium ( $K$ ) atoms in the gaseous state to form potassium ion ( $K^+$ )?

(I.E of potassium 419 kJ/mole)

⇒ Atomic mass of potassium is 39 g

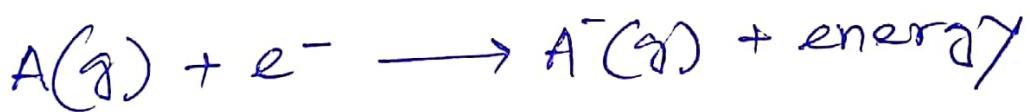


$$\begin{aligned}
 \text{39 g potassium require} &= 419 \text{ kJ/mole energy} \\
 \frac{1 \text{ g}}{39 \text{ g}} \cdot n &= \frac{419}{39} \text{ kJ/mole } n \\
 1.5 \text{ g} & \quad n = \frac{419 \times 1.5}{39} \\
 &= 16.1 \text{ kJ/mole energy}
 \end{aligned}$$

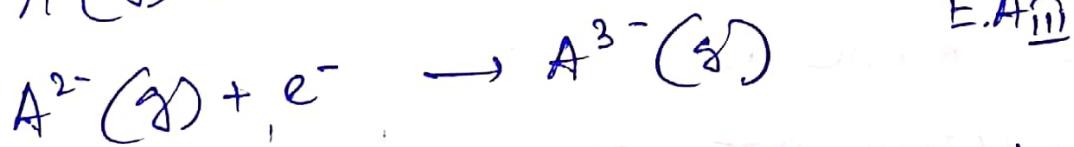
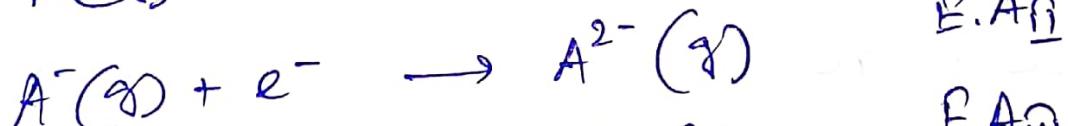
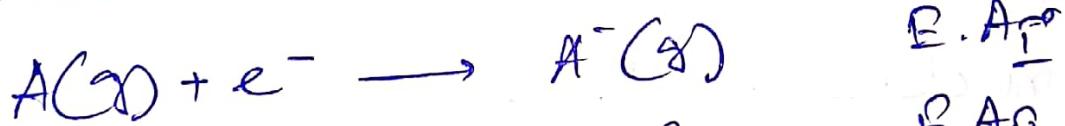
## Electron Affinity:

Atom not only lose electrons to form the positive ~~charge~~ ions but also gain electrons to form negative ions.

We know when an electron is removed from the gaseous atom, energy is required but when an electron is added to a neutral gaseous atom energy is released. This we can define as 'the amount of energy released when an electron is added to neutral gaseous atom is called electron affinity.'



## Successive Electron Affinity:



Electron affinity is an exothermic process because of energy released which give positive value and it's value is (-ve). But in case of successive electron affinity means affinity for the addition of 2nd, 3rd or next electrons to the anion after one electron has been added to the neutral atom.

Actually there is a lot of resistance put up by the anions to the addition of more electrons because of repulsive forces. So an electron can be added on a anion or negative charge ion is ~~less~~ to be required of energy or energy can be absorb. This process is endothermic. That's why successive electron affinity give negative value and  $\Delta H$  value is positive.

The factors that govern electron affinity of an element.

Electron affinity depends mainly upon the following factors -

i) Size of the atom: The smaller the size of atom, smaller will be the distance between the electron and nucleus. So the electrostatic force of attraction will be more to add an extra electron. Therefore extra electron added it release more energy so the electron affinity will be higher.

$$\text{Electron affinity} \propto \frac{1}{\text{size}}$$

ii) Nuclear charge: More the nuclear charge of the atom, more strongly will attract additional electron. Therefore as nuclear charge increases the electron affinity increases!

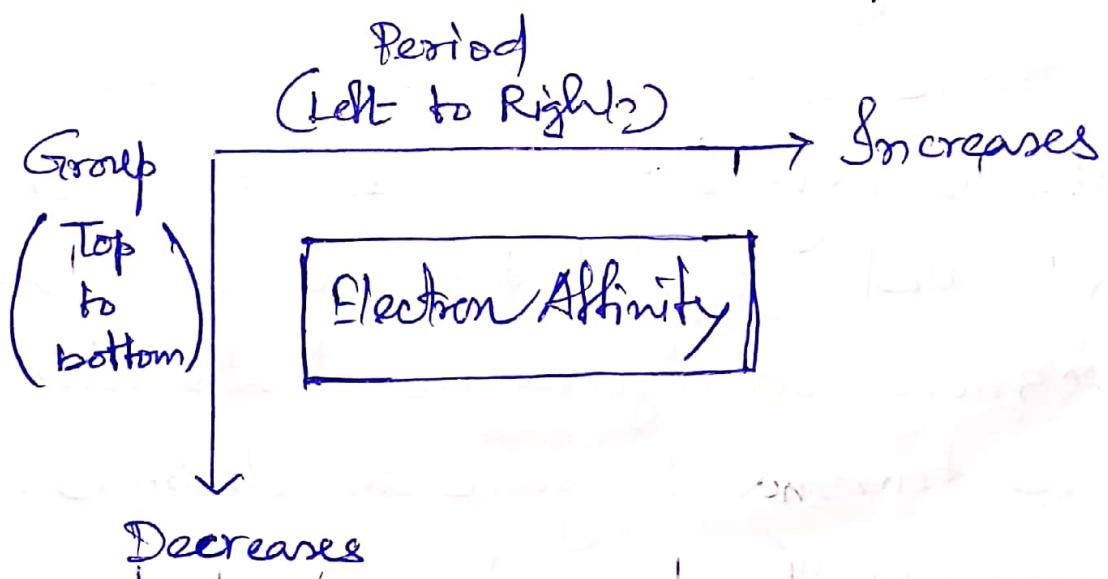
## E.A & Nuclear Charge

v) Electronic configuration's Atoms having stable electronic configuration, those having completely filled or half-filled outer orbitals do not show much tendency to add extra electron and have either zero or very low electron affinities.

Variation of electron affinity in the periodic table:-

Along a period :- The atomic size decreases while the nuclear charge increases. Therefore, the nucleus would have increased attraction for additional electron and electron affinity would be more.

Along a group :- The atomic size and nuclear charge both are increases on moving down the group. But overall the effect of these factors is that the effective nuclear charge for the attraction of the electron is decreases so that electron affinity decreases.



But in the variation of electron affinity in the periodic table having such exception there are -

Example i) Period-2

Elements - Li Be B C N O F Ne

Electronic config(v.s) -  $2s^1$   $2s^2$   $2s^2 p^1$   $2s^2 p^2$   $2s^2 p^3$   $2s^2 p^4$   $2s^2 p^5$   $2s^2 p^6$

According to the variation in period (left to right)  
electron affinity becomes & increases  
so the order of electron affinity is -

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

But in actual it shows different? (experimental data)

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

Here in this case only 'O' and 'F' are shows the actual rule but other elements are doesn't follow the actual variation. This is because 'Ne' is an inert gas (Noble gas) having highly stable electronic configuration and in case of 'N' and 'Be' both having half filled ~~and~~  $p$ -orbital and full-filled  $s$ -orbital & so they also have stable electronic configuration that's why they doesn't have tendency to gain an electron. In case ~~of~~  $B$  ~~and~~  $O$  They have tendency to loose an electron

rather than gain an electron so 'B' electron affinity is lesser and rest of the elements are follow the general tendency of variation in period. i.e.,  $\text{Li} < \text{C} < \text{O} < \text{F}$ .

## ii) Group-17

Group 17 elements are F, Cl, Br, I.

In general tendency as we down in the group the p electron affinity ~~do~~ become decreases so the order become  $\text{F} > \text{Cl} > \text{Br} > \text{I}$ . But in actual case this doesn't observed. 'F' has lesser electron affinity than Cl. Both having tendency to accept electron but Cl has higher space for having electron. In 'F' the 2nd shell is the outermost shell so the size of 'F' is small they ~~has~~ doesn't have ~~space~~ such space like Cl to for ~~having an~~ extra add an electron.

So the correct order is  $\text{Cl} > \text{F} > \text{Br} > \text{I}$ .

Cl has highest electron affinity value in periodic table.

\* Same trend follows in Group 14, 15, 16. In Group-16 'O' has lowest electron affinity.

## Electronegativity :-

Electronegativity is the ability of an atom in a molecule to attract to itself an electron pair that is shared with another atom.

Greater the ability of an atom to attract electron, larger is the value of electronegativity.

It is different from electron affinity which is shown in an isolated gaseous atom but electronegativity of an atom that may be bonded to one or more atoms in a molecule or complex ion.

Single atom does not show electronegativity.

Factors affecting the magnitude of electronegativity:-

The magnitude of electronegativity depends on the following factors -

i) Size of atom: The smaller the size of an atom, greater its tendency to attract towards itself the shared pair of electrons. Smaller atoms have greater electronegativity.

$$\text{Electronegativity} \propto \frac{1}{\text{atom}}$$

ii) Nuclear charge: In a same period higher nuclear charge having atom having higher value of electronegativity. Increasing nuclear charge atomic size decreases. So the electronegativity

become higher.

- iv) Number of inner shell's  $\rightarrow$  The atom with greater number of inner shells has less value of electronegativity than the atom with smaller number of inner shells.
- v) Charge on ~~ion's~~ Electronegativity varies with the change in the charge of the element. The element with more positive charge (cation) more value of electronegativity because of the size of the cation is smaller. Again in case of negatively charged ion (anion) less number of negative charge have more value of electronegativity here also cause of size.  
ex- for cation  $\text{Fe}^{3+}$  Electronegativity of  $\text{Fe}^{3+}$  is higher than  $\text{Fe}^{2+}$   
for anion Electronegativity of  $\text{N}^-$  is higher than  $\text{N}^{2-}$
- vi) Type of hybridisation  $\rightarrow$  The electronegativity of an atom also depends on the type of hybridisation which the atom undergoes in the formation of different bonds in the molecule. The electronegativity increases as the s-character in hybrid orbitals increases.

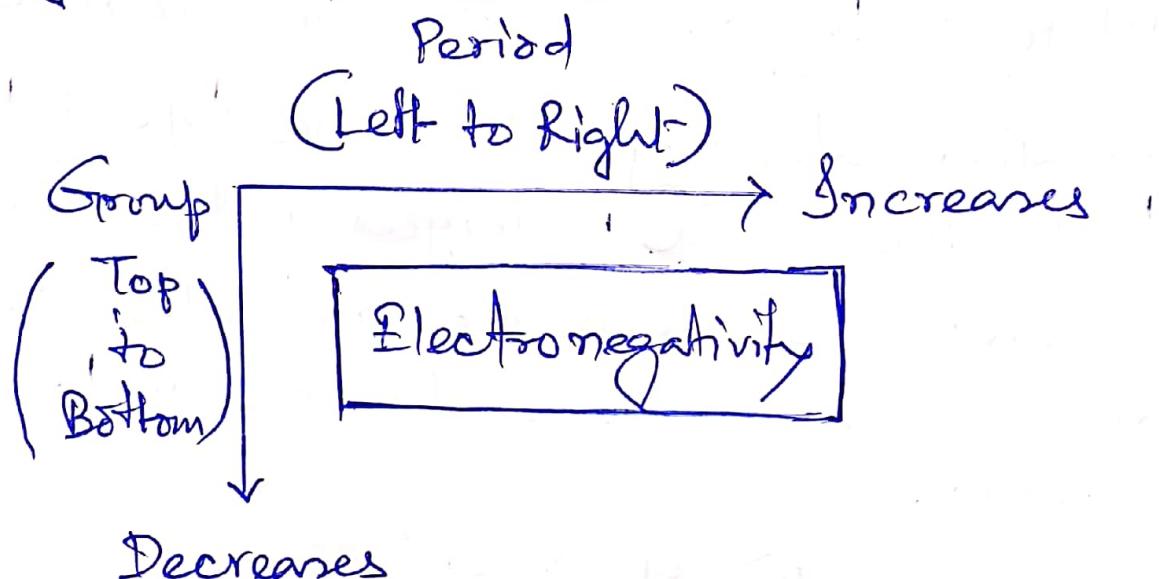


## Variation of Electronegativity in the Periodic Table:-

Along a period, Electronegativity increases from left to right in a period in the periodic table since nuclear charge increases and atomic radius decreases which cause electronegativity to increase across a period.

Along a group, The electronegativity decreases in going down a group due to increasing in atomic radius with increase in atomic number. The addition of extra inner shells in larger atoms screen the shared pair from the nucleus and thus the electron pair is attracted less by the atoms.

Some exceptions show in transition metals in going down the group.



In whole periodic table 'F' is the most-electronegative element.

Scale for measuring electronegativity:-

→ Pauling's Scale of electronegativity: In 1932

Linus Pauling proposed a scale of electronegativity. He based his scale on the difference between the measured bond energy of a molecule  $A-B$  [ $E_{(A-B)}$ ] and the energy excepted for the purely covalent bond  $A-B$  [ $E_{(A-B) \text{ cov}}$ ] that is

$$\Delta E = E_{(A-B)} - E_{(A-B) \text{ cov}}$$

According to him if the two atoms A and B have the same electronegativity value then the molecule  $AB$  is bonded by purely covalent bonds as in homo-nuclear molecules  $A_2$  or  $B_2$ . Then  $E_{(A-B) \text{ cov}}$  would be the mean of  $E_{(A-A)}$  and  $E_{(B-B)}$ , that is

$$E_{(A-B) \text{ cov}} = \frac{1}{2} [E_{(A-A)} + E_{(B-B)}]$$

$$= [E_{(A-A)} \times E_{(B-B)}]^{1/2}$$

$$\therefore \Delta E = E_{(A-B)} - [E_{(A-A)} \times E_{(B-B)}]^{1/2}$$

Pauling proposed empirical expression to correlate  $\Delta E$  with electronegativity difference

$$\chi_A - \chi_B = 0.208 (\Delta E)^{1/2}$$

$$= 0.208 \sqrt{E_{(A-B)} - \sqrt{E_{(A-A)} \times E_{(B-B)}}}$$

$\Delta E$  value's in kcal/mole.

If the  $\Delta E$  value's in KJ/mole then 8.1017 instead of 0.208.

where,  $\chi_A$  = Electronegativity of A

$\chi_B$  = Electronegativity of B

$E_{A-B}$  = Bond energy of the bond A-B

$E_{A-A}$  = Bond energy of the bond A-A

$E_{B-B}$  = Bond energy of the bond B-B

ii) Mulliken scale : According to Mulliken, the electronegativity of an atom is the arithmetic mean of its 1st ionisation energy and its electron affinity

$$\text{i.e., } \text{E.N} = \frac{(\text{I.E}) + (\text{E.A})}{2}$$

Two combining atoms with similar electronegativities form a pure covalent bond.

It is possible to calculate the electronegativity of an element on Pauling scale if its electronegativity is known on Mulliken scale by using the relationship

$$\text{Electronegativity on Pauling scale} \rightarrow \frac{\text{Electronegativity on Multiken scale}}{3.15}$$

iii) Alfred-Rochow scale: Alfred and Rochow proposed an empirical approach to electronegativity based on electrostatic force between the nucleus and electron. They defined electronegativity as electrostatic force ( $F$ ) exerted by the effective nuclear charge ( $Z_{\text{eff}}$ ) on the outermost electron at a distance ' $r$ ' from the nucleus. That is -

$$F \propto \frac{Z_{\text{eff}}}{r^2}$$

where  $r$  = covalent radius of the atom.

$Z_{\text{eff}}$  is calculated according to Slater's rules based on screening effect of intervening electrons.

Some empirical adjustments are then made to bring the calculated electronegativity coefficients in the same range of values as in the Pauling scale to obtain Alfred-Rochow electronegativities  $X_{\text{AR}}$  (AR for Alfred-Rochow).

$$X_{\text{AR}} = 0.359 \times \frac{Z_{\text{eff}}}{r^2} + 0.744$$

Advantages:

- i) Alfred-Rochow method depends on measuring covalent distance which are obtained with greater accuracy by x-ray diffraction. Therefore the  $X_{\text{AR}}$  values are quite accurate.
- ii) The Alfred-Rochow approach is based on the more fundamental and ~~less~~ reasonable dependence of

electrostatic force on distance.

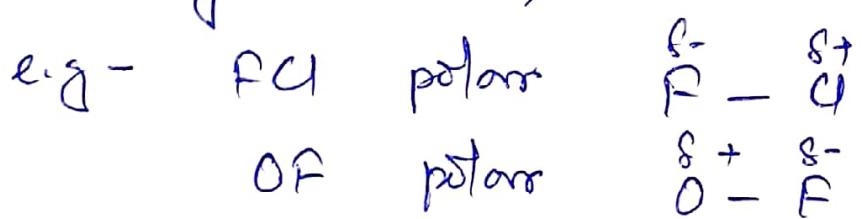
### Disadvantages:-

- i) Slater rules used for calculated  $Z_{eff}$  are empirical and may not give accurate values.
- ii) Covalent radii are inaccurate when the bond order is not known.

### Application of Electronegativity :-

#### Polar, Non-polar bond:-

Electronegativity is a useful concept which indicates the electron distribution between two atoms in a molecule. If two atoms have very similar electronegativities, that is, they have some tendency to attract electrons, the bond is said to be a non-polar bond, as found in a homonuclear diatomic molecules such as  $H_2$ ,  $F_2$ ,  $Cl_2$ . The greater the difference in the electronegativities of the two atoms forming a bond, the more polar is the bond.



#### Nature of bonding:-

Electronegativity values can be used to predict if a bond is non-polar then the

bonding between the atoms is covalent bond.  
 But when a bond is polar than the bonding between the atoms ~~is~~ is covalent or ionic.

Pauling derived an empirical relationship between electronegativity difference and percentage ionic character. This relationship is based on the ionic character present in covalent bond.

Percentage of ionic character

$$\text{present in covalent bond} = 16 |\Delta X| + 3.5 |\Delta X|^2$$

$$\Delta X = X_A - X_B \Rightarrow \text{difference of electronegativity.}$$

Example:- Find the percentage of ionic character in CsF

$$\text{E.N of } \text{Cs} = 0.7 \text{ and } \text{F} = 4.00$$

$$\begin{aligned}\text{Percentage of ionic character} &= 16 |\Delta X| + 3.5 |\Delta X|^2 \\ &= 16 |(\text{Cs} - \text{F})| + 3.5 |(\text{Cs} - \text{F})|^2 \\ &= 16 |0.7 - 4.00| + 3.5 |0.7 - 4.00|^2 \\ &= 90.91\%\end{aligned}$$

## Polarization

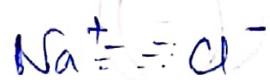
A covalent bond having some ionic character due to the difference in electronegativity of the two atoms. Similarly, ionic bond not at all pure ionic bond (100% ionic bond) they have some covalent character due to interaction between cation and anion.

In a covalent bond there are sharing of electron or shared pair of electron



Sharing of electron

But in a ionic bond complete transfer of electron occurs.



The bonding in ionic substances, we considered the coulombic attraction between two oppositely charged ions.

Anions are large in size than cations, therefore their electron clouds are less tightly bound. A small highly charged cation shall, therefore, distort the electron cloud of large anions. The electron cloud on the anion is pulled towards the cation in a

manner that it increases the electron density between the nuclei. This process is called polarization.

i) Electron cloud of anion gets distorted.

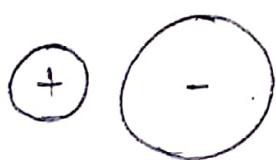
ii) More the polarization, more the covalent character.

The polarization effect produces covalence in molecule because there is some electron density in between the nuclei as in the sharing of electrons in a covalent bond.

The power of an ~~cation~~ ion to distort the other ion is known as its polarizing power.

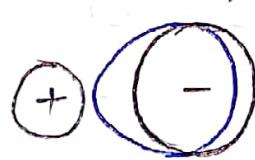
The tendency of the ion to distort is its polarizability.

The polarizing power to distort the other ion is for cation and the ~~tendency~~ tendency to distort is for anion called polarizability.



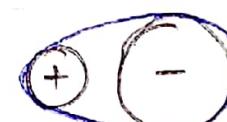
(A)

No polarization



(B)

Polarized anion



(C)

Polarization leading due to covalent bond

This results in deformation of electron cloud on anion, called polarization of anion. Due to small size of the cation, polarization of cation is not so much.

Fajan's rules to explain covalent character in ionic compounds:-

Or

Factors that govern polarization:-

Fajan proposed the following rules to determine the extent of polarization of an anion by a cation, that is, the extent of covalent character induced in an ionic compound.

i) Size of cation: Smaller the size of cation, ~~more~~ ~~stronger~~ ~~attraction~~ have high charged density and therefore it will be able to distort the electron cloud of the anion more effectively. So the small size cation have higher polarizing effect on anion than large size cation.

$$\text{Polarization} \propto \frac{1}{\text{Size of cation}}$$

e.g.  $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+ > \text{Cs}^+$   $\xrightarrow{\text{decreases}}$

ii) Size of anion: Large the size of anion polarizability increases because electron cloud not firmly held by its own nuclear charge and can be ~~more~~ easily polarized by the cation.

Polarization  $\propto$  size of anion.

e.g- Polarizability



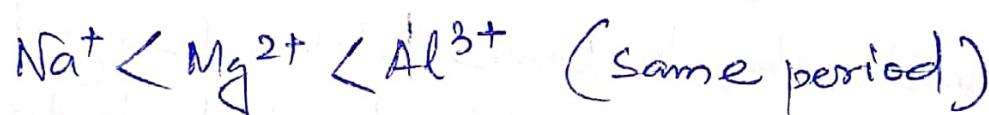
iii) Charge on cation's

Greater the charge on cation, more strongly it attracts the electron cloud of anion.

Higher charge become the smaller in size of cation so the nucleus having higher attraction power.

Polarization of Charge on cation

e.g- Polarizing power



iv) Charge on anion's

Greater the charge on anion, more easily its outermost shell electron cloud is attracted by cation.

Higher the charge on anion become the higher in size of anion so the nucleus are less tightly held the outermost electron.

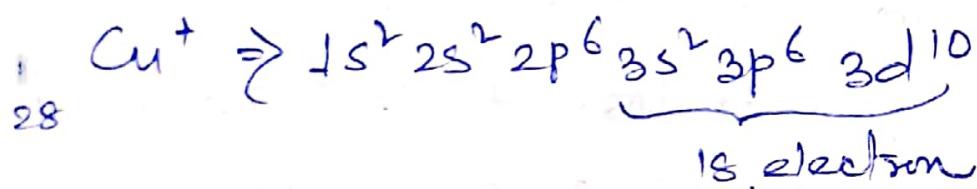
Polarization of Charge on anion

e.g- Polarizability

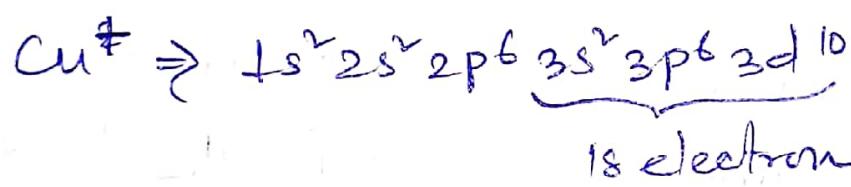
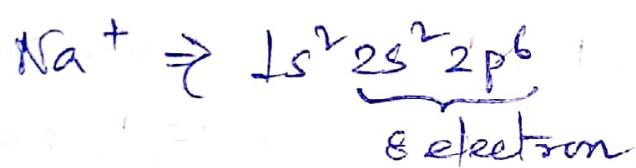


## → Pseudo Noble gas configuration's

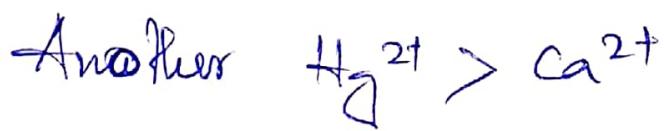
Cation with pseudo noble gas configuration valence shell having 18 electron.



Cation having pseudo inertgas(noble gas) configuration (18 electron in the outermost shell) has greater polarizing power than inertgas configuration (8 electron in the outermost shell).



Here in another reason in case of  $\text{Cu}^+$  having d-subshell, that is ~~become~~ become poor shielding effect. Due to poor shielding effect more effective nuclear charge, nucleus strongly attract the valence shell electron as well as more effectively distort the electron cloud of anion.



## Oxidation States :-

The common oxidation state of an element can be readily predicted from the electronic configuration of its atom. Oxidation states of different elements correspond to the gain or loss of electrons by their atoms so that they acquire a closed shell configuration of eight electrons ( $ns^2 np^6$ ). This tendency is particularly predominant in groups 1, 2 and 13 where the elements acquire noble gas configuration by losing electrons and thus show a single positive oxidation state to their group number. On the other hand, elements on the right side of the periodic table in group 15, 16 and 17 show negative oxidation states varying from -3 to 1. In the fourteenth group (14), the tendency is to form covalent compounds instead of gaining or losing electron.

Rules for determined oxidation number :-

The oxidation number is a measure of the extent of oxidation of an element in its compounds. It is determined by using a set of simple rules:

i) Any element in free state is assigned an oxidation number of zero.

e.g. H, P, S, Br, ~~Cl~~, ~~F~~

ii) The oxidation number of alkali metals elements is +1.

e.g.,  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$

iii) The oxidation number of alkaline earth metals elements is +2.

e.g.:  $\text{Be}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$

iv) The oxidation number of a monoatomic ion is equal to its charge.

e.g.:  $\text{Ca}^{2+}$  is assigned oxidation number equal to +2

$\text{Cl}^-$  is assigned oxidation number equal to -1

v) The sum of the oxidation number of all atoms in a neutral compound is equal to zero.

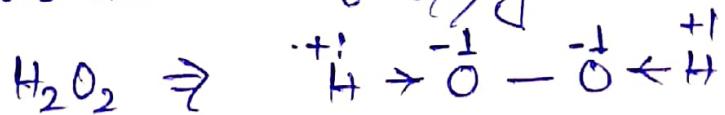
e.g.  $\text{KMnO}_4$  neutral compound oxidation number equal to zero.

vi) F, the most electronegative element, has an oxidation number of -1 in all its compounds. and other halogen group elements i.e; Cl, Br, I have an oxidation number of -1 except when they combined with a more electronegative element.

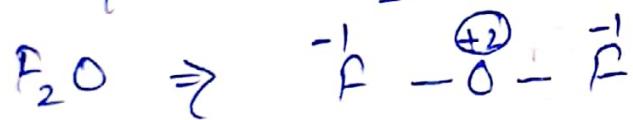
e.g.: In  $\text{ClO}^-$  ion the oxidation number Cl is +1.

vii) In general, Oxygen has an oxidation number -2 in its compounds. However there are three exceptions

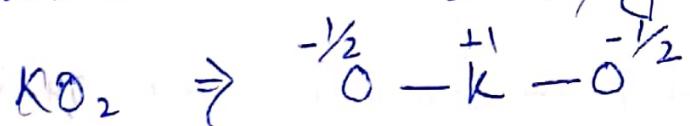
① When formation of a peroxide  $\text{H}_2\text{O}_2$  such as  $\text{H}_2\text{O}_2$ , if it containing oxygen-oxygen bond, the oxidation number of oxygen is -1.



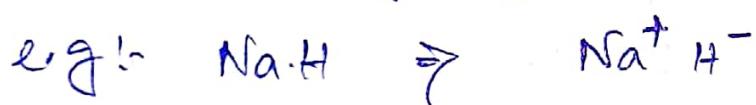
② When oxygen is combined with fluorine as in the compounds  $F_2O$ , its oxidation number is +2.



③ When formation of a superoxides like  $KO_2$ , the oxidation number of oxygen is  $-\frac{1}{2}$ .



viii) Hydrogen in its compounds exhibits an oxidation number of +1, when bonded with nonmetals. The exceptions occur when formation of metal hydride in which hydrogen has an oxidation number of -1.



ix) When an atom is bonded to another same electronegative atom, a molecule consisting of two identical atom. Each atom may have an oxidation number equal to zero. Similarly in  $P_4$ ,  $S_8$ , have oxidation number zero.

x) For complex ion the sum of oxidation numbers of all the atoms is equal to the charge on the ion.

e.g:- In  $PO_4^{3-}$  ion, The sum of oxidation number of P and 4 oxygen atom must be equal to -3.

~~Calculation of oxidation number~~

~~Keeping in mind the above rules we can calculate the oxidation number of any atom in a molecule or ion.~~

## ~~Step 1~~

## Coordination Compound

Before to know about coordination compound, take an idea about types of compounds -

i) Simple salts  $\rightarrow$  This type of compounds easily soluble in water and gives ions.

e.g. -  $\text{NaCl}$  breaks into  $\text{Na}^+$  and  $\text{Cl}^-$

ii) Double salt / Mixed salt  $\rightarrow$  This type of compounds are formed from mixed with two or more ~~other~~ simple salts. Those compounds lose their identity when dissolve in water and its give positive tests for each constituent ion.

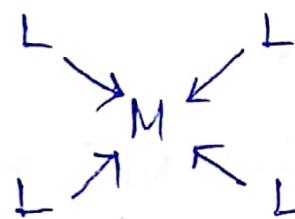
e.g. Mohr's salt  $[\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}]$  get dissociated into water and gives ~~not~~ tests for  $\text{Fe}^{2+}$ ,  $\text{NH}_4^+$ , and  $\text{SO}_4^{2-}$ .

iii) Coordination Compound  $\rightarrow$  Those compound which don't lose their identity in solution are called coordination or complex compounds. They only exists in crystal. The coordinate compound when dissolved in water doesn't give tests of each constituent ion.

e.g. Solution of Potassium ferrocyanide  $K_4[\text{Fe}(\text{CN})_6]$  in water doesn't give positive tests of  $\text{Fe}^{2+}$  and  $\text{CN}^-$  ions, rather a ferrocyanide ion  $[\text{Fe}(\text{CN})_6]^{4-}$  is formed.

In Coordination compound their are formation of coordinate bond (which is one type of covalent bond) in between lewis acid and lewis base.

Central metal atom bonded with ligand.



Important terms in Coordination compounds :-

- i) Ligands: The ion or neutral molecule attached to central atom in coordination compound is called ligand. Ligands are :-
- a) Ligands are neutral molecule or ions.
- b) Ligands have one or more electron pair.
- c) They donate electron pair to central metal atom.
- d) They are lewis base (lone pair donor)
- e) They form coordinate bond with central metal atom.

### Ligands

Inorganic ligands

(+)ve

e.g.  $\text{NO}_2^+$ ,  $\text{NO}_3^+$

(-)ve

e.g.  $\text{NH}_2^-$ ,  $\text{CN}^-$

Neutral

Organic ligands

e.g.:  $\text{C}_5\text{H}_5\text{N}$ ,  $\text{CH}_3\text{NH}_2$

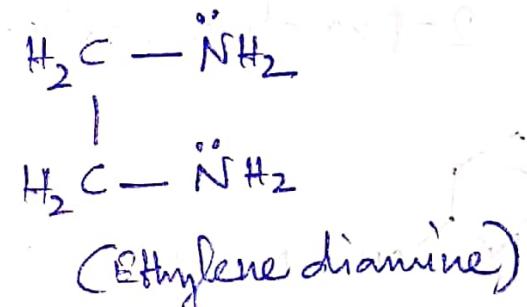
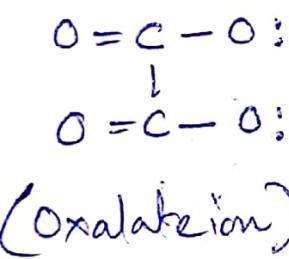
## Different types of ligands :-

1. Monodentate or Unidentate ligands:- A ligand is attached to the central metal atom only by one coordinate bond then the ligand is called as monodentate or unidentate ligand.

e.g:-  $\text{NO}_2^+$ ,  $\text{CN}^-$ ,  $\text{OH}^-$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}$  etc.

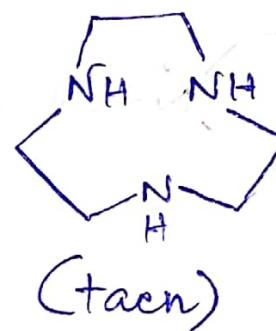
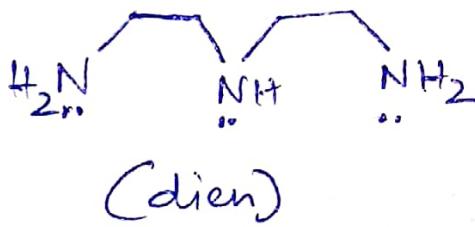
2. Bidentate ligands:- Ligands having two donor atom ~~center~~ are called bidentate ligand.

e.g:-  $\text{C}_2\text{O}_4^{2-}$  (oxalate ion), Ethylene diamine etc.



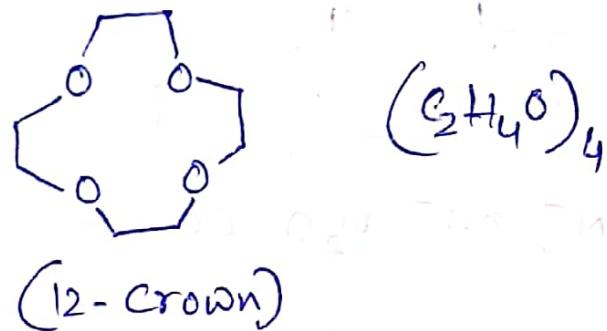
3. Tridentate ligands:- Ligands having three donor ~~center~~ atom are called tridentate ligands.

e.g:- Diethylene triamine (dien), 1,4,7-triazacyclononane (tacn)



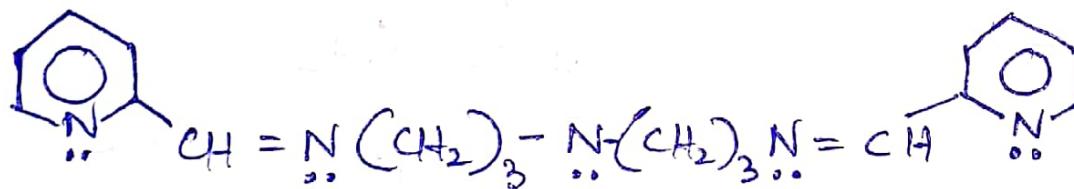
4. Tetradeinate ligands: Ligands having four donor atom are called tetradeinate ligands.

e.g.: Tetraoxacyclododecane (12-crown)



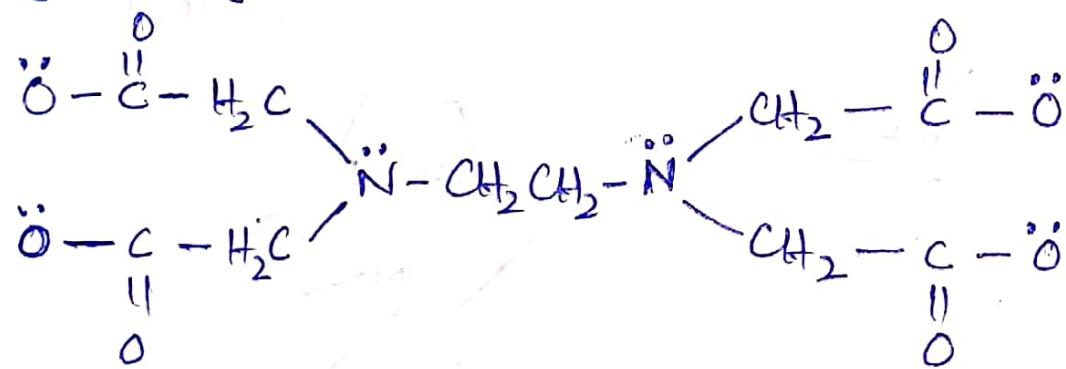
5. Pentadeinate ligands: Ligands having five donor atom are called pentadeinate ligands.

e.g.: 2-pyridine carboxaldehyde.



6. Hexadeinate ligands: Ligands having six donor atom are called hexadeinate ligands.

e.g.: Ethylenediaminetetraacetate (EDTA)



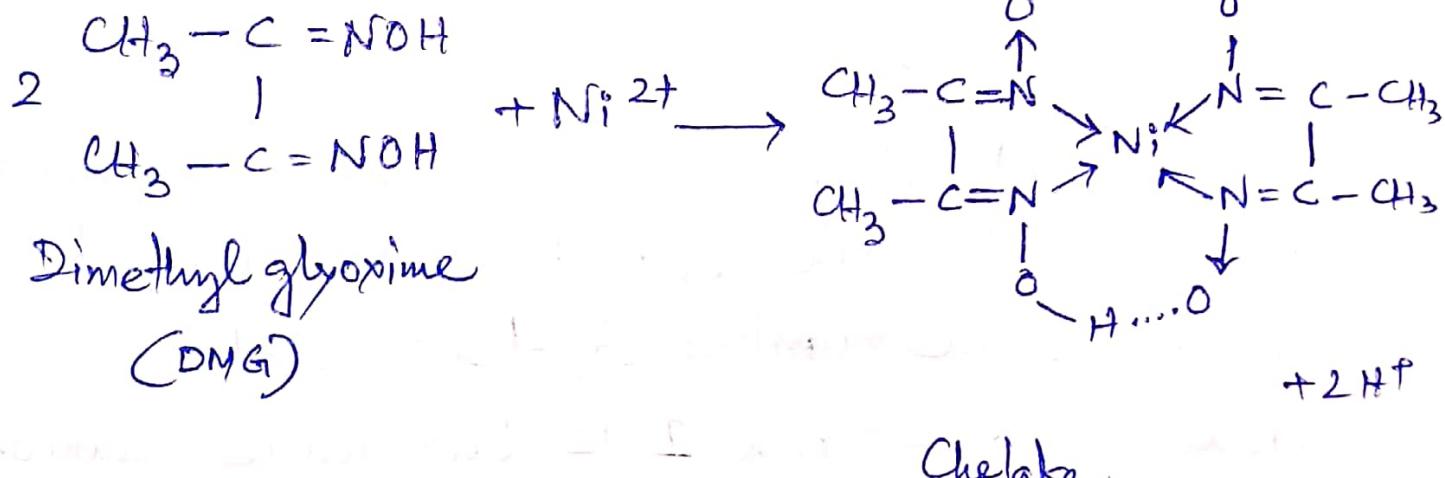
7. Ambidentate ligand: A monodentate ligand is coordinate to a ~~metal atom~~ central metal atom in two places, but not at the same time is called ambidentate ligand.

e.g.:  $\text{NO}_2^-$  can bind to the central metal atom/ion at either the nitrogen atom or one of the oxygen atoms.



8. Chelating ligands: Multidentate or polydentate ligand simultaneously coordinating to a central metal atom/ion through more than one side and formed one or more rings in their structure. Then the ligand is called chelating ligand. The ring structure compounds are called chelate and the process of formation is called chelation. Chelation increase the stability.

e.g.:-



Chelates have been classified as bidentate, tridentate, hexadentate depending upon whether the chelating

agent is bidentate, tridentate or hexadentate respectively.

i) Central metal atom:

- a) Metals are atoms or ion.
- b) Metals having electron deficiency.
- c) They accept electron pair from ligands.
- d) They are lewis acid (lone pair acceptor)

ii) Coordination sphere:

The central metal atom and ligands that are directly attached to it enclosed in square brackets are collectively known as coordination sphere. The ligands and metal atom inside the same square brackets behave as single constituent units.



iv) Coordination number:

Total number of coordination bond formed by ligands with central metal atom is known as coordination number of that metal ion. Coordination number varies from 2-12 but more common are four and six.

Determination of coordination number in different types of ligands:

### Types of ligands

1. Monodentate or Unidentate ligands

### Coordination number

No. of monodentate ligands × 1

2. Bidentate ligands

No. of bidentate ligands × 2

3. Tridentate ligands

No. of tridentate ligands × 3

4. Tetradentate ligands

No. of tetradentate ligands × 4

5. Pentadentate ligands

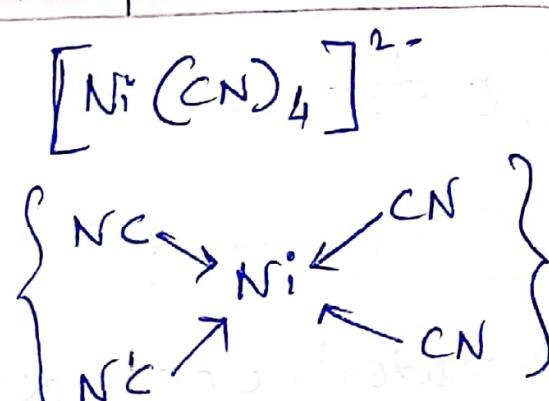
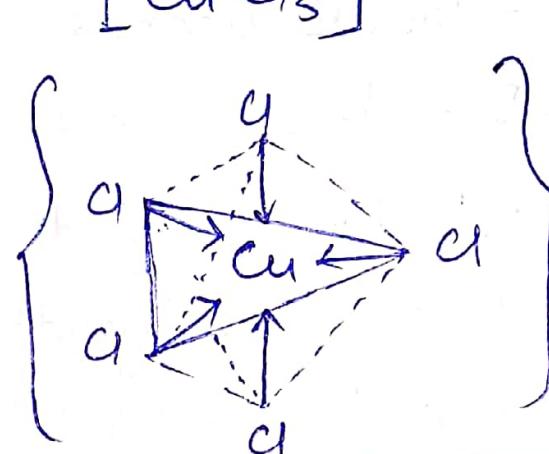
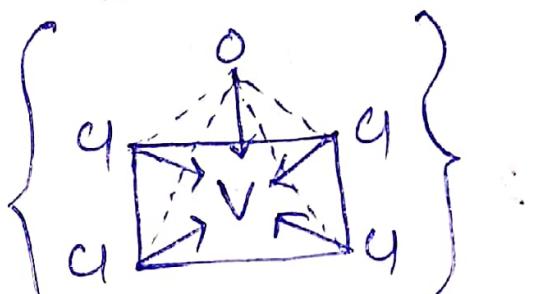
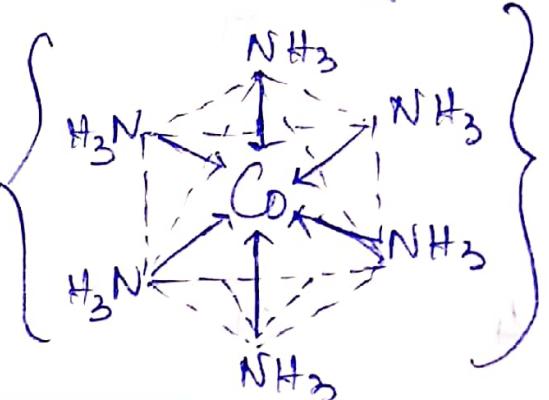
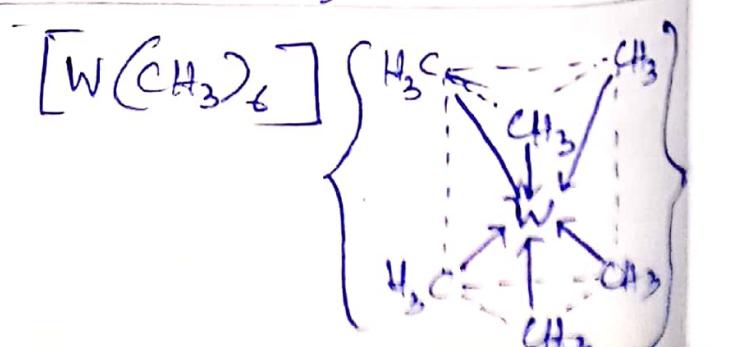
No. of pentadentate ligands × 5

6. Hexadentate ligands

No. of hexadentate ligands × 6

Coordination number determines the coordination geometry

C.N	Hybridisation	Geometry	Example with structure
2	$sp$	Linear	$[Ag(NH_3)_2]^+$ $\{ NH_3 \rightarrow Ag \leftarrow NH_3 \}$
3	$sp^2$	Trigonal planar	$[HgI_3]$ $\{ I \rightarrow Hg \leftarrow I \}$
4	$sp^3$	Tetrahedral	$[CuCl_4]^{2-}$ $\{ Cu \leftarrow Cl \leftarrow Cu \leftarrow Cl \}$

C.N	Hybridisation	Geometry	Example with Geometry
4	$d^2sp^2$	Square planar	$[Ni(CN)_4]^{2-}$ 
5	$d^2sp^3$	Trigonal bipyramidal	$[CuCl_5]^{3-}$ 
5	$d^2sp^3$	Square pyramidal	$[VOCl_4]^{2-}$ 
6	$d^2sp^3$	Octahedral	$[Co(NH_3)_6]^{3+}$ 
6	$sd^5$	Trigonal prismatic	$[W(CH_3)_6]$ 

# Hard and Soft Acids and Bases :-

HSAB principle:-

An acid-base reaction, according to Lewis concept involves the reaction between a donor (A) and an acceptor (B) as to form a complex as given below:



The formation of the stable complex between the donor (A) and the acceptor (B) depend upon the nature of the species (A and B) involved.

Pearson suggested a simple rule for predicting the stability of co-ordinate compound formed between acids and bases (metal ions and ligands) and is often termed as the HSAB principle.

It states that hard acids prefer to bond with hard bases and soft acids prefer to combine with soft bases.

Thus, hard acid will show the following order of preference for bonding with donor atoms or ions within a group.



Soft acids will show the following order of preference for bonding with donor atoms or ions within a group is observed.



Hard acids and bases are not easily polarizable and their interactions are predominately ionic. On the other hand, soft acids and soft bases are usually polarizable and hence their interactions are predominantly covalent.

## Classification of Acids and Bases as Hard and Soft:-

Pearson observed that it is possible to correlate acid-base interactions on the basis of hard and soft acid and bases. He observed that ~~large~~ ~~most~~ metal ions i.e., acids were small, compact and not very polarizable and these preferred ligands i.e., bases that were also small and less polarisable. He called these acids and bases as hard.

On the other hand, the ~~large~~ metal ions and the ligands they prefer, appear to be larger in size and more polarizable. He described these acids and bases as soft.

### Classification of acids:

A general classification of some common hard and soft acids along with some border line cases is given in Table 1.

Table 1. Classification of Lewis acids as hard and soft acids.

Hard acids	Soft acids	Border line acids
$H^+$ , $Li^+$ , $Na^+$ , $K^+$ $Be^{2+}$ , $Mg^{2+}$ , $Ca^{2+}$ , $Sr^{2+}$ $Al^{3+}$ , $Sc^{3+}$ , $Ga^{3+}$ , $In^{3+}$ , $La^{3+}$ $Cr^{3+}$ , $Co^{3+}$ , $Fe^{3+}$ , $As^{3+}$ , $Ce^{3+}$ $Si^{4+}$ , $Ti^{4+}$ , $Zr^{4+}$ , $Th^{4+}$ , $Pu^{4+}$ $BF_3$ , $BCl_3$ , $AlCl_3$ , $AlH_3$ , $Al(CH_3)_3$ $Cl^{3+}$ , $Cl^{7+}$ , <del><math>I^{5+}</math></del> , $I^{7+}$ $RCO^+$ , $CO_2$ , $NC^+$ $H \times (H\text{-bonding molecules})$	$Cu^{2+}$ , $Ag^+$ , $Au^+$ , $Tl^+$ , $Hg^+$ $Pt^{2+}$ , $Cd^{2+}$ , $Pt^{2+}$ , $Hg^{2+}$ , $Pt^{4+}$ $Ti^{3+}$ , $BH_3$ , $GaCl_3$ , $GaBr_3$ $GaI_3$ , $InCl_3$ $I^-$ , $Br^-$ , $HO^-$ , $RO^-$ $I_2$ , $Br_2$ , $ICN$ $O$ , $Cl$ , $Br$ , $I$ , $N$ , $RO$ , $RO_2$ $M^\circ$ (metal atom) $CH_2$ , carbenes	$Fe^{2+}$ , $Co^{2+}$ , $Ni^{2+}$ , $Cu^{2+}$ , $Zn^{2+}$ $Sb^{3+}$ , $Bi^{3+}$ , $NO^+$ $SO_2$ , $B(CH_3)_3$ , $GaH_3$ $Rh^{3+}$ , $Ir^{3+}$ , $Ru^{3+}$ $Rg^{3+}$ , $Sn^{2+}$ , $Pb^{2+}$

An inspection of Table 1. reveals that hard acids usually have the following characteristics:

- i) Hard acids are cations of smaller size
- ii) Hard acids are cations of higher oxidation state.  
(For example :  $Cl^{3+}$ ,  $Cl^{7+}$ ,  $I^{5+}$  and  $I^{7+}$ )

iii) Hard acids are molecules/cations with lesser number of valence electrons.

iv) Hard acids hold the valence electrons tightly and consequently are not easily polarizable.

In summary, hard acids bind strongly to a proton. Hard acids are small sized, compact and are not easily polarised.

Once again from the table.1. also reveals that soft-acids possess the following characteristics.

i) Soft-acids are cations of the large size or heavier elements

ii) Soft-acids are cations of lower charge

iii) Soft-acids are molecules/ions with large number of valence electrons.

iv) Soft-acids don't hold the valence electrons tightly and are, therefore, easily polarisable.

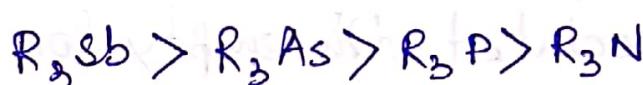
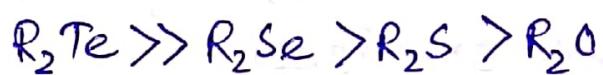
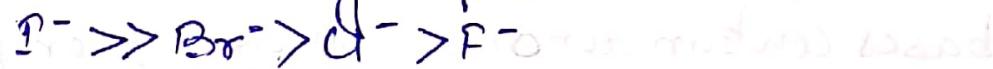
In summary, soft-acids are large sized and easily polarizable ions/molecules that bind strongly to highly polarisable ion/molecule.

It is important to note that there is no sharp division between hard and soft-acids. There are a number of Lewis acids ~~that~~ that are neither too hard nor too soft-acids.

Such types of acids that are neither ~~too~~ hard nor soft-are called borderline acids which are shown in Table.1.

Borderline acids have properties which are intermediate between that of a hard acid and a hard base. In case of borderline acids, the properties such size, oxidation states and polarizability of the cation/molecule are neither too low nor too high.

On the other hand, soft-acids will show the opposite trend and the following order of preference for binding the donor atoms/ions within a group is observed.



## Classification of bases:

A general classification of some commonly used ligands (i.e., Lewis bases) into hard and soft bases, along with the border line bases is presented in Table 2.

Table 2: Classification of Lewis bases:

Hard Bases	Soft-Bases	Border line Bases
$F^-$ , $Cl^-$	$H^-$ , $R^-$ , $I^-$	$Br^-$
$NH_3$ , $RNH_2$ , $N_2H_4$	$C_2H_4$ , $C_6H_6$	$C_6H_5N$ , $C_6H_5NH_2$
$ROH$ , $R_2O$ , $R_2C=O$ , $RO^-$	$RSH$ , $R_2S$ , $RS^-$	$N_2$ , $N_3^-$ , $NO_2^-$
$H_2O$ , $OH^-$ , $O_2^{2-}$	$CN^-$ , $SCN^-$ , $S_2O_3^{2-}$	$NO_2^-$ , $SO_3^{2-}$
$SO_4^{2-}$ , $PO_4^{3-}$ , $CH_3COO^-$ , $ClO_4^-$	$R_3P$ , $(RO)_3P$ , $R_3As$	$CO$ , $RNC$
$NO_3^-$		
$R = Alkyl$		

A glance at the table 2 reveals some of the important characteristics of hard bases:

- i) Hard bases bind strongly to the proton.
- ii) Hard bases contain donor atoms of high electronegativity.
- iii) The donor atoms in hard bases possess low polarizability.
- iv) The hard bases are not easily oxidized.
- v) Hard bases contain empty orbitals of high energy.

In summary, hard bases bind strongly to a proton. The donor atom in case of hard bases is of high electronegativity and of low polarizability.

A further inspection of table 2, reveals that the following features are observed in case of soft-bases:

- i) Soft-bases contain donor atoms of low electronegativity.
- ii) Soft-bases contain donor atoms of higher polarizability.
- iii) Soft-bases get easily oxidized.
- iv) Soft-bases are associated with empty low lying energy orbitals.

In brief, soft bases contain less electronegative non-metals (including C, S, P and I). The donor atoms in such bases possess donor atoms that are easily polarized.

Just as there are borderline acids, there are ~~are~~ borderline bases also. The properties of borderline bases are in between those of the soft and hard bases.

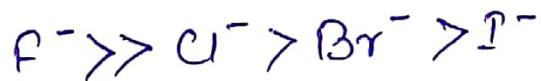
It is important to note that the categories are not rigidly divided. For example, the halide ions form a series from the very hard fluoride ion through the hard-borderline chloride ion to the borderline bromide ion and the soft iodide ion.

Pearson's HSAB principle:-

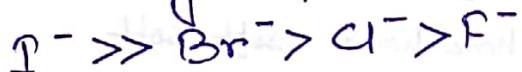
Pearson proposed a simple rule for predicting the stability of co-ordinate compound formed between acids and bases (metal ions and ligands) and is often termed as the HSAB principle.

It states that hard acids prefer to bond to hard bases and soft acids prefer to combine with soft bases.

Thus, hard acids will show the following order of preference for bonding with donor atom or ion within a group.



Soft acids will show the opposite trend and the following order of preference for bonding the donor atoms or ions within a group is observed.



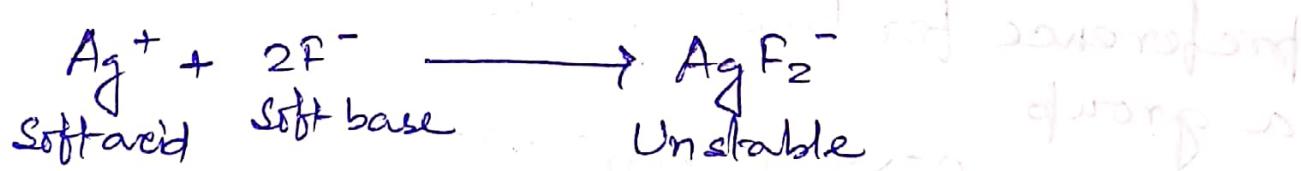
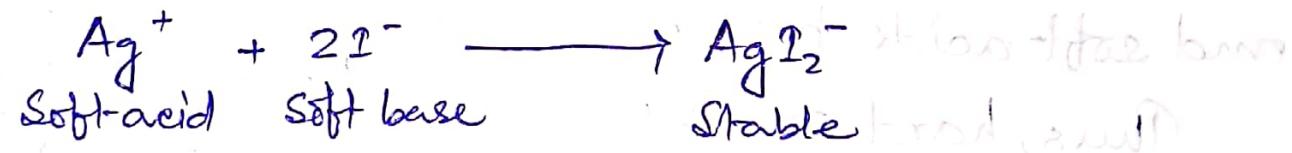
Hard acids and bases are not easily polarizable and their interactions are predominately ionic. On the other hand, soft-acids and soft-bases are usually polarizable and hence their interactions are predominantly covalent.

Applications of HSAB principle:-

a) Stability of complexes:- This principle explains the special stability of complexes formed by hard-hard and soft-soft-interactions. This has nothing to do with the actual acidic or basic strengths of acids or bases. For example, both  $\text{OH}^-$  and  $\text{F}^-$  are hard bases and although  $\text{OH}^-$  is a few stronger base than  $\text{F}^-$ , yet these are treated equally by the HSAB principle.

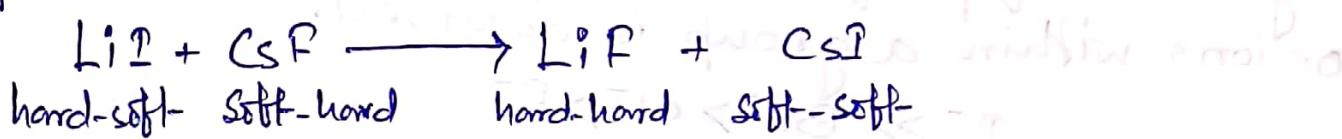
We can predict the stability of certain complexes on the basis of hard-hard and soft-soft-preferences.

For example, the complex between a soft-acid,  $\text{Ag}^+$  and soft-base  $\text{I}^-$  is quite stable contrast to the one between  $\text{Ag}^+$  and hard base  $\text{F}^-$ .



b) Course of reaction:- We can also predict the course of a reaction by the use of this principle.

For example, reaction between  $\text{LiI}$  and  $\text{CsF}$  always proceeds to give  $\text{LiF}$  and  $\text{CsI}$ .



There is preferential stability due to hard-hard and soft-soft combinations. Similarly reaction between  $\text{CaS}$  and  $\text{H}_2\text{O}$  proceeds towards the right to give  $\text{CaO} \cdot$



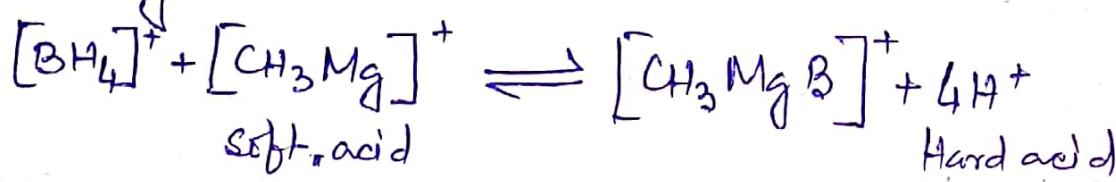
Formation of cuprous iodide by reaction between cupric iodide and cuprous fluoride is another example of hard-hard preference



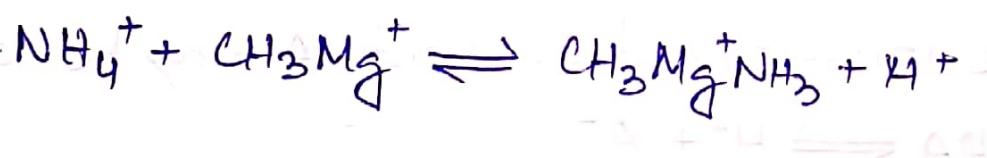
3) Poisoning of metal catalyst:- Soft metals (eg Pd, Pt etc) act as catalyst and they are easily poisoned by soft bases such as CO, P or As ligands because both (soft acid + soft base) form stable compound and block the active sites of catalysed.

d) Rate of chemical reactions: The HSAB principle can be correlated to the rate of chemical reaction. The rate of electrophilic and nucleophilic reaction depends upon the Hardness and Softness of the acids and bases.

e) Prediction of Hardness and Softness:- Suppose we have to predict the hardness or softness of base B in the following reaction



If equilibrium shift towards



If equilibrium shift towards right- Then B is a soft base (soft-acid + soft-base). If the equilibrium shift towards the left- Then A<sup>-</sup> is a hard base (hard acid + hard base)

The major limitations of HSAB principle:

- i) HSAB principle is too general and without any qualitative scale of measurement.
- ii) HSAB principle does not take into consideration the acidic or basic character of the compounds.
- iii) HSAB principle fails to explain the feasibility of the reaction and due to soft-soft interaction the following reaction should take place



$$\Delta H = 86 \text{ kcal/mole}$$

Inspite of the soft-soft- ( $\text{CH}_3^+ - \text{H}^-$ ) interaction this reaction should not proceed due to that their indicator acidity ( $\text{H}^+$ ) of proton.

# Molecular Geometry Chart

# of Electron Groups	Number of Lone Pairs	Electron Pair Arrangement	Molecular Geometry	Approximate Bond Angles
2	0	linear		180°
3	0	trigonal planar		120°
	1	bent		<120°
4	0	tetrahedral		109.5°
	1	trigonal pyramid		<109.5° (~107°)
	2	bent		<109.5° (~105°)
5	0	trigonal bipyramidal		90°, 120°
	1	see-saw		<90°, <120°
	2	T-structure		<90°
	3	linear		180°
6	0	octahedral		90°, 90°
	1	square pyramidal		90°, <90°
	2	square planar		90°