unit - 3

CLASSIFICATION OF ELEMENTS AND PERIODICITY IN PROPERTIES

Genesis of periodic classification

let us start with the very first theory of periodic table.

1) Doberiener's Triads -

The German chemist, Johann Dobereiner in 1800 first observed similarities in the elements on the basis of their properties. He saw that there are groups consisting of three elements (triads) which have similar chemicals and physical properties.

- In every group, the atomic weight of the middle element was half of the sum of the atomic weight of other two elements.
- Properties of the middle element were also at the halfway of both the elements. Dobereiner called this grouping method as the law of triads.
- Later on, it was found that this law was not true for every element and hence it was not successful.

Dobereiner's Triads

Element	Atomic weight	Element	Atomic weight	Element	Atomic weight
Li	7	Ca	40	Cl	35.5
Na	23	Sr	88	Br	80
K	39	Ba	137	I	127

2) Newland's octave -

- In 1865, after the failure of the Doberiene's triad the English chemist, John Alexander Newlands gave the law of octaves.

- According to him, elements can be arranged in ascending of their atomic weights. He also said that in this arrangement, every eight element of a row had similar properties to that of the first element of the same row, depicting the octaves of music.

- This law was also dismissed as it was only true for elements up to calcium.

Newland's octaves

Element	Li	Be	B	C	N	O	F
At. Wt	7	9	11	12	14	16	19
Element	Na	Mg	Al	Si	P	S	Cl
At. Wt	23	24	27	29	31	32	35.5
Element	K	Ca					
At. Wt.	39	40					

3) Mendeleev periodic Table -

- The real development in the periodic table took after the development of mendeleev periodic table.

- He gave a law which states that "properties of an element are the periodic function of their atomic masses"

- He arranged elements in periods (horizontal rows) and groups (vertical colums) in the increasing order of atomic weights. The verti-cal colum consists of elements that have similar properties.

- At the time of mandeleev, only 63 elements had been discovered. So At the same time, keeping his primary aim of arranging the elements of similar proper-ties in the group, he proposed that some of the elements were still undiscovered and therefore, He left several gaps in the table.

Modern Periodic Law and The Present Form of The Periodic Table

The modern periodic law states that the Physical and chemical Properties of the elements are the periodic Function of the atomic numbers. The various elements with similar properties repeat after certain regular intervals. This repetition occurs when you arrange the elements in order of their increasing atomic numbers

Long Form of Periodic Table

Numerous Forms of Periodic Table have been devised from time to time. Some Forms emphasise chemical reactions and valence, whereas others stress the electronic configuration of elements.

- A modern version, so called 'long form' of the periodic Table. of the elements, is The most convenient and widely used.
- The long form of the periodic Table is based upon the electronic configuration of the elements.
- The modern periodic table of elements consists of 18 vertical columns known as 'groups' and 7 Horizontal rows known as 'periods'
- the scientists have made this arrangements in a very perticular way. It keeps all the elements with similar electronic configuration

under each other in the same vertical column.

s - block

p - block

d - block

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	**Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	Ts	Og

f - block

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Fig : Long form of periodic Table

Groups in the periodic Table

- The 18 verticle colums in the modern periodic table are the groups.
- Each of the group consist of a mumber of elements having the same electronic configuration of the outermost shell.
- These groups are numbered from 1 to 18.

Periods in the periodic Table

- The long form of the periodic Table consists of 7 Periods.
- these are numbered as 1 to 7 from top to bottom.

- The first period consists of only two elements - Hydrogen and Helium.
- The 2nd and 3rd period consists of 8 elements each. On the other hand, the 4th and 5th consists of 18 elements each while the sixth period consists of 32 elements
- The 7th period is incomplete and like the 6th period would have a maximum of 32 electrons.
- There is a saparate pannel at the end bottom consists of 14 elements of the 6th period called the lanthanoids and 14 elements of the 7th period called the actinoids.

General Electronic configuration

- An electron in an atom is characterised by a set of four quantum numbers and the principle quantum number (n) defines the main energy level known as 'shell'

- The filling of electrons into different sub-shells, also referred to as 'orbitals' [s, p, d, f] in an atom.

- The distribution of electrons into orbitals of an atom is called its electronic configuration.

H = $1s^1$

Li = $1s^2 2s^1$ or $[He] 2s^1$

B = $[He] 2s^2 2p^1$

Na = $1s^2 2s^2 2p^6 3s^1$ or $[Ne] 3s^1$

s-block elements

The elements of Group 1 (alkali metals) and Group 2 (alkaline earth metals) which have ns^1 and ns^2 outermost electronic configuration belong to the s-Block Elements.

- They are all reactive metals with low ionization enthalpies. They lose the outermost electron(s) readily to form 1^+ ion or 2^+ ion.
- The metallic character and the reactivity increases as we go down the group.
- General configuration is ns^{1-2}
- Li and Be forms mainly covalent compounds; while outer elements mainly form Ionic compounds.

P- block Elements

- Group 13 to Group 18 are p-block elements. General electronic configuration of elements is $ns^2 np^{1-6}$

- mainly contain non-metals.

- At the end of the each period is a noble gas element with a closed valence shell ns^2np^6 configuration.

- Noble gases do not have any affinity (tendency to attract) to add or loose electron, are chemically almost unreactive.

- Group 16 (VIA) → chalcogens → ore forming
  Group 17 (VIIA) → Halogens → salt forming

These two groups of elements have highly negative electron gain enthalpies and readily add one or two electrons respectively.

The d- Block Elements (Transition Elements)

- These are the elements of Group 3 to Group 12 in the centre of the periodic Table.

- These are characterised by the filling of inner d orbitals by electrons and are therefore referred to as d-Block Elements.

- These elements have the general outer electronic configuration $(n-1)d^{1-10}ns^{0-2}$ except for Pd, where its electronic configuration is $4d^{10}5s^0$

- They are all metals.

- Zn, Cd and Hg which have the electronic configuration, $(n-1)d^{10}ns^2$ do not show most of the properties of transition elements.

- Elements of group 8, 9, 10 are commonly known as 'Ferrous Alloys' almost have same size.
- Elements of group - 11 : Cu, Ag, Au are known as 'COINAGE METALS'
- Transition elements form coloured complexen.
- Elements shows variable oxidation state, exhibit paramagnetism and oftenly used as catalysts.

F-block Elements
(Inner- Transition Elements)

The two rows of elements at the bottom of the Periodic Table, called the Lanthanoids - Ce (Z = 58) to Lu (Z = 71)

And Actinoids, Th $(Z = 90)$ to Lr $(Z = 103)$ are characterised by the outer electronic configuration $(n-2)f^{1-14}(n-1)d^{0-1}ns^2$.

- The last electron added to each element is filled in f-orbital. These two series of elements are hence called the Inner Transition Elements.

- They are all metals.

- Actinoid elements are radioactive. Many of the actinoid elements have been made only in nanogram quantities or even less by nuclear reactions.

Metals, Non-Metals and Metalloids

Metals -

- Metals comprise more than 78% of all known elements and appear on the left side of the periodic Table.
- metals are usually solids at room temperature. (except mercury)
- metals are good conductors of heat and electricity. They have high melting and Boiling points. They are malleable and ductile

Non - metals -

- Non- metals are located at the top Right hand side of the periodic Table.

- Non-metals are usually solids or gases at room temperature, with low melting and boiling points. (except boron and carbon)

- They are poor conductors of heat and electricity. most non-metals are brittle and are neither malleable nor ductile.

- The non-metallic character increases as we goes from left to right across the periodic table.

metalloids -

The change from metallic to non-metallic character shown by a thick zig-zag line. The elements bordering this line and running diagonally across the periodic table shows properties of both metals and non-metals. These elements are semi-metals or metalloids.

Trends in Physical Properties

a) Atomic Radius -

- The atomic radius of a chemical element is a measure of the size of its atom.

- Atomic radius is the distance from the center of the nucleus to the outermost isolated electron.

- Exact value of atomic radii can't be determine due to non well defined boundry. According to probability concept, probability of finding electron even at large distance from the nuleus is never zero.

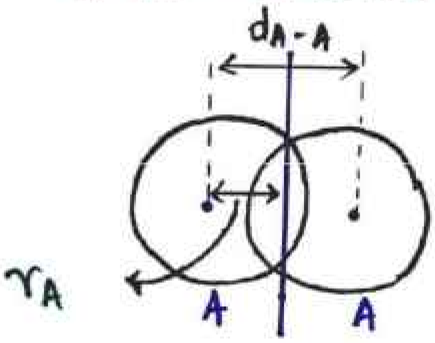
- size of an atom is affected by its neighbour, side atom and atmosphere.
- size of an atom also depends on type of bonding state. as well as size of an atom is determined in a particular bonding state.

Types of Radii -

1) covalent Radius -

A covalent radius is one-half the distance between the nuclei of two identicle atoms.

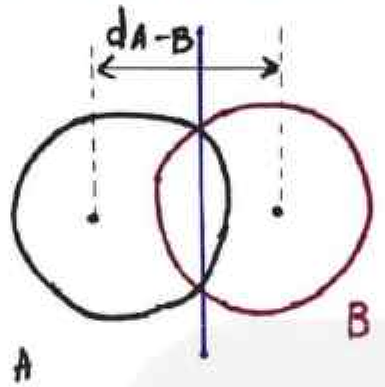
i) Homonuclear molecule



Bond length = d_{A-A}

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

2) Heteronuclear molecule



Bond length = d_{A-B}

$d_{A-B} = r_A + r_B - 0.09(\Delta EN)$

$\therefore \Delta EN$ = Electronegativity diff between both the atoms.

2) metallic Radius -

It is one-half the distance between nuclei of two adjacent atoms in a crystalline structure.

example : The distance between two adjacent copper atoms in solid copper is 256 pm ; hence the metallic radius of copper is assigned a value of 128 pm.

3) Vander waals Radius -

It is half of the distance between two non - bonding similar atoms belonging to non- bonding similar adjacent molecule.

- Van der waal radii is mainly determined for inert gases which do nof form compound.
- van der waal radii for any element can be defined.

van der wall Radius > Metallic Radius > covalent Radius

b) Ionic Radius

- The removal of electron from an atom results in the formation of a cation, Whereas gain of an electron leads to an anion.

- The Ionic Radius is distance from centre of ions upto which its effect can be felt.

- Ionic size $\propto$ -ve charge.

- Ionic size $\propto \frac{1}{+ve\ charge}$

- A cation is smaller than its parent atom because it has fewer electrons while its nuclear charge remains the same.

- The size of an anion will be larger than that of parent atom because the addition of one or more electrons would result in increased repulsion among the electrons and a decrease in effective nuclear charge.

c) Ionization Enthalpy -

Ionization Enthalpy of elements is the amount of energy that an isolated gaseous atom requires to lose an electron in its ground state.

- The first ionization enthalpy of element A is the energy required by an atom to form A^+ ions. The unit of ionization energy is given as $kJ\,mol^{-1}$

$$A(g) \longrightarrow A^+(g) + e^-$$

- We can define the second ionization enthalpy as the energy required to remove the second most loosely bound electron; it is the energy required to carry out the reaction.

$$A^+(g) \longrightarrow A^{2+}(g) + e^-$$

- You need to provide a specific amount of energy to remove an electron from an atom. Hence, the ionization enthalpies of chemical elements are always positive.

- The second most outer electron will be more attracted to the nucleus than the first outer electron. Therefore, the second ionization energy will always be more than the first ionization energy. In the same way, third ionization enthalpy will be greater than second one.

Factors for Ionization Enthalpies

- The force of attraction between electrons and the nucleus.
- The force of repulsion between electrons.

The effective nuclear charge felt by the outermost electrons will be less than the actual nuclear charge. This is because the inner electrons will shield the outermost electrons by hindering the path of nuclear charge. This effect is known as 'shielding' or 'screening' effect.

example : In Na, the $3s^1$ electrons will be shielded by its core electrons. $(1s^2, 2s^2, 2p^6)$

General periodic Trends.

- In a group, while moving from top to bottom it decreases.

- It increases from left to right across a period. This is due to the decrease in the size of atoms across a period.

d) Electron Gain Enthalpy

Electron gain enthalpy of an element is the energy released when a neutral isolated gaseous atom accepts an extra electron to form the gaseous, negative ion i.e, anion.

- We can denote it by $\Delta_{eg}H$. Greater the amount of energy released in the above process, higher is the electron gain enthalpy of the element.

- The electron gain enthalpy of an element is a measure of the firmness or strength with which an extra electron is bound to it.

- It is measured in electron volts per atom or KJ per mole. It can be endothermic or exothermic reaction when you add an electron to the atom.

Electron Gain Enthalpy	$KJ\ mol^{-1}$
FLUORINE	-333
CHLORINE	-348
BROMINE	-324
IODINE	-295
ASTATINE	-270.1

- Energy is released when an electron is added to the atom. Therefore, the electron gain enthalpy is negative.

- The electron gain enthalpy for halogens is highly negative because they can acquire the nearest stable noble gas configuration by accepting an extra electron.

- Noble gases have large positive electron gain enthalpy. This is because the extra electron is placed in the next higher principal quantum energy levels. Thus, The highly unstable electronic configu-ration is produced.

e) Electronegativity

Electronegativity of an element is the tendency of its atoms to attract the shared pairs of electrons toward itself in a covalent bond. The electronegativity of any given element depends upon the following factors:

1) State of hybridization : An sp-hybridized carbon is more electronegative than sp^2 hybridized carbon. This is, in turn, more electro negative than sp^3 hybridized carbon.

2) Oxidation state of the element : The electronegativity of an element increases with the oxidation state of the element.

3) Nature of substituents attached to the atom : The carbon atom in CF_3I aquires greater positive charge than in CH_3I .

- The electronegativity values for the elements increases along a period from left to right and decreases down a group .

- As we move along the period from left to right, nuclear charge increases and atomic radius decreases. However, When we move down the group, atomic radius as well as cleaning effect increases.

metallic and Non-metallic character

As the electronegativity increases, the non-metallic character increases. As the electronegativity decreases, the metallic character increases. Fluorine with the highest electronegativity of 4 is the most non-metallic element. and caesium with the lowest electronegativity of 0.7 is the most metallic element.

Periodic Trends in chemical properties

a) Periodicity of valence or oxidation states :

oxidation number is the number of