Chapter 01

Periodic Table and Periodic Properties

CONTENT

- Periodicity
- Long Form Of Periodic Table
- Ionisation Energy/ Enthalpy
- Electro-Negativity

- Development Of Modern Periodic Table
- Atomic Radius
- Electron Affinity (Ea) /Electron Gain Enthalpy ($\Delta H_{e.g}$)

PERIODIC TABLE OF THE ELEMENTS

PERIODICITY

Along a Period ($\longrightarrow$)
Along a Group ($\downarrow$)

$\longrightarrow$ Max.   Z $\longrightarrow$

Constant

Max.

Z* (effective due to screening) $\longrightarrow$

r_n (atomic, ionic radius) $\longleftarrow$ Cation smaller than atom, anion larger than atom
Fe, Co, Ni have size, also Zr, Hf

(I.P.) $\longrightarrow$ Be > B, N > O, inert gas max, $I_1 < I_2 < I_3$ ....

(Electronegativity) $\longrightarrow$ Inert gas zero

(Electron-affinity) $\longrightarrow$ Inert gas zero, Cl > F, S > O, P > N

(Hydration and Hydration Energy) $\longleftarrow$

(Size of Hydrated ion) $\longrightarrow$ (for cations)

(Polarising Power of cation) $\longrightarrow$ $Na^+ < Mg^{2+} < Al^{3+}$

(Polarising Power of anion) $\longleftarrow$ $N^{3-} > O^{2-} > F^-$

(Acidic nature of oxides) $\longleftarrow$

(Basic nature of oxides) $\longleftarrow$

(Reactivity) $\longleftarrow$

(Reducing Nature) $\longleftarrow$

$K^+ < Na^+ < Li^+$

➢ Isoelectric ions have different size.
➢ Inert pair effect is in p-block. Stability of higher oxidation state decreases and that of lower oxidation state increases going along a group. $Ge^{2+} < Sn^{2+} < Pb^{2+}$
➢ Reducing nature of hydride increases in a group and decreases in a period.

Facts to be remembered :

1. Seven Periods:

1st Period	:	2 elements	:	Shortest period
2nd & 3rd Period	:	8 elements	:	Short period
4th & 5th period	:	18 elements	:	Long period
6th period	:	32 elements	:	Longest period
7th period	:	Incomplete period		

2. 18 groups

Alkali Metals   :   IA / 1st group
Alkaline earth metals   :   IIA / 2nd group

⎫ s-block

Coinage Metals   :   IB / 11th group

Pnicogens   :   VA / 15th group

Chalcogens   :   VIA / 16th group

Halogens   :   VIIA / 17th group

Noble gases or inert gases or zero group   : 18th group

3. Configurations:

s–Block   : $ns^1 – ns^2$
p–Block   : $ns^2 np^{1–6}$ ⎫ Representative elements
d-Block   : $(n-1)d^{1–10}$ $ns^{0\ or\ 1–2}$ ⎫ transition elements

f–Block   : $(n-2)f^{0-14}$ $(n-1)d^{0, 1\ or\ 2}$ ns^2 $\rbrack$ Inner transition elements

4. Non metal liquid at room temperature = Bromine
5. Metal liquid at room temperature = Mercury
6. Metals with very low Melting point
   Ga = 29.8°C
   Cs = 28.5°C
   Fr = 27.0°C
7. Tungsten is
   (a) Most tensile (b) Highest boiling metal   (c) Highest melting metal
8. Oxygen is the *most abundant element* & Al is the *most abundant metal*
9. Carbon is the *highest* boiling non-metal. (4827°C)
10. Osmium and Iridium are the *densest* elements & Lithium is the *lightest* metal : d = 0.54gm/cc
11. Silver is the *best conductor of electricity*. Copper is the *second best conductor of electricity*
12. Diamond is the *hardest* substance known.
13. Osmium & Ruthenium shows *maximum Oxidation state* : +8
14. Tin(Sn) has maximum number of isotopes: 10 isotopes
15. Fluorine is the *most electronegative element* & Cesium is the *most electropositive element*.
16. Inert pair effect is exhibited by 13th, 14th & 15th group elements. That too from 4th period & down.
17. Diagonal relationship is between:

   Li   Be   B   C

   Na   Mg   Al   Si
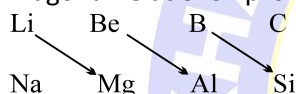
18. Elements of 2nd & 3rd period are known as *Typical elements*.
19. The typical elements of 3rd period are also known as *Bridge elements*.

   Prediction of Period, Group and Block of a Given Element

   The period, group and block of an element can be easily predicted from its electronic configuration as follows :

   (i) The period of an element corresponds to the principal quantum number of the valence shell.

   (ii) The block of an element corresponds to the type of orbital which receives the last electrons.

   (iii) The group of an elements is predicted from the number of electrons in the valence shell or/and penultimate shell last but one, i.e. (n–1) as follows :

   (a) For s-block elements, group number is equal to the number of valence electrons.

   (b) For p-block elements, group number is equal to 10 + number of electrons in the valence shell.

   (c) For d-block elements, group number is equal to the number of electrons in (n–1) d-subshell + number of electrons in valence shell (nth shell) .

DEVELOPMENT OF MODERN PERIODIC TABLE

(a) Dobereiner's Triads :

He arranged similar elements in the groups of three elements called as triads, in which the atomic mass of the central element was merely the arithmetic mean of atomic masses of other two elements or all the three elements possessed nearly the same atomic masses

$$\begin{bmatrix} Cl & Br & I \\ 35.5 & \boxed{80.0} & 127 \end{bmatrix} \quad \frac{35.5 + 127}{2} = 81.2 \quad \text{At. wt of Br}$$

$$\begin{bmatrix} Ca & Sr & Ba \\ 40 & \boxed{87.5} & 137 \end{bmatrix} \quad \frac{40 + 137}{2} = 88.5 \quad \text{At. wt of Sr}$$

$$\begin{bmatrix} Li & Na & K \\ 7 & \boxed{23} & 39 \end{bmatrix} \quad \frac{7 + 39}{2} = 23 \quad \text{At. wt of Na}$$

It was restricted to few elements, therefore, discarded

Other examples – (K, Rb, Cs), (P, As, Sb), (S, Se, Te), (H, F, Cl), (Sc, Y, La)

(b) Newland's Law of Octave :

He was the first to correlate the chemical properties of the elements with their atomic masses.

According to him if the elements are arranged in the order of their increasing atomic masses the eighth element starting from given one is similar in properties to the first one.

This arrangement of elements is called as Newland's law of Octave.

Li Be B C N O F

Na Mg Al Si P S Cl

K Ca

This classification worked quite well for the lighter elements but it failed in case of heavier elements and, therefore, discarded

Drawback or Limitation :

(a) This rule is valid only upto Ca. because after Ca due to presence of d-block element there is difference of 18 elements instead of 8 element.

(b) After the discovery of Inert gas and included in the periodic table it becomes the 8th element from Alkali metal so this law had to be dropped out.

(c) He failed in the case of heavier metals as Fe has been placed atoms with O and S.

(d) Newland placed Co and Ni in the same slot as that F, Cl, Br to fit elements in the table despite having dissimilar properties.

(c) Lothar Meyer's Classification :

He determined the atomic volumes by dividing atomic mass with its density in solid states. He plotted a graph between atomic masses against their respective atomic volumes for a number of elements. He found the following observations.
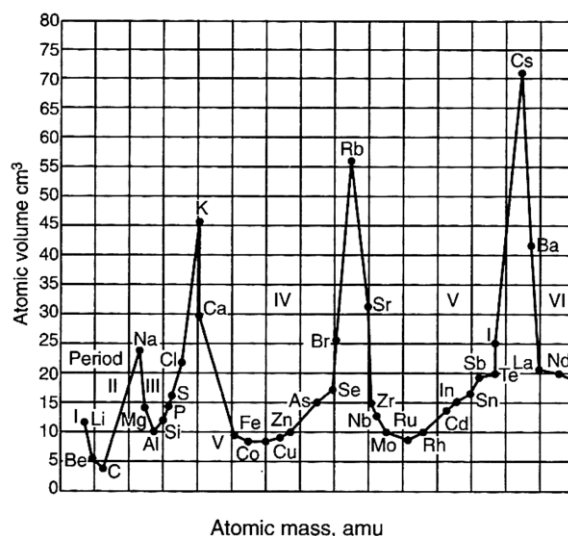
Lothar Meyer's Curve

(i) Elements with similar properties occupied similar positions on the curve.

(ii) Alkali metals having larger atomic volumes occupied the crests.

(iii) Transitions elements occupied the trough.

(iv) The halogens occupied the ascending portions of the curve before the inert gases.

(v) Alkaline earth metals occupied the positions at about the mid points of the descending portions of the curve.

On the basis of these observations he concluded that the atomic volumes (a physical property) of the elements are a periodic function of their atomic masses. It was discarded as it lacks practical utility.

(d) Mendeleev's Periodic Table :

Mendeleev's Periodic's Law

According to him the physical and chemical properties of the elements are a periodic function of their atomic masses.

He arranged then known elements in order of their increasing atomic masses considering the facts that elements with similar properties should fall in the same vertical columns and leaving out blank spaces where necessary.

The table is divided into nine vertical columns called groups and seven horizontal rows called periods.

Periods	No. of Elements	Called as
1st n = 1	2	Very short period
2nd n = 2	8	Short period
3rd n = 3	8	Short period
4th n = 4	18	Long period
5th n = 5	18	Long period
6th n = 6	32	Very long period
7th n = 7	19	Incomplete period

The groups were numbered as I, II, III, IV, V, VI, VII, VIII and Zero group

Each group up to 7th is divided into A & B sub groups 'A' sub group elements are called normal elements and 'B' sub groups elements are called transition elements.

The 8th groups consisted of 9 elements in three rows.

Merits of Mendeleev's Periodic table :

(i) It has simplified and systematized the study of elements and their compounds

(ii) It has helped in predicting the discovery of new elements on the basis of the blank spaces given in its periodic table. Mendeleev's left the gap under aluminium and a gap under silicon, and called these elements **Eka-Aluminium** and **Eka-Silicon.**

(iii) Atomic weights of elements were corrected. Atomic weight of Be was calculated to be 3 × 4.5 = 13.5 by considering its valency 3, was correctly calculated considering its valency 2 (2 × 4.5 = 9).

Other corrections of doubt full atomic weights eg. U, Be, In, Pt, Au.

Demerits in Mendeleev's Periodic Table :

(i) Position of hydrogen is uncertain. It has been placed in lA and VIIA groups because of its resemblance with both the groups.

(ii) No separate positions were given to isotopes.

(iii) It is not clear whether the lanthanides and actinides are related to IIA or IIIB group.

(iv) Order of increasing atomic weights is not strictly followed in the arrangement of elements in the periodic table. For e.g.–Ar(At.wt.39.94) is placed before K(39.08) and Te (127.6) is placed before I (126.9)

(v) Similar elements were placed in different groups(Cu IB and Hg IIB) and the elements with different properties were placed in same groups(alkali metals IA and coinage metals IB)

(vi) It didn't explained the cause of periodicity.

⎯⎯⎯⎯⎯⎯⎯⎯◇◇◇◇◇◇◇◇◇◇◇◇◇⎯⎯⎯⎯⎯⎯⎯⎯

LONG FORM OF PERIODIC TABLE

MODERN PERIODIC LAW (MOSELEY'S PERIODIC LAW)

Physical and chemical properties of elements are the periodic functions of their atomic number. If the elements are arranged in order of their increasing atomic number, after a regular interval, element with similar properties are repeated.

Cause of Periodicity:

The periodic repetition of the properties of the elements is due to the recurrence of similar valence shell electronic configuration after certain regular intervals. For example, alkali metals have same electronic configuration ns^1, therefore, have similar properties.

The long form of periodic table is the contribution of Range, Werner, Bohr and Bury

This table is also referred to as Bohr's table since it follows Bohr's scheme of the arrangements of elements into four types based on electronic configuration of elements

The periodic table is divided into 18 groups and 7 periods.

(i) Each period consists of a series of elements having same valence shell.

(ii) Each period corresponds to a particular principal quantum number of the valence shell present in it.

(iii) Each period starts with an alkali metal having outermost electronic configuration ns^1.

(iv) Each period ends with a noble gas with outermost electronic configuration ns^2np^6 except Helium having outermost electronic configuration $1s^2$.

(v) The number of elements in a period is equal to the number of necessary electrons to acquire ns^2np^6 configuration in the outermost shell of first element (alkali metal) of the period. First period contains two elements.

(vi) Each period starts with the filling of new energy level.

(vii) henry Moseley observed regularities in the characteristics X-ray spectra of the elements. A plot of $\sqrt{v}$ (where v is frequency of X-rays emitted against atomic) number (Z) gave a straight line and not the plot of $\sqrt{v}$ us atomic mass. He thereby showed that the atomic number is a more fundamental property of an element that its atomic mass.

$\sqrt{v}$ = a + (z – b)

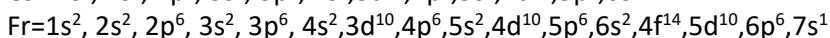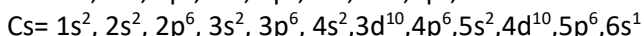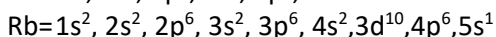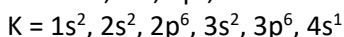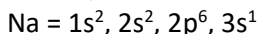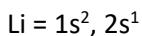v = frequency of light

a, b = constant

z = atomic no.

DESCRIPTION OF GROUPS –
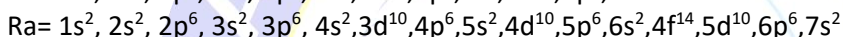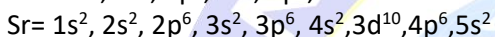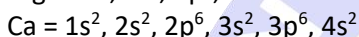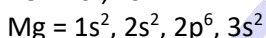
1st/IA/Alkali metals :

H = 1s^1

Li = 1s^2, 2s^1

Na = 1s^2, 2s^2, 2p^6, 3s^1

K = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1

Rb=1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2,3d^{10},4p^6,5s^1

Cs= 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2,3d^{10},4p^6,5s^2,4d^{10},5p^6,6s^1

Fr=1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2,3d^{10},4p^6,5s^2,4d^{10},5p^6,6s^2,4f^{14},5d^{10},6p^6,7s^1
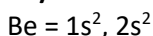
General electronic configuration = **ns**^{1}(n = Number of shell)

Number of valence shell e$^-$ = 1

2nd/IIA/Alkali earth metals :

Be = 1s^2, 2s^2

Mg = 1s^2, 2s^2, 2p^6, 3s^2

Ca = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2

Sr= 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2,3d^{10},4p^6,5s^2

Ba= 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2,3d^{10},4p^6,5s^2,4d^{10},5p^6,6s^2

Ra= 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2,3d^{10},4p^6,5s^2,4d^{10},5p^6,6s^2,4f^{14},5d^{10},6p^6,7s^2
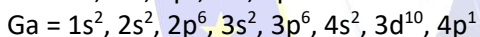
General electronic configuration = **ns**^{2}

Number of valence shell e$^-$ = 2

13th/IIIA/Boron Family :

B = 1s^2, 2s^2, 2p^1

Al = 1s^2, 2s^2, 2p^6, 3s^2, 3p^1

Ga = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^1

In=1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6,5s^2,4d^{10},5p^1

Tl=1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6,5s^2,4d^{10},5p^6,6s^2,4f^{14},5d^{10},6p^1

Nh=1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6,5s^2,4d^{10},5p^6,6s^2,4f^{14},5d^{10},6p^6,7s^2,5f^{14},6d^{10},7p^1
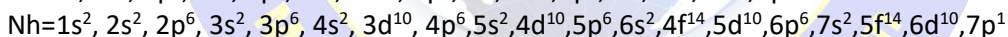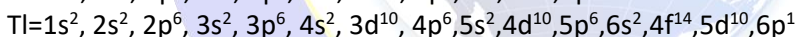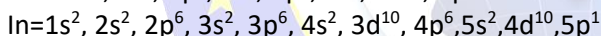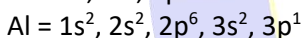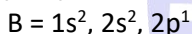
General electronic configuration = **ns**^{2} **np**^{1}

Number of valence shell e$^-$ = 3

14th/IVA/Carbon Family :

C = 1s^2, 2s^2, 2p^2

Si = 1s^2, 2s^2, 2p^6, 3s^2, 3p^2

Ge = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^2

Sn= 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6,5s^2,4d^{10},5p^2

Pb=1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6,5s^2,4d^{10},5p^6,6s^2,4f^{14},5d^{10},6p^2

Fl=1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6,5s^2,4d^{10},5p^6,6s^2,4f^{14},5d^{10},6p^6,7s^2,5f^{14},6d^{10},7p^2
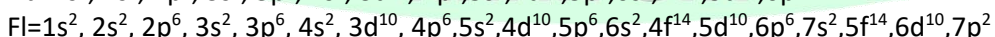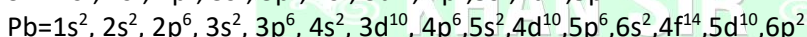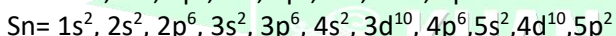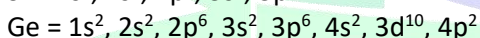
General electronic configuration = **ns**^{2} **np**^{2}

Number of valence shell e$^-$ = 4

15th/VA/Nitrogen family/Pnicogen : (Used in fertilizer as urea)

N = 1s^2, 2s^2, 2p^3

P = 1s^2, 2s^2, 2p^6, 3s^2, 3p^3

As = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^3

Sb= 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6,5s^2,4d^{10},5p^3

Bi=1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6,5s^2,4d^{10},5p^6,6s^2,4f^{14},5d^{10},6p^3

Mc=1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6,5s^2,4d^{10},5p^6,6s^2,4f^{14},5d^{10},6p^6,7s^2,5f^{14},6d^{10},7p^3
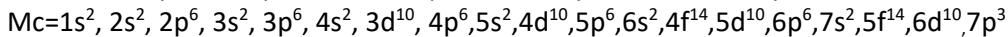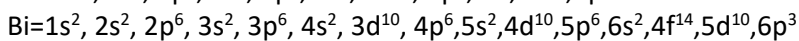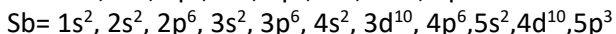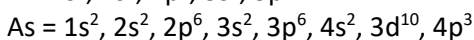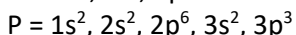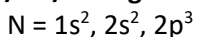
General electronic configuration = **ns**^{2} **np**^{3}

Number of valence shell e^- = 5

16th/VIA/Oxygen family/Chalcogen : (Ore forming)

O = $1s^2, 2s^2, 2p^4$

S = $1s^2, 2s^2, 2p^6, 3s^2, 3p^4$

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

Te= $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^4$

Po= $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2, 4f^{14}, 5d^{10}, 6p^4$

Lv= $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2, 4f^{14}, 5d^{10}, 6p^6, 7s^2, 5f^{14}, 6d^{10}, 7p^4$

General electronic configuration = **$ns^2\, np^4$**

Number of valence shell e^- = 6

17th/VIIA/Halogen family/Halogens : (Salt forming)

F = $1s^2, 2s^2, 2p^5$

Cl = $1s^2, 2s^2, 2p^6, 3s^2, 3p^5$

Br = $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^5$

I= $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^5$

At= $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2, 4f^{14}, 5d^{10}, 6p^5$

Ts= $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2, 4f^{14}, 5d^{10}, 6p^6, 7s^2, 5f^{14}, 6d^{10}, 7p^5$

General electronic configuration = **$ns^2\, np^5$**

Number of valence shell e^- = 7

18th/Zero group/Inert gases/Noble gases :

Ne = $1s^2, 2s^2, 2p^6$

Ar = $1s^2, 2s^2, 2p^6, 3s^2, 3p^6$

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

Xe= $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6$

Rn= $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2, 4f^{14}, 5d^{10}, 6p^6$

Og= $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2, 4f^{14}, 5d^{10}, 6p^6, 7s^2, 5f^{14}, 6d^{10}, 7p^6$

General electronic configuration = **$ns^2\, np^6$** (except. He)

Number of valence shell e^- = 8

Important Points :

(a) 2nd period elements (Li, Be, B) Shows diagonal relationship with 3rd period elements (Mg, Al, Si), so (Li, Be, B) are called Bridge elements. Because of same ionic potential (Ionic potential = Charge/Radius) value they shows similarity in properties.
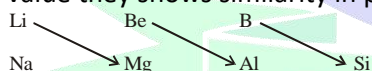
(b) 3rd period elements (Na, Mg, Al, Si, P, S, Cl) are called typical elements because they represent the properties of other element of their respective group.

(c) In 6th period all types of elements are included (s, p, d & f)

(d) No inert gas in 7th period.

(e) Normal elements present in all periods.

(f) Atomic No. of last inert gas element is 86.

(g) Long form of modern periodic table can be divided into four portions.

    1. Left portion – IA & IIA – s-block.

    2. Right portion – IIIA to VIIA + zero group – p-block.

    3. Middle portion – IIIB to VIIB + VIII + IB + IIB – d-block.

    4. Bottom portion – IIIB – f-block elements

(h) The group containing most electro positive elements – IA GROUP

(i) The group containing most electro negative elements – VIIA GROUP

(j) The group containing maximum number of gaseous elements – ZERO (18th) GROUP

(k) The group in which elements have generally ZERO valency – ZERO (18th) GROUP

(l) In the periodic table –

Number of Gaseous elements   - 11 (H, N, O, F, Cl + Noble gases)

Number of Liquid elements   - 6 (Cs, Fr, Ga, Hg, Br, Uub)

Bromine is the only non-metal which exists in liquid form.

All remaining elements are solid.

(m) Ist period has all the elements in gaseous form (H, He)

(n) 0/18th group have all the elements in gaseous form.

(o) 2nd period contains maximum number of gaseous elements. They are 4 : N, O, F, Ne

(p) IIIB/3rd group is called longest group having 32 elements including Sc, Y 14 Lanthanides and 14 Actinides

La .... Lanthanides (14)

Ac .... Actinides (14)

Nomenclature of elements :

(a) IUPAC gave names to elements above atomic No. 100 as follows -

0	1	2	3	4	5	6	7	8	9
nil	un	bi	tri	quad	pent	hex	sept	oct	enn

(b) In all the elements suffix is - ium

e.g.

Atomic No.	IUPAC Name	Symbol
101	Un nil Unium	Unu
102	Un nil bium	Unb
103	Un nil trium	Unt
104	Un nil quadium	Unq
105	Un nil pentium	Unp
106	Un nil hexium	Unh
107	Un nil septium	Uns
108	Un nil octium	Uno
109	Un nil ennium	Une
110	Un un nilium	Uun

Merits of long form of periodic table -

(a) Position of isotopes - Atomic No. of isotopes are similar, so different isotopes can be placed at same place in periodic table.

(b) (Ar - K) (Co - Ni) (Te - I) are now in increasing order of atomic number.

(c) Lanthanides and actinides are in IIIB group.

(d) In modern periodic table diagonal line separates out metals, metalloids and non metals.

(e) Elements of same group have same general formula of electronic configuration of outer most shell.

Demerits of long form of periodic table -

(a) Position of hydrogen is still controversial.

(b) 'He' is a inert gas but it has different electronic configuration than other inert gas elements.

(c) Lanthanides and actinides are still not placed in main frame.

(d) Isotopes have different physical properties but have same place in periodic table.

CLASSIFICATION OF ELEMENTS :

Bohr classification - Elements can be divided in four parts on the basis of electronic configuration.

(i) Inert gas elements -

(a) The elements in which ultimate orbit is completely filled up are called inert gas elements.

(b) General electronic configuration is ns^2p^6 (Except He = $1s^2$)

(c) Because of most stable configuration, they are very less reactive. Hence known as noble gas or inert gas.
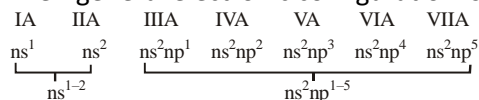
(d) These elements are present in '0' group or 18th group and 1 to 6th period of periodic table.

(e) Number of inert gas elements are 6(One in each period upto 6th) He, Ne, Ar, Kr, Xe, Rn

(ii) Normal or Representative elements -

(a) The elements in which ultimate orbit is incomplete, while penultimate orbits are complete are called normal elements.

(b) Their general electronic configuration is :

IA	IIA	IIIA	IVA	VA	VIA	VIIA
ns^1	ns^2	ns^2np^1	ns^2np^2	ns^2np^3	ns^2np^4	ns^2np^5

ns^{1-2} $\qquad$ ns^2np^{1-5}

(c) These elements lies in group   IA to VIIA and period Ist to 7th

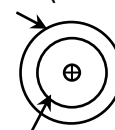(d) Elements of 2nd period known as bridge elements.

(e) Elements of 3rd period (Na, Mg, Al, Si, P, S and Cl) are called typical elements. These are 7 in numbers.

SPOT LIGHT ● ● ●

ultimate shell (Outer)

➢ The outermost shell of an atom is known as ultimate shell.

➢ The shell that is just before the ultimate shell is penultimate shell.

penultimate shell (Inner)

(iii) Transition elements -

The elements in which both ultimate (n) as well as penultimate shells (n – 1) are incomplete either in atomic state or in some oxidation state are called transition elements.

Note:

According to this concept, Zn, Cd, Hg and Uub are not transition elements because they do not have incomplete penultimate shell either in atomic state or in some oxidation state.

$Zn = [Ar]\ 3d^{10}\ 4s^2$

$Zn^{+2} = [Ar]\ 3d^{10}$
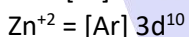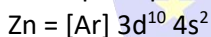
(a) group – IIIB to VIIB + VIII + IB + IIB

Periods – 4th to 7th

(b) Electronic configuration $(n – 1)d^{1–10}\ ns^{1\ or\ 2}$

(c) Total number of d-block elements = 40

Total number of transition elements = 36 (Except Zn, Cd, Hg and Uub)

Note:

All transition elements are d-block elements but all d-block elements are not transition elements.

(iv) Inner transition elements -

(a) The elements in which all the three shells that is ultimate (n) penultimate (n – 1) and pre or anti penultimate (n – 2) shell are incomplete are called inner transition elements.

$_{58}Ce = [Xe]\ 6s^2,\ 5d^1,\ 4f^1$
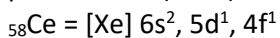
(b) Electronic configuration - $(n – 2)f^{0,1 – 14}\ (n – 1)d^{0\ or\ 1}\ ns^2$

(c) These are 28 in number.

(d) Group – IIIB

(e) Period – 6th & 7th

(f) Inner transition elements are divided into two series.

Lanthanide series/Rare earth elements/Lanthenones (Ce$_{58}$ – Lu$_{71}$ 14 elements)

The first element of this series is Cerium & not Lanthanum.

In these elements, last electron enters into 4f subshell.

They are present in IIIB group and 6th period of the periodic table.

Promethium ($_{61}$Pm) is the only lanthanide which is synthetic and radioactive in nature.

Actinide series/Man made elements/Actinones (Th$_{90}$ – Lw$_{103}$ 14 elements)

The first element of this series is Thorium & not Actinium.

In these elements, last electron enters into 5f subshell.

They are present in IIIB group and 7th period of the periodic table.

All the actinides are radioactive in nature.

First three elements (Th, Pa, U) are found in nature while others are synthetic in nature.

After U$_{92}$ i.e. from $_{93}$Np onwards elements are called transuranic elements because :

They are heavier than uranium.

They are derived from uranium by nuclear reactions.

Classification on The Basis Of Sub Shell In Which Last e⁻ Enters

(i) s-block elements -
(a) In these elements last electron enters in s-subshell.
(b) Groups – IA, IIA (He)
(c) Period – 1 to 7th
(d) Electronic configuration – ns^{1-2}
   IA group n = 1 to 7
   IIA group n = 2 to 7
(e) Total s-block elements are (14) including H and He
(f) Total s-block metals are (12) (excluding H & He) H & He are non-metal.

General characteristics of s-block elements :
(a) s-block elements are soft metal, that is why these elements have low melting and boiling point.
(b) Their oxides and hydroxides are basic in nature.
(c) They act as reducing agent.
(d) They have very low ionisation energy and highly electropositive so, they form ionic compound.
(e) Flame of these elements have the property of showing different colour.

(ii) p-block elements -
(a) Last e⁻ enters in p-sub shell
(b) Group – IIIA (13) to VIIA(17) + 0 group (18) (except He)
(c) Period – 2nd to 6th
(d) Electronic configuration – $ns^2\, np^{1-6}$
(e) Total p-block elements – (30)

Characteristic of p-block elements :
(a) p-block possesses all three kind to elements i.e. metals, non-metals and metalloids.
(b) Oxides of non-metals are acidic in nature.
(c) They form covalent compounds mostly.
(d) They are oxiding in nature.

(iii) d-block elements -
(a) Last e⁻ enters in (n – 1)d subshell
(b) Group – IIIB – VIIB, VIII, IB, IIB or group 3 to 12 (IUPAC)
(c) Period – 4th to 7th
(d) Electronic configuration – $(n-1)d^{1-10}\, ns^{0,1\ or\ 2}$

(e) Total d-block elements – (40)

Total transition elements – (36). If 112 elements are included in periodic table.

(f) IIB elements (Zn, Cd, Hg, Uub) are d-block elements but not transition elements.

General characteristics of d-block elements –

(a) They all are metals, which are very hard having high melting and boiling point.

(b) Elements of this block situated in between 's' and p-block elements. So the character of this block elements lie between s and p-block elements

(c) They show variable oxidation - state, eg. Mn = Mn^{+2}, Mn^{+3}, Mn^{+4}, Mn^{+5}, Mn^{+6}, Mn^{+7}

(d) They form ionic and covalent bond both.

(e) They are good conductor of heat and electricity and form complex compounds.

(f) Metals, which have unpaired electrons show paramagnetism.

(g) They form alloys and most of the elements act as catalyst.

(iv) f-block elements -

(a) Differentiating e^- enters in $(n-2)f$ subshell.

(b) Group – IIIB

(c) Period – 6th and 7th

(d) From at. no. 58 - 71, 6th period ; Lanthanide series $4f^{0-14}\ 5d^{0\ or\ 1\ or\ 2}\ 6s^2$

90 - 103 7th period; Actinide series $5f^{1-14}\ 6d^{0\ or\ 1}\ 7s^2$

(e) Total number of f-block elements – (28)

(f) All the actinides are radioactive elements.

(g) Transuranic actinides are man made elements ($Np_{93} - Lw_{103}$)

(h) Lanthanides are found rarely on earth so these are called rare earth metals.

General characteristics of f-block elements-

(a) All the f-block elements are heavy metals.

(b) It shows high melting and boiling point.

(c) The most common oxidation state of these elements is +3.

(d) The elements of 5f series are radioactive in nature.

Determination of period, block and group of an element -

(i) Period No. - The period no. of the element can be predicted from the principal quantum no. (n) of the valence shell.

e.g. electronic configuration of iodine is :

$1s^2 2s^2 2p^6$, $3s^2 3p^6 3d^{10}$, $4s^2 4p^6 4d^{10}$, $5s^2 5p^5$. Therefore the period number of iodine is 5 as the valence shell configuration is $5s^2 5p^5$.

(ii) Block No. - The type of orbital which receives the last electron known as **block no.**

e.g. An element 'X' has its electronic configuration is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^8$. As the last electron enters in the d-orbital, therefore it is a d-block element.

(iii) Group No. - It is predicted from the number of electrons in the valence shell and penultimate shell as follows.

(a) For s-block elements, group number is equal to the number of electrons in the valence shell after the noble gas core.

e.g. An element 'Y' having electronic configuration $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$ or [Ar] $4s^2$ has two electron in valence shell and it is a s-block element. Therefore it belongs to group 2.

(b) For p-block element, the group number is equal to 10 + number of electrons in valence shell.

e.g. An element 'Z' with electronic configuration as $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^3$ has five electrons in its valence shell and belongs to p-block.

Therefore its group number is 10 + 5 = 15. It belongs to group VA of the Mendeleev's periodic table.

(c) For d-block elements group number is equal to the number of electrons in $(n-1)$d sub-shell and valence shell.

e.g. An elements 'A' having electronic configuration as.

$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$. So its group number will be $10 + 1 = 11$.

Predicting atomic no. of the successive member in a group or family –

(i) Magic Numbers –

Knowing the at. no. of the first member of a group, we can write that at. no. of the subsequent elements by adding given magic no. For example

Group	1	2	3	4, 5, 6, 7, 8, 9, 10, 11, 12	13, 14, 15, 16, 17	18
	IA	IIA	IIIB		IIIA IV V VI VII	'0'gp
I+	2	–				8
II+	8	8			8	8
III+	8	8			18	18
IV+	18	18	18	18	18	18
V+	18	18	18	32	32	32
VI+	32	32	32	32	–	–
VII						

PERIOD (down arrow)

(ii) In group IA – Atomic no. of H is 1 at. no. of other element will be as follows –

Magic no. $\underbrace{H_1\ 1+2=3}_{2}$ $\underbrace{Li\ 3+8=11}_{8}$ $\underbrace{Na\ 11+8=19}_{8}$ $\underbrace{K\ 19+18=37}_{18}$ $\underbrace{Rb\ 37+18=55}_{18}$

Periodicity

(i) The regular gradation in properties from top to bottom in a group and from left to right in a period is called periodicity in properties.

(a) In a period, the ultimate orbit remain same, but the no. of e⁻ gradually increases.

(b) In a group, the no. of e⁻ in the ultimate orbit remains same, but the values of n (shell) increases.

(ii) Causes of periodicity -

(a) The cause of periodicity in properties is due to the same outermost shell electronic configuration coming at regular intervals.

(b) In the periodic table, elements with similar properties occur at intervals of 2, 8, 8, 18, 18 and 32. These numbers are called as magic numbers.

PERIODIC PROPERTIES

VALENCY :

It is defined as the combining capacity of the elements. The word valency is derived from an Italian word "Valentia" which menas combining capacity.

Old concept : Given by : **Grankland**

Valency with respect to Hydrogen and Chlorine : $\boxed{\text{Valency of } H = 1}$

It is defined as the number of hydrogen or Chlorine atoms attached with a particular element.

	IA	IIA	IIIA	IVA	VA	VIA	VIIA
	NaH	MgH$_2$	AlH$_3$	SiH$_4$	PH$_3$	H$_2$S	H-Cl
	NaCl	MgCl$_2$	AlCl$_3$	SiCl$_4$	PCl$_3$	SCl$_2$	Cl-Cl
Valency	1	2	3	4	3	2	1

Note: Valency w.r.t. H across the period increases upto 4 and then again decreases to 1.

Valency with respect to oxygen : $\boxed{\text{Valency of 'O'} = 2}$

It is defined as twice the number of oxygen atoms attached with a particular atom.

IA	IIA	IIIA	IVA	VA	VIA	VIIA
Na$_2$O	MgO	Al$_2$O$_3$	SiO$_2$	P$_2$O$_5$	SO$_3$	Cl$_2$O$_7$

Valency	1	2	3	4	5	6	7

Note: Valency with respect to oxygen increases from 1 to 7 across the period. Valency w.r.t. 'O' is equal to the group number.

New concept : This concept is based on the electronic configuration. According to this concept valency for IA to IVA group elements is equal to number of valence shell e^- and from VA to zero group, it is [8–(number of valence e^-)].

Valency = No. of valence e^- Valency = (8 – No. of valence e^-)

	IA	IIA	IIIA	IVA	VA	VIA	VII	0
	ns^1	ns^2	ns^2np^1	ns^2np^2	ns^2np^3	ns^2np^4	ns^2np^5	ns^2np^2
Valence shell e^-	1	2	3	4	5	6	7	8
Valence	1	2	3	4	3	2	1	0

$$(8 – 5) = 3 \qquad\qquad (8 – 8) = 0$$

Note: All the elements of a group have same valencies because they have same number of valence shell electrons.

DENSITY:

(a) In a group volume of an atom increases along with atomic weight but atomic weight increases more than atomic volume, So density increases in a group.

$$\text{Density (D)} = \frac{\text{Mass}}{\text{Volume}} = \frac{M}{V}$$

(b) **In period -** Density first increases till maximum and then decreases. (s-block to d-block increases, d-block to p-block decreases)

(c) **In group -** From top to bottom in a group density increases regularly

    e.g.   In VIIA gp - F and Cl are gases (Low density)

                 Br is liquid (density 3.19 gm/cm^{-3})

                 I   is solid (density 4.94 gm/cm^{-3})

(d) From s-block to p-block packing capacity and strength of bond increases.

(e) **Exceptions -** The density of Na and Mg is greater than K and Ca respectively. This can be explained by inner shell configuration :

IA	IIA		
Li	Be		
Na	Mg	Na	$1s^2 2s^2 2p^6 3s^1$
K	Ca	K	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^0 4s^1$

In K, $3d^{10}$ orbital is vacant, 3rd orbit has the capacity to hold $18e^-$ but it has only $8e^-$. Due to empty orbital atomic volumes increases and so density decreases

Mg > Ca > Na > K

(f) Li is the lightest metal known.

(g) Highest density of solid metal Ir (22.63 gm/cc) and Os (22.6 gm/cc) and liquid metal Hg(13.6 gm/cc)

(h) **Order of density of elements**

    Li < K < Na < Rb < Cs   {In K and Ca density is less due to empty d-orbitals in inner shells}

    Ca < Mg < Be < Sr

    Sc < Y < La

Ti < Zr < Hf

Zn < Cd < Hg

BOILING POINTS AND MELTING POINTS :

(a) It is a property of aggregate of atoms and not of a single atom.

i.e. why it is a molecular property.

(b) **In period -** Along the period from left to right B.P. and M.P. first increases then decreases.

Alkali metals – Crystal structure BCC (low B.P. & M.P.)

Transition metals – .... " .... FCC (High B.P. & M.P.)

$\begin{bmatrix} \text{Inert gases ....Lowest B.P. \& M.P. (Vander wall force)} \\ \text{Transition elements................ Highest M.P.} \end{bmatrix}$

Metals $\begin{bmatrix} \text{W(Tungston)Max. M.P. (3410°C)} \\ \text{Hg(Mercury)Lowest M.P. (−38°C)} \end{bmatrix}$

Non Metals $\begin{bmatrix} \text{Carbon(In tha form of diamond)Highest M.P. (3727°C)} \\ \text{Helium Lowest M.P. (−270°)} \end{bmatrix}$

In group -

(a) In **s-block** elements B.P. & M.P. decreases down the group.

Li, Na (solid) → Cs, Fr (liquid)

It is due to more repulsion of non-bonding electrons which weakens the metallic bond.

(b) In **d-block** elements B.P. & M.P. increases down the group (due to lanthanide contraction, zeff increases and hence bond energy increases)

(c) In **p-block** elements

i. From IIIA – IVA group B.P. & M.P. decreases down the group and from VA to '0' group, B.P. & M.P. increases down the group. (Atomic or molecular wt $\propto$ vander wall force).

ii. B.P. and M.P. of monoatomic molecules are lesser than diatomic molecules. '0' group < Halogens.

iii. Atomic solid non metals like B, C and Si has higher B.P. and M.P. due to strong covalent bond.

iv. B.P. & M.P. of molecular solids are less because of weaker vander wall force among molecules eg. I_2.

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ATOMIC RADIUS :

(a) It is distance between outermost e⁻ and nucleus.

(b) Half of the nuclear distance between two atoms is defined as atomic radius.

(c) X-ray diffraction, e⁻ diffraction method and nuclear magnetic resonance (NMR) spectrum methods are used to determine internuclear distance or bond length.

Atomic radius = $\dfrac{\text{Inter nuclear distance}}{2}$

(d) Atomic radius depends on the type of chemical bond between atoms in a molecule. These are :

(i) Covalent radius   (ii) Ionic radius   (iii) Metallic radius   (iv) Vander waal's radius

(i) Covalent radius : (SBCR Single Bonded Covalent Radius)

(a) Covalent bonds are formed by overlapping of atomic orbitals.

(b) Internuclear distance is minimum in this case.

(c) Covalent radius is the half of the internuclear distance between two singly bonded homo atoms e.g. internuclear distance of A–A(A_2) molecule is (d_{A-A}) and covalent radius is r_A then

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

$r_A = \dfrac{d_{A-A}}{2}$

e.g. – In Cl_2 molecule, internuclear distance is 1.98 Å so $r_{Cl} = \dfrac{1.98}{2} = 0.99$ Å

(d) SBCR of O, N and C etc. elements can be determined by taking H_2O_2, N_2H_4, C_2H_6 respectively.

Case I - For Heteroatomic molecule with no. E.N. difference.

For A – B molecule Electronegativities of A & B are approximately equal e.g. C – I

E.N. of C & I are approx equal (2.5) internuclear distance of C – I is 2.13Å

$d_{C-I} = r_C + r_I$ (r_C is 0.77Å)

∴ $r_I = 2.13 - 0.77 = 1.36$Å

Case II- Heteroatomic molecule with Δ E.N. difference more :

Schomaker and Stevenson law :

If in a diatomic molecule electronegativities of A – B have more difference. Then actual bond length will be reduced.

As per schomaker & Stevenson – The reduction in bond length depends on the difference in electronegativities of atoms by following manner -

$d_{A-B} = r_A + r_B - 0.09 (X_A - X_B)$

Here X_A is E.N. of A & X_B is E.N. of B

e.g. -   If bond length of F_2 = 1.44Å, Bond length of H_2 = 0.74Å.

Find out the bond length of H – F ?   (EN of F is 4.0, EN of H is 2.1)

Solution- $d_{H-F} = r_F + r_H - 0.09 (X_F - X_H)$

∵ $r_{F-F} = 1.44/2 = 0.77$Å, $r_{H-H} = 0.72/2 = 0.37$Å

∴ $d_{H-F} = 0.77 + 0.37 - 0.09 (4.0 - 2.1) = 1.09 - (0.09 \times 1.9) = 1.09 - 0.171 = 0.919$Å

Example: A given compound A_2 whose total d_{A-A} is 1.4 Å. The atomic (covalent) radius of an atom A is –

(A) 0.7 Å   (B) 0.5 Å   (C) 0.2 Å   (D) 0.1 Å

Ans.   **(A)**

Solution: $r_A = \dfrac{d_{A-A}}{2} = 1.4/2 = $ **0.7 Å**

Example: A compound AB whose electronegativity difference is 1.9. Atomic radius of A and B are 4 and 2 Å. The distance between A & B means d_{A-B} is –

(A) 6.72 Å   (B) 5.82 Å   (C) 6.9 Å   (D) 7.5 Å

Ans.   **(B)**

Solution: Given r_A = 4 Å

r_B = 2Å

Δx = 1.9

By the formula $d_{A-B} = r_A + r_B - .09 (\Delta x)$

= 4 + 2 − .09 × 1.9

= 6 − 0.171

= **5.82 Å**

(ii) Ionic Radius :

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(A) Cationic radius :

(a) When an neutral atom loses e^- it converts into cation (+ve charged ion) Atomic radius > Cationic radius because after loosing e^- no. of e^- reduces, but no. of protons remains same, due to its Zeff increases, hence electrons pulls towards nucleus and atomic radius decreases, moreover after loosing all the electrons from the outer most shell, penultimate shell becomes ultimate shell which is nearer to nucleus so size decreases.

(b) Size of cation $\propto \dfrac{1}{\text{Magnitude of the charge or Zeff}}$

e.g. $Fe > Fe^{+2} > Fe^{+3}$

$Pb^{+2} > Pb^{+4}$

$Mn > Mn^{+2} > Mn^{+3} > Mn^{+4} > Mn^{+5} > Mn^{+6} > Mn^{+7}$

(B) Anionic radius :

(a) When neutral atom gains e^- it converts into anion. Anionic radius > Atomic radius

(b) In an anion e^- are more than protons so effective nuclear charge reduces, and inter electronic repulsion increases, which also increases screening effect. So distance between e^- and nucleus increases and size of anion also increases.

e.g. Z of fluorine is 9

	F	F⁻
Proton	9	9
e^-	9	10

so $\dfrac{Z}{e} = \dfrac{9}{9} = 1$ $\dfrac{9}{10} = 0.9$ As Z_{eff} of F⁻ is less than F so size of F⁻ > F

(c) Size of iso electronic species:

– Those species having same no. of e^- but different nuclear charge forms isoelectronic species.

– for isoelectronic species the atomic radius increases with decrease in nuclear charge

	K^+	Ca^{+2}	Ar	S^{-2}	Cl^-
Z	19	20	18	16	17
e	18	18	18	18	18
$\dfrac{z}{e}$	$\dfrac{19}{18}$	$\dfrac{20}{18}$	$\dfrac{18}{18}$	$\dfrac{16}{18}$	$\dfrac{17}{18}$

Order of radius: $(S^{-2} > Cl^- > Ar > K^+ > Ca^{+2})$, $(N^{3-} > O^{2-} > F^- > Ne > Na^{+2} > Mg^{+2} > Al^{+3})$

(iii) Metallic radius :

(a) Half of the nuclear distance between two adjacent metallic atoms in crystalline lattice structure.

(b) There is no overlapping of atomic orbitals

(c) so metallic radius > Covalent radius

(d) Metallic radius $\propto \dfrac{1}{\text{Metallic bond strength}}$

(e) More metallic radius → loose crystal packing → less bond strength

(body centered packing)

(f) Less metallic radius → Tight crystal packing FCC → High bond strength

(Hexagonal close packing)

(iv) Vander Waal's radius :

(a) Those atoms (like noble gases) which are not bonded with each other, experiences a weak attractive force to come nearer.

(b) the half of the distance between the nuclei of adjacently placed atoms in solid state of a noble gas is Vander Waal's radius.

(c) Vander Waal radius > Covalent radius.

(d) Inert gas have only Vander Waal radius.

(e) In molecules of nonmetals both covalent and Vander Waal radius exists.

Cl_2 molecules
Covalent radius = 0.99Å
Vander Waal radius = 1.80Å

Covalent radius

Vander Waal distance
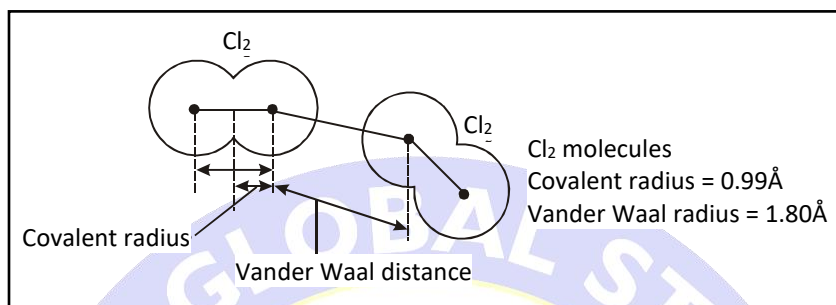
$$\text{Vander Waal radius} = 2 \text{ covalent radius}$$

(f) VWR > Metallic R > Covalent R

(g) Vander Waal force of attraction $\propto$ Molecular wt. or atomic weight (in inert gases)

(h) In a period from left to right VWR decreases.

(i) In a group from top to bottom its values increases.

(v) Factors affecting atomic size are :

(a) $$\boxed{\text{Atomic radius} \propto \frac{1}{\text{Effective nuclear charge}}}$$ e.g.   Li > Be > B > C > N > O > F

(b) $\boxed{\text{Atomic radius} \propto \text{No. of shells}}$ e.g.   Li < Na < K < Rb < Cs

(c) $\boxed{\text{Atomic radius} \propto \text{Screening effect}}$

(d) $$\boxed{\text{Atomic size} \propto \frac{1}{\text{Magnitude of +ve charge}}}$$ e.g. $Mn > Mn^{+2} > Mn^{+3} > Mn^{+4}$

$\boxed{\text{Atomic size} \propto \text{Magnitude of} -\text{ve charge}}$ e.g. $O < O^- < O^{-2}$

(e) $$\boxed{\text{Atomic radius} \propto \frac{1}{\text{Bond order}}}$$ e.g. $> N - N < > - N = N - > N \equiv N$

(vi) Periodic variation of atomic size :

i- Across a period – It decreases from left to right in a period as nuclear charge increases

e.g. Li > Be > B > C > N > O > F < Ne

ii- In a group – It increases from top to bottom in a group as number of shell increases

e.g. Li < Na < K < Rb < Cs

Exceptions : Transition elements

(a) From Sc_{21} to Zn_{30} in first transition series Z_{eff} continuously increases, but atomic size does not decreases continuously.

(b) From Sc_{21} to Mn_{25} size decreases

(c) From Fe_{26} to Ni_{28} size almost constant
Nuclear charge $\simeq$ Screening effect

(d) From Cu_{29} to Zn_{30} size increases. so nuclear charge is less effective than screening effect.

(vii) Lanthanide Contraction :

(a) Outermost electronic configuration of inner transition elements is
$(n-2)f^{1-14}, (n-1)s^2p^6d^{0-1}, ns^2 \ (n = 6 \ to \ 7)$

(b) e^- enters in $(n-2)$ f orbitals

(c) Mutual screening effect of e^- is very less, because of complicated structure of f-orbital

(d) Nuclear charge increases by one (+1) in lanthanides and actinides so atomic size of these elements slightly decreases. it is known as lanthanide contraction.
Here Nuclear charge > Screening effect.

(e) In transition series Ist 2nd and 3rd

	III$_B$	IV$_B$	
size	Sc	Ti $\downarrow$	size increases
Increases	Y	Zr ⎫	Equal due to lanthanide contraction
	La	Hf ⎭	

Radii 3d < 4d $\approx$ 5d except III B.

(viii)   Orders of atomic and ionic radii -

$H^+ < H < H^-$

$I^+ < I < I^-$

$Ti < Zr \approx Hf$

$Sc < Y < La$

$Na^+ < Ne < F^-$

$Be < Li < Na$

$Ni < Cu < Zn$

$Sc > Ti > V > Cr$

$Ar > Na > Cl$

$Cu < Au < Ag$

SPOT LIGHT

1. The alkali metals which are present at the extreme left of the periodic table have the largest size in a period.

2. The halogens which are present at the extreme right of the periodic table have the smallest size.

3. The size of the atoms of inert gases are, however, larger than those of preceding halogens because in inert gases van der Waals' radii are taken into consideration.

4. In transition series, the decrease in size is small as the additional electrons in $(n-1)$d levels effectively screen much of the nuclear charge on the ns electrons.

5. In 4f-series, there is continuous decreases in size with increase in atomic number. This decrease is termed Lanthanide contraction.

6. In a group of normal elements, there is continuous increase in size with increase in atomic number.

7. In a group of transition elements, there is an increase in size from first member to third member to second member as expected but from second member to third member, there is very small change in size and sometimes sizes are same. This is due to Lanthanide contraction.

8. Van der Walls' radius > Metallic radius > Covalent radius covalent radius is used for non-metals. Metallic or crystal radius is used for metal atoms and van der Wall's radius for noble gases.

9. Radii of Al and Ga are nearly equal inspite of the fact that both belong to same group. This is due to the presence of ten d-block elements before Ga. In d-block elements, the screening effect of d-electrons is low and thereby nuclear charge attracts valence electrons strongly and reduces the size considerably.

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IONISATION ENERGY/ENTHALPY

Ionisation energy (IE), sometimes also called ionisation potential (IP), of an element is defined as the amount of energy required to remove an electron from an isolated gaseous atom of that element resulting in the formation of positive ion.

$$M(g) \xrightarrow{(IE)} M^+(g) + e^-$$
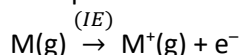
- $(IE)_1$, $(IE)_2$, $(IE)_3$...are respectively first, second, third ...ionisation energies required to remove first, second, third.....electron from the isolated gaseous atoms.

  $(IE)_1 < (IE)_2 < (IE)_3 < ....$

FACTORS AFFECTING IONISATION ENERGY

(IE) variation in a period and group may or not be regular and can be influenced by :

(A) Size of the Atom :

In a small atom, the electrons are tightly held while in a larger atom, the electrons are less strongly held, the Coulombic force of attraction F being

$$F = \frac{kZe^2}{r^2}$$

Where Ze is charge on nucleus, e the electrons charge, r the atomic radius and k the constant. Thus the ionistion energy decreases as the size of the atom increases.

(B) Effective Nuclear Charge (Z*) :

As given above the force of attraction between the nucleus and the outermost electron increases with increase in nuclear charge. Greater the effective nuclear charge, greater energy required to pull the electrons from the atom. Here (IE) increases with increase in nuclear charge.

(C) Shielding effect (σ) :

The electrons in the inner shells act as a screen or shield between the nucleus and the electrons in the outer most shell. This is called shielding effect. The larger the number of electrons in the inner shells , greater is the screening effect and smaller the force of attraction and thus (IE) decreases.

(D) Penetration Effect :

An s electron penetrates nearer to the nucleus, and is therefore more tightly held than a 'p' electron, and a 'd' electron is more tightly held than f electron. Other factors being equal, ionisation energies are in the order $s > p > d > f$.

(E) Electronic Configuration :

If an atom has full filled or half-filled orbitals, its (IE) is higher than expected normally from its position in the periodic table.
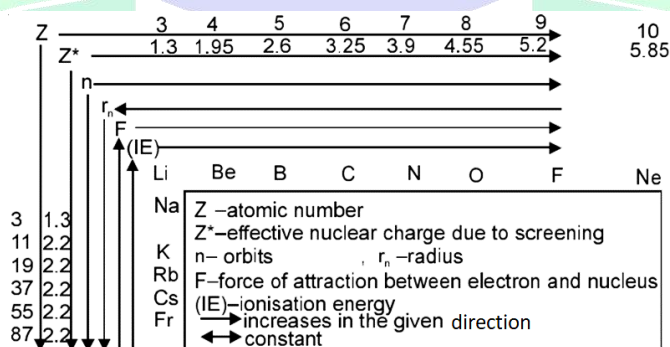
Variation of (IE) in a group and period

Example: I.E. of one H atom is 2.18×10^{-18}J. The I.E. of H atom in kJ mole^{-1} is –

(A) 1505 kJ mole^{-1} (B) 1310 kJ mole^{-1} (C) 1608 kJ mole^{-1} (D) None

Ans.   **(B)**

Solution: I.E. = 2.18 × 10^{-18} × 6.022 × 10^{23} = 1.31 × 10^6 J mole^{-1} = **1310 kJ mole^{-1}**.

Example: Which of the following order is correct of reducing strength –

(A) Cs > Rb > K > Na > Li (B) Li > Na > K > Rb > Cs
(C) Li > Cs > Rb > K > Na (D) None of these

Ans. **(C)**

Solution: Li is the best reductant in IA group because oxidation potential of it is very high and Li$^+$ (aq.) is most stable, since Li$^+$ is small cation. They have greater hydration energy. Hence the above process occurs easily.


DETECTIVE MIND ● ● ● ●

1. The radius of cation (positive ion) is always smaller than the atomic radius of the parent atom.
$$M^+ < M$$
2. The radius of anion (negative ion) is always larger than the atomic radius of the parent atom of the parent atom.
$$A^- > A$$
3. On moving down the group, the ionic radii of ions having same charge increase as atomic number increase.
$$Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$$
4. In a period of representative elements the ionic radii of ions having same charge decreases as atomic number increase.
5. Variation of ionic radii in transition series is small and not smooth.
6. Radii of tripositive lanthanide ions decreases regularly along the series.
7. In a set of species having same number of electrons (isoelectronic), the ionic size decreases with increase in nuclear charge.
$$N^{3-} > O^{2-} > F^- > Na^+ > Mg^{2+} > Al^{3+}$$
8. The size of the cations of the same element decreases with the increase of positive charge.
$$Cr^{2+} > Cr^{3+} ; Fe^{2+} > Fe^{3+} ; Pb^{2+} > Pb^{4+}$$
9. H$^+$ and Cs$^+$ are the smallest and largest cations respectively.
10. F$^-$ and I$^-$ are the smallest and largest monovalent anions respectively.
11. If a cation forms compounds with different coordination numbers, the radius of the cation will be higher with higher coordination number.

C.N.	4	6	8
Ionic radius of Li$^+$(Å)	0.73	0.90	1.06

12. Ionic radii of Al^{3+} and Ga^{3+} are similar inspite of the fact both belong to same group. This is due to d-effect. Similarly, ionic radii of Zr^{4+} and Hf^{4+} are almost equal inspite of the fact that both belong to same group. This is due to lanthanide contraction.

◇◇◇◇◇◇◇◇◇◇◇◇

ELECTRON AFFINITY (EA) /ELECTRON GAIN ENTHALPY ($\Delta H_{e.g}$)

Electron affinity (E.A) is the amount of energy released when an additional electron as added to the outer most shell of an isolated gaseous atom to form anion.

$X_{(g)} + e^- \longrightarrow X^-_{(g)} + E.A.(I)$
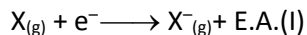
$\Delta H_{e.g}$ (first electron gain enthalpy) = –ve (negative)

*   Generally addition of first electron in an isolated gaseous atom is an exothermic process [except stable electronic configuration]

$\Delta H_{e.g} = -E.A$

For addition of first electron = $\Delta H_{eg_1} = -ve$

$E.A_1 = +ve$

*   the second electron is added to gaseous anion against the electrostatic repulsion between the electron being added and the gaseous anion

$X^-_{(g)} + e^- \xrightarrow[\quad]{+Energy \quad EA\,(II)} X^{2-}_{(g)}$
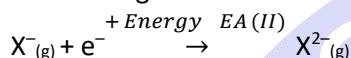
• addition of second electron is an isolated gaseous atom is always on "endothermic" process.

$\Delta H_{eg_2} = +ve$

$E.A_2 = -ve$

$\Delta H_{e.g_1} + \Delta H_{e.g_2} \text{.......} = +ve$

• Formation of polynegative anion O^{-2}, N^{-3}, C^{-4} etc is always an endothermic process

EXCEPTIONS :

(a) Electron affinity values of second period elements (N, O, F) are smaller than the electron affinity values of third period elements (P, S, Cl). The electron being added experiences comparatively more repulsion because of high value of charge densities of second period elements due to much smaller size. and thus the electron affinity value of second period elements decreases. For example the electron affinity of fluorine is less than chlorine.

(b) Electron affinity of alkaline earth metals (group 2) are almost zero. It is because of completely filled s–orbitals in their valence shells.

(c) Nitrogen has low electron affinity values. The atom of these elements have stable exactly half filled p–orbitals.

(d) Electron affinity of noble gases is zero. It may be attributed to the stable completely filled valence shell electronic configurations.

ELECTRO-NEGATIVITY(EN)

(i) The tendency of an atom to attract shared electrons towards itself is called electronegativity.

(ii) EN and EA both have tendency to attract electrons but electron affinity is for isolated atoms. Where as electronegativity is for bonded atoms.

(iii) A polar covalent or ionic bond of A – B may be broken

as (a) $A - B \longrightarrow A^- : + B^+$ (EN A > EN B)

or (b) $A - B \longrightarrow A^+ + :B^-$ (EN A < EN B)

depending on their tendency to attract bonded electron.

(iv) There is no unit of electronegativity as EN is tendency of a bonded atom not an energy

(v) Pauling explained it first time.

(vi) In Pauling's scale, elements having almost same electronegativity are –

N = Cl = 3.0

C = S = I = 2.5

P = H = 2.1

Cs = Fr = 0.7

Be = Al = 1.5

Linus Pauling developed a method for calculating relative electronegativities of most elements. According to Pauling

$$\Delta = X_A - X_B = 0.208 \sqrt{E_{\cdot A-B} - \sqrt{E_{A-A} \times E_{B-B}}}$$

E_{A-B} = Bond enthalpy/ Bond energy of A – B bond.

E_{A-A} = Bond energy of A – A bond

E_{B-B} = Bond energy of B – B bond

(All bond energies are in kcal / mol)

$$\Delta = X_A - X_B = 0.1017 \sqrt{E_{\cdot A-B} - \sqrt{E_{A-A} \times E_{B-B}}}$$

(vii) **Mulliken's scale :** Electronegativity can be regarded as the average of the ionisation energy (IE) and the electron affinity (EA) of an atom (both expressed in electron volts).

$$\chi_M = \frac{IE + EA}{2}$$

[Paulings's electronegativity χ_P is related to Mulliken's electronegativity χ_M as given below.

$\chi_P = 1.35 \, (\chi_M)^{1/2} - 1.37$

Mulliken's values were about 2.8 times larger than the Pauling's values.]

(viii) EN of some other elements are as follows –

H						
2.1						
Li	Be	B	C	N	O	F
1.0	1.5	2.0	2.5	3.0	3.5	4.0
Na	Mg	Al	Si	P	S	Cl
0.9	1.2	1.5	1.8	2.1	2.5	3.0
K						Br
0.8					2.8	
Rb					I	
0.8					2.5	
Cs						
0.7						
Fr						
0.7						

– Small atoms are normally having more EN than larger atoms.

(ix) **Factors Affecting electronegativity :**

(a) **Atomic size -**

$$\text{electronegativity} \propto \frac{1}{\text{Atomic size}}$$

(b) **Effective nuclear charge (Z_{eff}) -**

Electronegativity $\propto Z_{eff}$

(c) **Hybridisation state of an atom -**

Electronegativity $\propto$ % of s character in hybridised atom

$$sp \quad > \quad sp^2 \quad > \quad sp^3$$

s character	50%	33%	25%
Electronegativity	3.25	2.75	2.5

Because s-orbital is nearer to nucleus so by increasing s-character in hybridisation state, EN also in creases.

(d) Oxidation state -

Electronegativity $\propto$ oxidation state

$Mn^{+2} < Mn^{+4} < Mn^{+7}$

$O^- < O < O^+$

$Fe < Fe^{+2} < Fe^{+3}$
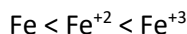
- As atomic radius decreases by increasing oxidation state of cation species, EN increases.
- In anionic species, the order of electronegativity is $O^{-2} < O^- < O$

(e) Electronegativity does not depends on filled or half filled orbitals, because it is a tendency to attract bonded electron, not to gain electron from out side.

(x) Periodic table & Electronegativity :

(a) Electronegativity decreases down the group.

(b) In period on moving from left to right EN increases.

Exceptions -

– **'O' group** – Electronegativity of '0' group is always zero, because inert gas do not form molecule.

(c) Electronegativity of Cs and Fr in 6th and 7th period (IA) are equal, it is because from $_{55}$Cs to $_{87}$Fr only one shell but nuclear charge (No. of proton) increases by +32.

(d) So effect of nuclear charge balanced the effect of increase in number of shell.

Electronegativity of F > Cl but electron affinity of Cl > F

So Fluorine is called **Black sheep** element.

(e) In group of IIB elements (Zn, Cd, Hg) value of electronegativity increases down the group, because of lanthanide contraction

(f) In IIIA group, value of electronegativity increases down the group, because of transition contraction (+ 18 charge)

EN of Ga > EN of Al

(xi) Application of electronegativity :

(A) Metallic and non metallic nature -
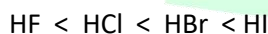
Low electronegativity $\longrightarrow$ Metals

High electronegativity $\longrightarrow$ Non metals

Metallic character increases down the group but decreases along a period.

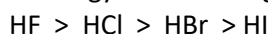**(B) Bond length -**

$$\Delta EN \propto \frac{1}{Bond\ length}$$

Here Δ EN = difference in electronegativities of bonded atoms

HF < HCl < HBr < HI

– HF has minimum bond length because of much difference in the electronegativities of H and F.

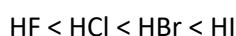**(C) Bond energy** - By increasing ΔEN bond length decreases and hence bond energy increases.

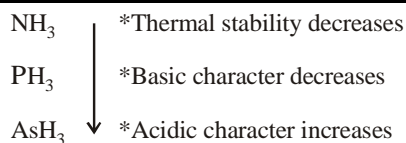Bond energy $\propto$ Electronegativity difference

HF > HCl > HBr > HI

(D) Acidic strength of hydrides -

Bond energy (Strength) $\propto$ stability of molecule.

– Order of stability of hydrohalides is

HF > HCl > HBr > HI and so order of their acidic strength will be -

HF < HCl < HBr < HI

– In VA group -

NH_3 | *Thermal stability decreases

PH_3 | *Basic character decreases

AsH_3 ↓ *Acidic character increases

In PH_3 and AsH_3 there is less difference in the electronegativities of X_A and X_B, so their bond energy decreases and hence acidic character (losing H^+ ion) increases.

(E) Reactivity -

Bond energy $\propto$ Stability $\propto \dfrac{1}{\text{Reactivity}}$

As bond energy $\propto$ difference of electronegativities

So, Δ Electronegativity $\propto$ Stability $\propto \dfrac{1}{\text{Reactivity}}$

$$\xrightarrow[\text{Reactivity}]{HF < HCl < HBr < HI}$$

– HI is most reactive hydrohalides or strongest acid among all hydrohalides.

(F) Nature of bonds -

(a) It can be determined by Hanny & Smith formula -

Ionic % = $16(X_A - X_B) + 3.5(X_A - X_B)^2$

Here X_A = Electronegativity of A

X_B = Electronegativity of B

If $X_A - X_B \geq 2.1$ Ionic % > 50% i.e. Ionic bond

If $X_A - X_B \leq 2.1$ Ionic % < 50% i.e. covalent bond

(b) Gallis experimental values are -

$X_A - X_B \geq 1.7$ Ionic

$X_A - X_B \leq 1.7$ Covalent

– If $X_A = X_B$; then A – B will be non polar, e.g. H – H, F – F

If $X_A > X_B$ and difference of EN is small then

$A^{\delta-}$ —— $B^{\delta+}$ bond will be polar covalent

e.g. H_2O ($H^{\delta+}$ —— $O^{\delta-}$ —— $H^{\delta+}$)

– If $X_A \gg X_B$ and $X_A - X_B$ ΔEN is high then, $A^- \longrightarrow B^+$ bond will be polar or ionic

e.g. Na^+Cl^-

– In HF, $X_A - X_B = 1.9$, which is more than 1.7, even then it is covalent compound.

(G) Nature of hydroxides -

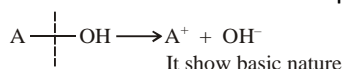(a) As per Gallis, In AOH if electronegativity of A is more than 1.7 (Non metal) then it is acidic in nature.

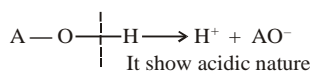(b) If electronegavity of 'A' is less than 1.7 (metal) then AOH will be basic in nature

e.g. | | NaOH | ClOH |
|---|---|---|
| X_A | 0.9 | 3.0 |
| Nature | Basic | Acidic |

(c) If $X_A - X_O \geq X_O - X_H$

then AO bond will be more polar and will break up as

$A \!-\!\!\!|\!-\! OH \longrightarrow A^+ + OH^-$
        It show basic nature

(d) If $X_A - X_O \leq X_O - X_H$

$$A — O \!\!\mid\!\! —H \longrightarrow H^+ + AO^-$$
It show acidic nature

e.g. In NaOH

$X_0 - X_{Na}$ (2.6) > $X_0 - X_H$ (1.4)

So hydroxide is basic

In ClOH –

$X_O - X_{Cl}$ (0.5) < $X_O - X_H$ (1.4)

So hydroxide is acidic

(H) Nature of oxides - Consider an oxide AO

If $X_A - X_O$ > 2.3   Basic oxide

If $X_A - X_O$ = 2.3   Amphoteric oxide

If $X_A - X_O$ < 2.3   Acidic oxide

(a) Along a period acidic nature increases.

(b) Down the group basic nature increases

Li Be B C N O F

Na Mg Al Si P S Cl

$X_A - X_O$ > 2.3   ↓ $X_A - X_O$ < 2.3

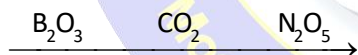Basic $X_A - X_O$ = 2.3   Acidic

           Amphoteric

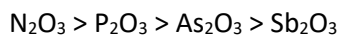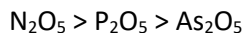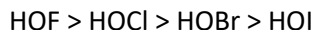i.e. when in periodic table the distance between the element and oxygen increases, basic character increases.

NO_2 > ZnO > K_2O

$\longrightarrow$

acidic character decreases

– BeO, Al_2O_3, ZnO, SnO, PbO, SnO_2, PbO_2, Sb_2O_3 etc. are amphoteric oxides.

– CO, H_2O, NO, N_2O are neutral oxides.

Acidic strength of oxide and oxyacid ∝ EN

$\xrightarrow{\hspace{1cm}}$ B_2O_3 CO_2 N_2O_5

EN increase, acidic nature increase

H_3BO_3 < H_2CO_3 < HNO_3

SO_3 H_2SO_4 EN ↓

SeO_3 H_2SeO_4 Acidic ↓

TeO_3 ↓ H_2TeO_4 ↓

H_3PO_4 > H_3AsO_4 > H_3SbO_4

H_2SO_3 > H_2SeO_3 > H_2TeSO_3

HOF > HOCl > HOBr > HOI

$HClO_4$ > $HBrO_4$ > HIO_4

N_2O_5 > P_2O_5 > As_2O_5

N_2O_3 > P_2O_3 > As_2O_3 > Sb_2O_3
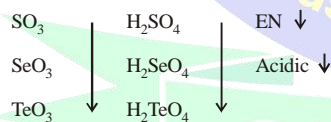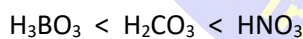
Acidic nature ∝ oxidation state

Acidic properties increases with increasing oxidation state of an element

$HClO_4$ > $HClO_3$ > $HClO_2$ > HClO

HNO_3 > HNO_2

H_2SO_4 > H_2SO_3

SO_3 > N_2O_3

$Sb_2O_3 < Sb_2O_5 < N_2O < NO < NO_2 < N_2O_5$
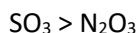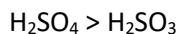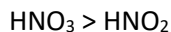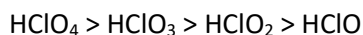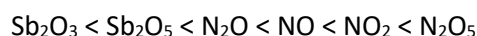
(I) Hydrolysis of AX - Where A = Other element

and X = Halogen

(a) If electronegativity of X > Electronegativity of A then on hydrolysis product will be HX.

– In example (BCl_3), EN of Cl > EN of B

$PCl_3 + 3HOH \longrightarrow 3HCl + H_3PO_3$

$PCl_3 . Cl_2 + H_2O \longrightarrow 2HCl + POCl_3$

$POCl_3 + 3HOH \longrightarrow 3HCl + H_3PO_4$

(b) If electronegativity of X < electronegativity of A then on hydrolysis product will be HOX (hypohalous acid)

e.g. Cl_2O

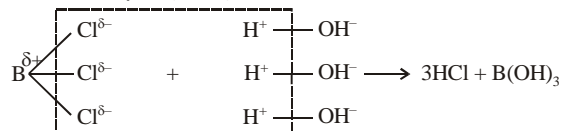So On hydrolysis –
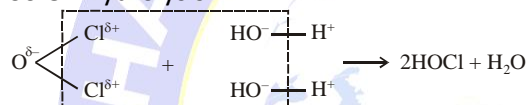
Example: Give the correct order of electronegativity of central atom in following compounds -

(a) $CH_3 - CH_3$ (b) $CH_2 = CH_2$ (c) $CH \equiv CH$

The correct order is –

(A) a > b > c (B) c > a > b (C) c > b > a (D) b > c > a

Ans: **(C)**

Solution: % -S- character

in $CH_3 - CH_3$ = sp^3 = 25 %

in $CH_2 = CH_2$ = sp^2 = 33.33 %

in $CH \equiv CH$ = sp = 50 %

So, the electronegativity order is :

$CH \equiv CH > CH_2 = CH_2 > CH_3 - CH_3$

Example: Which of the following compound has highest value of bond length –

(A) CsF (B) CsBr (C) CsI (D) CsCl

Ans. **(C)**

Solution: The ΔE.N. of CsI is minimum.

Difference Between Electron Gain Enthalpy And Electronegativity

S.NO.	ELECTRON GAIN ENTHALPY	ELECTRONEGATIVITY
1.	It is the tendency of an isolated atom to attract electron.	It is the tendency of an atom in a combined state, i.e., in molecule to attract the shared pair of electrons.
2.	It can be measured experimentally.	It is a relative number and cannot be determined experimentally.
3.	Its units are electron volts per atom or kilo joules per mole or kilo joules per mole or kilo calories per mole.	It has no unit but merely a number.

4.	It is a constant quantity for a particular element	Electronegativity of an element is not constant. It depends on a number of factors such as hybridized state, oxidation state, etc.
5.	Its periodicity is not regular in a period or a group	The periodicity is regular in a period but so regular in group.

DETECTIVE MIND ● ● ● ˙

1. In each period, alkali metals show lowest first ionization enthalpy. Cesium has the minimum value.
2. In each period, noble gases show highest ionization enthalpy. Helium has maximum value of first ionization enthalpy.
3. The representative elements show a large range of values of first ionization enthalpies, metals having low and non-metals have high values. The following is the trend:

   IA $<$ IIA $>$ IIIA $<$ IVA $<$ VA $>$ VIA $<$ VIIIA

   (1)   (2)   (13)   (14)   (15)   (16)   (17)

   Li < Be > B < C < N > O < F

   Na < Mg > Al < Si < P > S < Cl

   In any period, inert gas has maximum value of first ionization enthalpy.
4. Largest jump in IE_1 and IE_2 is in the case of alkali metals as ns^1 configuration changes into inert gas configuration. The trend in the values of IE_2 and 2nd and 3rd periods is the following :

   IE_2 Li > Ne > O > F > N > B > C > Be

   IE_2 Na > Ar > Cl > S > P > Al > Si > Mg
5. The largest jump between IE_2 and IE_3 is for alkaline earth metals.
6. The IE_1 of Al and Ga are almost equal as they have nearly same atomic radii.
7. Ionisation enthalpies of the atoms having filled or half filled shells have higher values. For example, N has higher IE_1 than O. Be, Mg, inert gases, etc., have high IE_1 values.
8. Successive ionization enthalpies of an atom have higher values.

   $IE_1 < IE_2 < IE_3$ .....

◇◇◇◇◇◇◇◇◇◇◇◇◇

QUICK FOLLOW UP ● ● ● ●

PERIODIC TABLE

is organized into

Genesis of periodic classifications

Periods (Rows)

Group 1 -18 (Column)

Block (s, p, d, f)

1. Doberneiner's triads

2. Newlands' law of octaves

3. Lothar Meyer's curve

4. Mendeleev's Periodic Law

5. Modern Periodic Law

The most important ones are given the "family" names

the s-block & p-block together constitute the

which include

Alkali metals   halogens

Alkaline earths   Noble gases

Actinides (second f-block)

Transition Metal (d-block)

Lanthanides (first f-block)

"REPRESENTATIVE ELEMENTS"

PERIODIC TRENDS IN PROPERTIES OF ELEMENT

Trends in Physical Properties

→ **Atomic radii:**
  ➤ Along a period, decreases
  ➤ Within a group, increases

→ **Ionisation enthalpy:**
  ➤ Along a period, increases
  ➤ Within a group, decreases

→ **Electron gain enthalpy:**
  ➤ Along a period, increases
  ➤ Within a group, decreases

→ **Electronegativity:**
  ➤ Along a period, increases
  ➤ Within a group, decreases

Exceptions:
→ Δ_{eg} H of Be, Mg Ca, N and inert gases is positive.
Ar and Kr have the same value of Δ_{eg} H.
Δ_{eg} H of F is less – ve than Cl.
Δ_{eg} H of O is less – ve than S.

Trends in Chemical Properties

→ **Valence electrons**
  ➤ Along a period, increases from 1 to 8
  ➤ Within a group, same

→ **Strength of oxy-acids of non-metals:**
  ➤ Along a period, increases
  ➤ Within a group, decreases

→ **Basic character of hydrides:**
  ➤ Along a period, decreases
  ➤ Within a group, (non-metal) decreases (metals increases)

→ **Acidity of oxides:**
  ➤ Along a period, increases
  ➤ Within a group, decreases

→ **Anomalous behaviour of the elements of II period :**

Diagonal relationship: Some elements of period II show similarities with the period III elements placed diagonally to different groups.

e.g. , Li and Mg, Be and Al