

### PERIODICITY-PERIODIC PROPERTIES:

- Repetition of properties after intervals of atomic number values 2, 8, 18 and 32 is called periodicity. The properties are called periodic properties.

### ATOMIC RADIUS:

- The distance between the centre of the nucleus and electron cloud of the outermost energy level is called the atomic radius.
- It cannot be measured directly.
- It can be measured from the inter nuclear distance of bonded atoms using x-ray diffraction techniques.
- The atomic radius depends on factors like
  - 1) the number of bonds formed by atom
  - 2) nature of bonding
  - 3) oxidation state

### CRYSTAL RADIUS OR ATOMIC RADIUS:

- It is applicable for metal atoms.
- Half of the distance between the nuclei of two adjacent atoms in metallic crystal is called crystal radius.
- It is measured in angstrom units  
( $1 \text{ \AA} = 10^{-8} \text{ cm} = 10^{-10} \text{ m}$ ) or nanometres.  
( $1 \text{ nm} = 10^{-9} \text{ m} = 10^{-7} \text{ cm}$ )

### COVALENT RADIUS:

- This is used for non metals which form covalent bonds.
- It is half of the distance between the nuclei of two atoms connected by a covalent bond in a homonuclear molecule.
- Crystal radius is slightly greater than the covalent radius.

### VANDERWAAL'S RADIUS:

- It is used for molecular substances in the solid state only.
- It is half of the distance between the nuclei of two adjacent nonbonded atoms in neighbouring molecules.
- Vanderwaal's radius is greater than the covalent radius as the Vanderwaal's forces are weak.
- Vanderwaal's radius is approximately 40% greater than the covalent radius.

### TREND :

- The atomic radius increases down the group due to the addition of new shells and increase in screening effect.
  - The atomic radius decreases from left to right in a period due to the increase in nuclear positive
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charge.

- In a given period alkali metal is the largest atom and halogen is the smallest atom.
- Since the inert gas atoms are non bonded their atomic radius should be taken as the Vanderwaal's radius.
- Thus in every period inert gas atom is larger than halogen.
- In 2<sup>nd</sup> period inert gas atom is the largest and in other periods alkali metal atom is the largest.
- The decrease in atomic radius of transition elements is less than expected due to the screening effect of  $(n - 1)d$  electrons.
- Thus transition metals have similar atomic radii.
- In transition families, atomic radius increases normally from 3d to 4d series. But there after it doesn't change much due to lanthanide contraction.

#### LANTHANIDE CONTRACTION:

- In inner transition elements the differentiating electron enters into 'f' orbitals of the antepenultimate shell.
- As the atomic number increases in lanthanides due to the dispersed shape of f-orbitals and their poor shielding effect the atomic and ionic radii steadily decrease. This is called lanthanide contraction.
- Lanthanide contraction is also observed in 5d transition series.
- The atomic radius of 5d transition elements are very close to those of 4d transition elements due to Lanthanide contraction.
- As a result 4d and 5d transition elements are more similar in properties when compared to 3d and 4d transition elements e.g. Zr and Hf resemble most closely to each other than other elements.

#### IONIC RADIUS:

- The distance between the nucleus and the outermost  $e^-$  in an ion.
- When an atom loses one or more electrons a positive ion is formed.
- The cation is smaller in size than the neutral atom.
- The ionic radius is smaller than the atomic radius.
- As the number of electrons removed from the atom increases, the ionic radius is further decreased.

ATOMIC RADIUS	IONIC RADIUS
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|---------------|---|
| i) Na 1.86 Å  | Na <sup>+</sup> 1.02 Å                          |
| ii) Fe 1.17 Å | Fe <sup>2+</sup> 0.76 Å Fe <sup>3+</sup> 0.64 Å |

- If an atom gains electrons negative ion is formed (anion).
  - The negative ion is bigger in size than the neutral atom.
  - The size of anion increases with increase in negative charge.
  - With increase in  $z/e$  ratio ionic radius decreases.
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- In cations, the  $z/e$  ratio is greater than 1 and in anions, the  $z/e$  ratio is less than 1. (charge per electron =  $z/e$ )
- The atomic radius of chlorine atom ( $0.99 \text{ \AA}$ ) is much smaller than that of chloride ion ( $1.81 \text{ \AA}$ ).

### ISOELECTRONIC SPECIES:

- Ionic species having the same number of electrons is called isoelectronic species.
- In isoelectronic series the size decreases with the increases in nuclear positive charge.

Ion	$\text{C}^{4-}$	$\text{N}^{3-}$	$\text{O}^{2-}$	$\text{F}^-$	$\text{Na}^+$	$\text{Mg}^{2+}$	$\text{Al}^{3+}$	$\text{Si}^{4+}$
Ion Radius ( $\text{\AA}$ )	2.60	1.71	1.40	1.36	0.95	0.65	0.50	0.41

- In isoelectronic series, size decreases with increase in number of protons.
  - Smallest atom is 'H'
  - Largest atom is Fr
  - Smallest cation is  $\text{H}^+$
  - Smallest anion is  $\text{H}^-$
  - Largest cation is  $\text{Cs}^+$
  - Largest anion is  $\text{I}^-$

### IONIZATION POTENTIAL OR IONIZATION ENERGY:

- The minimum amount of energy required to remove the most loosely bound electron from an isolated gaseous atom is called its first ionization potential ( $I_1$ ).  $\text{M(g)} \xrightarrow{I_1} \text{M}^+(\text{g})$
- The energy required to remove an electron from a unipositive ion is called its second ionization potential ( $I_2$ ).  $\text{M}^+(\text{g}) \xrightarrow{I_2} \text{M}^{2+}(\text{g})$
- The number of ionisation potentials of an atom is equal to its atomic number.
- The second ionization potential is greater than the first ionization potential.
- With the successive removal of electrons ionization potential increases due to increased nuclear charge.
- $I_1 = 13.6 \times z^2$  ( $z$  = effective nuclear charge)
- Ionization potential is measured in eV/atom and ionization energy is measured in kJ/mole  
 $(1 \text{ eV/atom} = 96.45 \text{ kJ mole}^{-1} \text{ or } 1 \text{ eV/atom} = 23.06 \text{ kcal/mole})$
- Ionization energies are determined from spectral studies as well as from discharge tube experiments.

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- Ionization potential depends on the following factors.
    - 1) Atomic radius.
    - 2) Nuclear positive charge
    - 3) Screening effect or shielding effect.
    - 4) Extent of penetration of valence electrons.
    - 5) Completely or half-filled sub shells.
  - Ionization potential decreases as the atomic radius increases.
  - Ionization potential increases as the nuclear positive charge increases.

#### SCREENING EFFECT:

- The protection given by the inner electrons to the valence electrons from the nucleus is called screening effect.
  - As the inner electrons increase in number, screening effect increases and the ionization potential decreases.
  - The extent of penetration of orbitals towards the nucleus follows the order  $s > p > d > f$  for a given principle quantum number  $n$ .
  - With increase in the extent of penetration, I.P. increases.  $s > p > d > f$ .
  - Atoms having completely filled and half filled orbitals are more stable and need more energy for ionization.
  - Be has greater ionisation potential than B due to the completely filled s-orbital.
  - Nitrogen has greater ionization potential than oxygen due to the half filled p-orbitals.
- $I_1$  of 2<sup>nd</sup> period:  $\text{Li} < \text{B} < \text{Be} < \text{C} < \text{O} < \text{N} < \text{F}$
- $I_2$  of 2<sup>nd</sup> period:  $\text{Be}^+ < \text{C}^+ < \text{B}^+ < \text{N}^+ < \text{F}^+ < \text{O}^+ < \text{Li}^+$

#### TREND OF IONIZATION POTENTIAL:

- Ionization potential decreases down the group due to increase in size and increases in screening effect.
  - Ionisation potential increase in a period from left to right due to decrease in size and increase in nuclear charge.
  - In any given period, alkali metal has less. I.P. value and inert gas has highest I.P. value.
  - In transition series I.P. value slowly  $\uparrow$  due to less screening effect of  $(n - 1)d$  electrons.
  - Alkali metals have low I.P values. Lowest I.P. value is for Cs.
  - Noble gases have high I.P values. Highest I.P. value is for He.
  - In transition families I.P. value  $\downarrow$  from 3d to 4d and slightly increases there after due to lanthanide contraction.
  - The  $I_1$  values of 1<sup>st</sup> few elements:
  - $\text{He} > \text{Ne} > \text{F} > \text{Ar} > \text{N} > \text{Kr} > \text{O}$  etc.
  - I.P. curve is obtained by plotting I.P. Vs atomic number.
  - In I.P. curve, peaks are occupied by Inert gases.
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- Troughs are occupied by alkali metals.
  - Ascending portions are occupied by II-A group metals.
  - Descending portions are occupied by VII-A group elements.

#### ELECTRON AFFINITY:

- The amount of energy released when an electron is added to a neutral gaseous atom is called electron affinity.
- Energy is released when the first electron is added to the neutral atom.
- The energy is required to add the second electron or  $e^-$ s to uninegative ion.
- Therefore for most of elements  $E_1$  values are negative (energy released) and for all the elements  $E_2$ ,  $E_3$  etc values are positive (energy absorbed).
- Even  $E_1$  values are positive for some elements due to their stable configurations. E.g.: 'O' group elements, Be, Mg, N.
- Numerically  $I_1$  of atom 'M' is equal to  $E_1$  of  $M^+$  ion.
- Numerically  $E_1$  of atom 'M' is equal to  $I_1$  of  $M^-$  ion.
- They cannot be determined directly.
- They are calculated indirectly using Born-Haber cycle.
- Electron affinity is measured in  $\text{kJ mol}^{-1}$  or  $\text{eV / atom}$ .
- Electron affinity depends on
  - (i) **Size:** E.A increases with decrease in size
  - (ii) **Nuclear charge:** E.A. increases with increase in nuclear charge
  - (iii) **Screening effect:** EA decreases with increase in screening effect.
  - (iv) **Electronic configuration:** Atoms with stable electronic configuration have zero or negative electron affinities.
  - (v) **Number of valence electrons in valence shell.** E.A increases with increase in the number of valence  $e^-$ s.

#### TREND:

- E.A. decreases from top to bottom in a group due to increase in size and increase in nuclear charge.
  - But in most of the groups, the 1<sup>st</sup> element has abnormally low E.A. value than that of the remaining elements, eg.  $F < Cl$ ,  $O < S$ .
  - $EA \uparrow$  from left to right in a period due to  $\downarrow$  in atomic size and  $\uparrow$  in nuclear charge.
  - In every period halogen has highest E.A value.
  - $E_1$  trend of few elements:  $Cl > F > Br > I > S > Si$ .
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## APPLICATIONS OF E.A.:

- (i) We can predict the ability of atom into anion.
- (ii) Oxidising power of element.
- (iii) We can predict the tightness of binding an electron to the valence shell.

## ELECTRONEGATIVITY:

- The tendency of an atom to attract the shared electron pair towards itself in a molecule is called its electro negativity.
- Electron affinity is the property of an isolated atom and electronegativity is the property of a bonded atom.
- Electron affinity is absolute phenomenon electro negativity is relative phenomenon.
- Electron affinity has units and electronegativity has no units.
- Electron affinity of an element is fixed and electronegativity is slightly variable.
- Electronegativity depends on
  - i) **Size of atom:** EN. decreases with increase in size of atom
  - ii) **Nuclear charge:** E.N. increases with increase in nuclear charge
  - iii) **Screening effect:** E.N. decreases with increase in screening effect.
  - iv) **Number of valence electrons:** E.N increases with increase in number of valence e<sup>-</sup>s.
  - v) **S-character of hybrid orbital:** E.N. increases with increase in S-character of hybrid orbital.

## TREND:

- Electronegativity decreases with increase in size and increase in screening effect in a group from top to bottom.
- Among all groups, I-A group has least E.N. and VII-A group has highest E.N. Values.
- Electronegativity increases with decrease in size and increase in nuclear charge in a period from left to right.
- In a given period I-A element has least E.N. and VII-A element has highest E.N. value.
- 'O' group elements have zero E.N values.
- E.N of the 1<sup>st</sup> few elements:  
 $F > O > N \approx Cl > Br > C \approx I > H$
- In Pauling's scale electroegativities are calculated from the bond energies.

## SCALES OF ELECTRONEGATIVITY :

### Pauling scales :

- It is widely accepted scale.
  - $X_A - X_B = 0.208 \cdot \sqrt{\Delta}$  if  $\Delta$  is in kcal/mole or
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- $X_A - X_B = 0.1017\sqrt{\Delta}$  if  $\Delta$  is in kJ/mole.
  - $X_A$  and  $X_B$  are the electronegativities of two elements A and B.
  - $\Delta$  -difference between calculated and experimental bond energies of A – B bond.

$\Delta$  = ionic - resonance energy

$\Delta$  = polarity of A - B bond.

- In the determination of electronegativities of other elements. Hydrogen is reference element.
- Fluorine is the most electronegative and Cs is the least electronegative.
- Electronegative value of Hydrogen is 2.1.

#### MULLIKAN SCALE:

- Mullikan suggested that the electronegativity of an element is the average of its ionization energy and electron affinity.

$$E.N = \frac{\text{ionization energy} + \text{electron affinity}}{2} \text{ (eV/atom)}$$

(E.N = Electronegativity)

- These values are about 2.8 times greater than the values on Pauling's scale.
- The commonly accepted electronegativity values are obtained from the formula.

$$E.N = \frac{\text{ionization potential} + \text{electron affinity}}{544} \text{ (kJ/mole)}$$

- Mulliken scale is not much useful due to the following drawbacks.
  - i) It is applicable only for monovalent elements.
  - ii) As per Mulliken scale, Inert gases should possess higher E.N values.

#### Conversion:

$$1 \text{ Unit of Pauling} = \frac{1 \text{ unit of Mulliken}}{2.8}$$

#### APPLICATIONS OF ELECTRONEGATIVITY:

- i) If the electronegativity difference of the bonded atoms is greater than or equal to 1.7, the bond is ionic. If the electronegativity difference is less than 1.7 the bond is covalent or polar covalent.
  - ii) Electronegativity values are useful in writing the formulae of compounds.
  - iii) In calculation of oxidation states.
  - iv) In predicting oxidising power of elements.
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## VALENCY:

- Valency was introduced by Mendeleev.
- Valency is the combining capacity i.e. number of bonds formed by an atom.
- Valency of an element can be defined as the
  - i) number of hydrogens with one atom of element combines.
  - ii) number of chlorine atoms with which one atom of element combines.
  - iii) double the number of oxygen atoms with which one atom of element combines.
- Valency of a given group element will be same in general.
- Highest valency of an element will never exceed its group number.
- Valency of an element may be equal to its group number or  $8 - \text{group number}$ .
- Valency of a given period elements will be different and it changes by 1 unit from one element to next element.
- w.r.t. oxygen. Valency increases from 1 to 7 in a period.
- w.r.t. hydrogen, valency increases from 1 to 4 and then decreases towards the end of the period.
- For zero group elements valency is zero
- Valency is a whole number without positive or negative sign.

## OXIDATION STATES:

- The charge which an atom appears to be possessed in a molecule or ion is called its oxidation state.
  - Oxidation state may be positive or negative or a fraction or zero.
  - For s-block elements oxidation number is equal to the group number.
  - p-block elements show different oxidation states which often differ by 2 units.
  - The s-electron pair in the valence shell of the heavier elements of p-block show reluctance in bond formation. This is called inert pair effect.
  - In p-block group III elements have a common oxidation state of +3.
  - For thallium +1 oxidation state is more stable than +3 oxidation state, due to inert pair effect.
  - Group IV elements show +4 and +2 oxidation states.
  - Group V elements show +5 and +3 oxidation states.
  - The common oxidation state shown by group VI elements is -2.
  - The other oxidation states shown by VI group elements are +2, +4 and +6.
  - Halogens are the most electronegative elements and show the common oxidation state -1.
  - Fluorine always shows the oxidation state -1.
  - The other halogens show positive oxidation state +1, +3, +5 and +7.
  - The common oxidation state of transition or d-block elements is +2 due to the  $ns^2$  electronic
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configuration.

- Ruthenium (Ru) and osmium (Os) show the highest oxidation state of +8.
- Carbon show the lowest oxidation state of -4.
- f-block elements or inner transition elements show the common oxidation state of +3.
- The highest oxidation state shown by any element is equal to its group number.

#### **ELECTROPOSITIVE NATURE:**

- The tendency of an element to lose an electron is called its electro positivity.
- Electro positivity is a metallic character.
- Smaller the ionization potential greater the electropositive character.
- More electropositive metals form ionic compounds.
- Strongly electropositive metals readily liberate hydrogen from water and dilute acids.
- More electropositive metals form strong basic oxides and hydroxides.
- The ions of strong electropositive metals do not undergo hydrolysis.
- Electropositive nature increases down the group and decreases along a period.
- Alkali metals are the most electropositive metals.
- Strong electropositive elements are strong reducing agents.

#### **Metallic and nonmetallic nature:**

- Metallic nature means electropositive nature
- Most electropositive or most metallic is Cs.
- Non-metallic nature means electronegative nature.
- Most electronegative or most non-metallic is F.
- Metallic nature increases and non-metallic nature decreases down the group.
- Metallic nature decreases and non-metallic nature increases along a period.

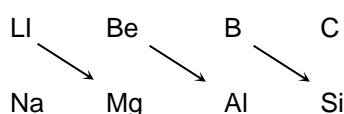
#### **Acidic and basic nature of oxides:**

- In general, metal oxides are basic and dissolve in water to form hydroxides. e.g.:  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ,  $\text{CaO}$ ,  $\text{BaO}$ .
  - Alkali metal oxides are the most basic oxides.
  - Oxides of nonmetals are acidic and dissolve in water to form acidic solutions e.g.:  $\text{CO}_2$ ,  $\text{SO}_2$ ,  $\text{P}_2\text{O}_3$ ,  $\text{Cl}_2\text{O}_7$  etc.
  - Oxides of halogens are the most acidic oxides.
  - Oxides which show both acidic and basic properties are called amphoteric oxides.
  - Metalloids and a few metals form amphoteric oxides. e.g.:  $\text{BeO}$ ,  $\text{ZnO}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{SnO}$ ,  $\text{SnO}_2$ ,  $\text{PbO}$ ,  $\text{PbO}_2$ ,  $\text{As}_2\text{O}_3$ ,  $\text{Sb}_2\text{O}_3$ .
  - Basic nature of oxides increases and acidic nature decreases down the group.
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- Across a period acidic nature increases and basic nature decreases in oxides.
  - The 2<sup>nd</sup> period element which forms most acidic oxide is nitrogen (N<sub>2</sub>O<sub>5</sub>)
  - The 3<sup>rd</sup> period element which forms most acidic oxide is chlorine (Cl<sub>2</sub>O<sub>7</sub>)
  - Among all, the most acidic oxide is Cl<sub>2</sub>O<sub>7</sub> and most basic oxide is Cs<sub>2</sub>O.
  - Fluorine does not form oxides, instead it forms fluorides eg. O<sub>2</sub>F<sub>2</sub> and OF<sub>2</sub>.

#### DIAGONAL RELATIONSHIP:

- The lighter elements of short periods show similarities with the diagonally arranged ones. This is called diagonal relationship.



- This is found between 2<sup>nd</sup> and 3<sup>rd</sup> period elements.
- Diagonal relation is weaker than group similarities.
- Diagonal relation disappears beyond IV-A group.
- Diagonal relation is due to
  - i) similar ionic sizes and similar electronegativity values.
  - ii) similar polarising power.

$$\text{Polarising power} = \frac{\text{Charge}}{(\text{radius})^2}$$

#### Trend of Melting and Boiling Points:

- In a period MP's and BP's will increase first and decrease towards the end of period.
- In a group MP's and BP's will decrease from top to bottom in IA, IIA, IIIA, IVA.
- In VA, VIA, VIIA and zero groups, MP's and BP's will increase from top to bottom.

#### TREND OF ATOMIC VOLUME:

- Atomic volume is the volume occupied by 1 gram – atom of element.
- In a group atomic volume increases from top to bottom.
- In a period atomic volume first decreases and then increases towards the end.

#### TREND OF DENSITY:

- In a group density increases from top to bottom due to increase in atomic mass.
  - In a period density increases from left to right due to decrease in atomic size.
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