Unit 1: Atomic Structure and Periodicity of Elements

Syllabus:

Periodicity of elements: s, p, d, f block elements, the long form of periodic table.

Detailed discussion of the following properties of the elements, with reference to s- and p-block.

(a) Effective nuclear charge, shielding or screening effect, Slater rules, variation of effective nuclear charge in periodic table.

(b) Atomic radii (van der Waals)

(c) Ionic and crystal radii.

(d) Covalent radii (octahedral and tetrahedral)

(e) Ionization enthalpy, Successive ionization enthalpies and factors affecting ionization energy. Applications of ionization enthalpy.

(f) Electron gain enthalpy, trends of electron gain enthalpy.

(g) Electronegativity, Pauling's/ Mulliken's/ Allred Rachow's/ and Mulliken-Jaffé's electronegativity scales. Variation of electronegativity with bond order, partial charge, hybridization, group electronegativity. Sanderson's electron density ratio.

Mendeleev’s Periodic Law:
According to Mendeleev’s periodic law, the physical and chemical properties of elements are periodic functions of their atomic weights.

Disadvantages of Mendeleev’s Periodic Table:

1. Position of hydrogen: It has been confirmed that hydrogen has many characters which match with halogen elements too. But it is only placed in Group IA. Thus position of hydrogen is not clear.

2. Position of isotopes: Since in Mendeleev’s periodic table elements have been arranged according to their atomic masses, isotopes (more than one element) are placed at a one place which is confusing.

3. Position of the isobar: Since in Mendeleev’s periodic table elements have been arranged according to their atomic masses, different elements having different atomic numbers but same mass number (isobars) are placed at one place which is again confusing.

4. No attempts were made to separate metals from non-metals.

5. Dissimilar elements placed together in the same group: Elements showing different chemical properties have been placed together in the same group. For example Li, Na, k and Cu, Ag, Au have been placed in Group IA.

MODERN PERIODIC TABLE:

Moseley’s experiment confirmed that atomic number of an element and square root of the frequency of X-ray of that element (which is obtained when various elements were bombarded with cathode rays) are directly proportional to each other. This triggered the chemist to modify the old periodic law.

- According to modern periodic law, “The properties of elements are the periodic function of their atomic numbers”
- In modern periodic table, the **horizontal lines are periods** and the **vertical lines are groups**.
- The periodic table has total **7 periods** and **18 groups**.
- If elements are arranged in increasing order of their atomic numbers, there is repetition of properties after 2, 8, 18, and 32 elements.
- There are two elements in the first period, eight elements in each of the second and third periods, eighteen elements in each of fourth and fifth period, thirty two elements in the sixth period and only nineteen elements till now in the seventh period.

Advantages of the Long Form of the Periodic Table:

(a) The table is based on a more fundamental property i.e. atomic number.

(b) It correlates the position of elements with their electronic configuration more clearly.

(c) The completion of each period is more logical. In a period, as the atomic number increases, the energy shells are gradually filled up until an inert gas configuration is reached.

(d) It eliminates the even and odd series of IV, V and VI periods of Mendeleev's periodic table.

(e) The position of VIII group is also justified in this table. All the transition elements have been brought to the middle as the properties of transition elements are intermediate between s-and p-block elements.

(f) Due to the separation of two sub-groups, dissimilar elements do not fall together. One vertical column accommodates elements with same electronic configuration thereby showing same properties.

(g) The table completely separates metals and non-metals. Non-metals are present in upper right corner of the periodic table.

(h) There is a gradual change in properties of the elements with increase in their atomic numbers i.e., periodicity of properties can be easily visualized. The same properties occur after the intervals of 2, 8, 8, 18, 18 and 32 elements which indicates the capacity of various periods of the table.

(i) The greatest advantage of this periodic table is that this can be divided into four blocks namely s-, p-, d- and f-block elements.

(j) This arrangement of elements is easy to remember and reproduce.

Defects of the Long Form of the Periodic Table:

(a) The position of hydrogen is still disputable as it was there in **MENDELEE**V periodic table in group IA as well as IVA & VIIA.

(b) Helium is an inert gas but its configuration is different from that of the other inert gas elements

(c) Lanthanide and actinide series could not be adjusted in the main periodic table and therefore they had to be provided with a place separately below the table.

Period-The details about the seven periods are as follows:-

Period	**Atomic number**		**Number of elements**
	From	**To**	
First	H (1)	He (2)	2
Second	Li (3)	Ne(10)	8
Third	Na (11)	Ar (18)	8
Fourth	K (19)	Kr(36)	18
Fifth	Rb (37)	Xe (54)	18
Sixth	Cs (55)	Rn (86)	32 (including lanthanides)
Seventh	Fr (87)	Ha (105)	19 (including actinides)

Group: The modern periodic table has 18 vertical columns and according to CAS system there are 16 groups having the following number of elements.

Group	**Number of Elements**
(a) I A group	**7 (H, Li, Na, K Rb, Cs, Fr) Alkali metals**
(b) II A group	**6 (Be, Mg, Ca, Sr, Ba, Ra) Alkaline earth metals**
(c) III A group	**5 (B, Al, Ga, In, Tl) Boron family**
(d) IV A group	**5 (C, Si, Ge, Sn, Pb) Carbon family**
(e) V A group	**5 (N, P, As, Sb, Bi) Nitrogen family**
(f) VI A group	**5 (O, S, Se, Te, Po) Oxygen family (Chalcogen)**
(g) VII A group	**5 (F, Cl, Br, I, At) Halogen family**
(h) Zero group	**6 (He, Ne, Ar, Kr, Xe, Rn) Inert elements**
	32 (Sc, Y, La, Ac & 14 lanthanide elements & 14 actinide elements.)
(i) III B group	**These are elements of IIIB group, which could not be accommodated in one column and therefore written separately outside the periodic table.**
(j) IV B group	**4 (Ti, Zr, Hf, Rf)**
(k) V B group	**4 (V, Nb, Ta, Db)**
(l) VI B group	**3 (Cr, Mo, W)**
(m) VII B group	**3 (Mn, Tc, Re)**
(n) VIII (3) group	**9 (Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, Pt)**
(o) I B group	**3 (Cu, Ag, Au)**
(p) II B group	**3 (Zn, Cd, Hg)**

Periodicity of Elements (Cause of Periodicity):

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

Looking at the elements of alkali metals in the modern periodic table, it's not difficult to realize that every element here has a similar outer electronic configuration. This repetition in similar outer electronic configurations after certain regular interval (as the atomic number increases while arranging the elements in the periodic table) is the cause of periodicity in properties of elements. This is because the chemical behavior of elements is due to the electrons in the outer most shells. Since all the elements in a particular group have similar outer electronic configuration their chemical behavior are almost same.

CLASSIFICATION OF PERIODIC TABLE BASED ON BLOCKS

1. **s-block Elements:**
   - ✓ Elements of groups 1 and 2 including He in which the last electron enters the s-orbitals of the valence shell are called s-block elements.
   - ✓ There are only **14 s-block elements** in the periodic table.

Characteristics:

(a) The electronic configuration of outermost shell of s-block elements is ns^1 (alkali metals; group 1) or ns^2 (alkaline earth metals; group 2)

(b) The valence of group I elements is +1 and those of group II elements is +2.

(c) These are soft metals having low melting points and boiling points.

(d) Most of these form ionic compounds on account of their lower ionization energy.

(e) Most of these metals (except Be & Mg) and their salts imparts characteristic colour to the flame e.g., sodium imparts a golden yellow colour; potassium imparts violet colour to the flame.

(f) These are highly reactive elements and are strong reducing agents.

(g) All are good conductors of heat and electricity.

2. **p-block Elements:** Elements of groups 13-18 in which the last electron enters the p orbitals of the valence shell are called p-block elements.

   Characteristics:

   (a) The electronic configuration of the outermost shell of p-block elements (group 13, 14, 15, 16, 17 and 18) is $ns^2\ np^{1-6}$.

   (b) These elements include metals and non-metals with a few metalloids. The metallic character, however, decreases along the period but increases down the group.

(c) These possess relatively higher ionization energy which tends to increase along the period but decreases down the group.

(d) Most of them form covalent compounds.

(e) Most of these elements show negative (except some metals) as well as positive oxidation states (except F).

(f) The oxidizing power of these elements increases along the period but decreases down the group.

3. **d-Block Elements:** There are three complete series and one incomplete series of d-block elements.
   These are:
   - 1st or 3d-transition series which contains ten elements with atomic number 21-30 ($_{21}Sc$-$_{30}Zn$).
   - 2nd or 4d-transition series which contains ten elements with atomic numbers 39-48 ($_{39}Y$-$_{48}Cd$).
   - 3rd or 5d transition series which contains ten elements with atomic numbers 57 and 72-80 ($_{57}La$, $_{72}Hf$-$_{80}Hg$).
   - 4th or 6d transition series which is incomplete at present and contains only nine elements. These are $_{89}Ac$, $_{104}Rf$, $_{105}Ha$, Unh (Seaborgium, Z = 106), $_{107}Bh$ (Bohrium), $_{108}$ Hs (Hassium), $_{109}Mt$ (Meitnerium), Ds (Darmstadtium, Z= 110) and Cn (Copernicium, Z = 112) or Ekamercury. The element, Z = 111 has not been discovered yet. Thus, in all, there are 39 d-block elements.

Characteristics:

(a) The electronic configuration of outermost shell of d-block elements is $\mathbf{ns^{0-2}}$ followed with $\mathbf{(n-1)\ s^2p^6d^{1-10}}$.

(b) All (except Hg) are hard, ductile metals with high melting and boiling points.

(c) All of these are good conductors of heat and electricity.

(d) Their ionization energies are higher than s-block elements but lesser than p-block elements.

(e) Most of the transition metals form coloured ions (Zn^{2+}, Hg^{2+}, Cd^{2+} are colourless.)

(f) These elements show variable oxidation states.

(g) Most of these elements possess catalytic activity.

(h) Metals and their ions are generally paramagnetic due to the presence of unpaired electrons.

(i) Most of the transition metal ions possess the tendency to form complex ions.

(j) Most transition metals form alloys.

4. f -block Elements:

f-Block elements are also called inner-transition elements. In these elements, the f-subshell of the inner-penultimate is progressively filled up. There are two series of f-block elements each containing 14 elements.

The fourteen elements from $_{58}$Ce - $_{71}$Lu in which, 4f-subshell is progressively filled up are called **lanthanides or rare elements**.

Similarly, the fourteen elements from $_{90}$Th – $_{103}$Lr in which, 5f-subshell is progressively filled up are called actinides.

Characteristics:

(a) The electronic configuration of outermost shell of f-block elements is **ns^2**, followed with **$(n–2)f^{1–14}$, $(n–1)\ d^{0–2}$.** **{i.e. $(n-2)f^{1-14}(n-1)d^{0-1}$, ns^2}**

(b) All are metals.

(c) **Lanthanoids are also known as rare earth elements whereas most of the members of actinoid series are known as transuranic elements (made artificially).**

(d) These show variable valency.

(e) These form coloured ions.

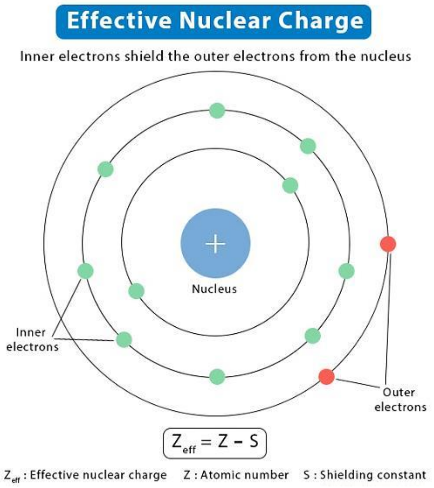
(f) Actinoids are radioactive.

(g) These also form complexes.

EFFECTIVE NUCLEAR CHARGE

According to Coulomb's law, the attractive electrostatic force between the nucleus and the electron depends on the nuclear charge, electron charge, and electron-nucleus distance. However, Coulomb's law is only suitable for single-electron atoms or ions.

For a multi-electron atom, the calculations are complicated as the forces need to be added vectorially. Overall, the outer electrons experience a lower force and a reduced nuclear charge due to shielding by the inner electrons. ***This reduced charge is known as the effective nuclear charge. It is called effective because the shielding prevents the outer electrons from experiencing the full charge.***



Effective Nuclear Charge and Nuclear Charge:

The actual nuclear charge is the atomic number multiplied by the proton charge.

On the other hand, **the effective nuclear charge** is the net charge on the nucleus that attracts the valence electrons towards itself.

The effective nuclear charge is always less than the actual nuclear charge.

WHAT IS THE SCREENING/SHIELDING EFFECT?

In an atom containing a multielectron, the electrons present in the valence shell are attracted towards the nucleus and these electrons are repelled by the electrons which are repelled by the electrons allocated in the inner shell. Due to this, the actual force of attraction between the nucleus and the valence electrons is reduced by the repulsive force which is acting in the opposite direction. **This decrease in the force of attraction exerted by the nucleus on the valence electrons resulting from the presence of electrons from the availability of electrons in the inner shells is known as the shielding effect**. The shielding effect occurs between the sublevels between the same principal energy level.

An electron in the s sublevel shields electrons present in the p sublevel of the same principal energy level. This is due to the spherical shape of the s orbital. It can be explained by the shielding effect example of a lithium atom. A lithium atom contains three protons and three electrons. The electronic configuration of lithium is $1s^2 2s^1$, two electrons are present in the first principal energy level and one electron (valence electron) in the second principal energy level. The valence electron is partially shielded by the attractive force of the nucleus by the two electrons present in the inner shell. The removal of the valence electrons becomes easy due to the shielding effect.

Order of Screening Effect:

The order of screening effect is s > p > d > f. The shielding effect experienced by the outermost electrons increases as the number of electron shells increases.

As the screening effect of orbitals reduces from s-orbital to f-orbital in an atom due to the geometry of the orbital.

SLATER'S RULE:

The effective nuclear charge for any electron in the configuration of an atom may be calculated with the help of following correlation:

$$\boxed{Z_{eff} = Z_{actual} - S}$$

where **S** is the screening constant or the shielding constant whose magnitude determines the extent to which the electron is screened or shielded by other electrons in the atom from the nuclear charge.

The screening constant is evaluated by the following empirical rules known as Slater's Rule:

1. The shielding effect or screening effect of each electron of 1s orbital is 0.30.

2. The shielding effect of each electrons of ns and np i.e. electron of the outermost orbit, is 0.35.

3. The shielding effect of each electron of s, p or d orbitals of the penultimate orbit (n – 1) is 0.85.

4. The shielding effect of each electron of s, p, d or f orbital of the inner penultimate orbit (n – 2) and below this is 1.0

Rules to determine shielding constant based on Slater's values:

1. Write the electronic configuration for the atom

2. Group electronic configurations by n value as shown:

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

3**.**

Case 1: The value of s for an electron residing in an ns or in np orbitals

To calculate **S** assign the values

(a) 0.35 for each of the remaining electrons is the nth shell

(b) 0.85 for each of the electrons in (n−1)th shell

(c) 1.0 for each of the electrons present in the rest of inner shells

(d) There will be no contribution to the value of s by the electrons residing in orbitals/shell having higher value of their principal quantum number than the orbital containing the electrons for electrons for which s is being calculated.

(e) If s is being calculated for an electron of 1s orbital, there will be a contribution of 0.30 from other single electrons in 1s orbitals (for H and He only)

Net S = sum of all the above contribution made by electrons

Case 2: The value of σ for an electron residing in (n – 1)d orbitals of (n – 1)th shell of an atom or an ion

(a) There will be no contribution to the value of s by the electrons residing in ns orbitals in ns orbital.

(b) Each of the remaining electrons present in (n – 1) d orbitals, makes a contribution of 0.35

(c) Each of the electrons present in the (n – 1)s, (n – 1)p orbitals and inner shells [i.e. 1st 2nd, 3rd,….(n – 2)th shells] makes a contribution of 1.0

Thus :

σ for a (n – 1)d electron = 0.35 × [No. of the electrons in (n – 1)d orbitals] + 1.0 × [No. of electrons in (n – 1)s, (n – 1)p orbitals and inner shells]

Electrons to the outer of the electron of interest do not shield.

Example 1: calculate the effective nuclear charge for outermost electron of fluorine?

Ans: Fluorine electronic configuration is: $1s^2 2s^2 2p^5$ or $(1s)^2(2s, 2p)^7$

There are 2 electrons in n=1.

There are 7 e in n=2 but this includes the electron of interest.

Since electron of interest would not shield itself so subtract 1 leaving 6 electrons that we count in n=2.

There aren't any other electrons.

$\Phi = 2 \times 0.85+6 \times 0.35 = 3.8$;

Zeff = Z – S = 9-3.8 =5.2

The Zeff on the outer most electron of fluorine is 5.2.

It means outer most electron of Fluorine experience charge of 5.2 units although its nucleus has 9 protons.

EXAMPLE 2: Calculate the effective nuclear charge for 4s electron in calcium ?

Ans: Ca: $1s^2\ 2s^2 2p^6 3s^2\ 3p^6\ 4s^2$ or $(1s)^2(2s,2p)^8(3s,3p)^8\ (4s,4p)^2$

Count number of electrons in outermost shell = 1 ; because one electron is the one over which we are calculating the shielding constant.

$\Phi = 1.00 n_{n-2} + 0.85\ n_{n-1} + 0.35\ n_0$

$\Phi = 2 \times 1.00 + 8 \times 1.00 + 8 \times 0.85 + 1 \times 0.35 = 17.15$;

$Z_{eff} = Z – S = 20-17.38 = 2.85$

The Z_{eff} of Ca is 2.85.

Example 3: What is the screening constant for the last electron in Sc?

Sol: 1s2 2s2 2p6 3s2 3p6 3d1 4s2

Last electron is in 4s orbital.

The shielding effect for one electron of 4s = 0.35

Electrons of 3rd shell = 9; their contribution = 9 × 0.85

Contribution of 2nd and 1st shell = 10 × 1

Total = 0.35 + 9 × 0.85 + 10 × 1 = 18

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35.3 = 18

z* = z – S = 21 – 18 = 3

VARIATION OF EFFECTIVE NUCLEAR CHARGE IN PERIODIC TABLE.

The Z_{eff} for electrons in a given shell and subshell increases as the atomic number increases; this tendency is observed both across and down the periodic table.

Understanding trends in valence Z_{eff} is important for valence electrons since the valence Z_{eff} determines atomic/ionic characteristics and chemical reactivity. As the valence shell and/or subshell change as the atomic number increases, the trends in the valence Z_{eff} are not simple.

Down the Group:- As we go down the group of the periodic table, the valence Z_{eff} increases as the atomic number increases down the group.

Along a period:

Periods 1-3 (s and p only): As we go across periods 1-3, the shell remains constant as Z increases and the subshell changes from s to p. In these periods, there is a gradual increase in valence Z_{eff} . For example, the effective nuclear charge of magnesium is 3.31 at the periphery while the effective nuclear charge of chlorine is 6.12 at the periphery. This indicates that Z_{eff} increases along a period.

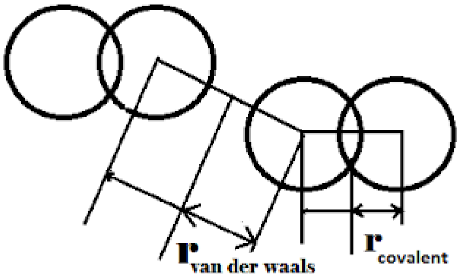
In periods 4 and 5 in the d subshell, effective nuclear charge shows an exceptional change in 4d subshell.

ATOMIC RADIUS

Atomic Radius: It refers to the distance between the centre of the nucleus of the atom to the outermost shell containing electrons. It is measured by electron diffraction method in angstrom (A°) or picometer (pm) unit.

i. Vander Waal's Radii:

- Van der Waals radius is defined as half of the internuclear separation of two non-bonded atoms of the same element on their closest possible approach. The term is used for non- metals (covalent compound) and noble gases.
- It is half of the distance between two successive nuclei of two covalently bonded molecules of like atoms or two successive molecules of inert gases.
- **Vander Waals radius = 1/2 × Internuclear distance between two successive nuclei of two covalent molecules.**



ii. Crystal Radius or Metallic Radius:

- The term is usually used for metals.
- It is defined as half of the distance between two successive nuclei of two adjacent metal atoms in the metallic closed packed crystal lattice.

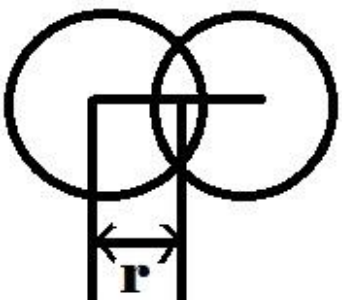
iii. Ionic Radius:

- This term is used in case of ions.
- It is the distance of outermost shell of an anion or cation from its nucleus.
- In other words, it is defined as the effective distance from the nucleus of the ion which is under influence in an ionic bond.

iv. Covalent Radius:

- Normally, this term is used for non-metals
- It is defined as half of the distance between two successive nuclei of two covalently bonded atoms in a molecule

Covalent radius = 1/2 × Internuclear distance between two covalently bonded like atom (d)



- **Covalent Single Bond Radius For Homonuclear Molecules**: It is defined as one half of the distance between the nuclei of two covalently bonded atoms (bonded with a single bond) of the same element in a homonuclear molecule such as H_2, F_2, Cl_2 etc.

r = 1/2 (Internuclear distance between two bonded atoms)

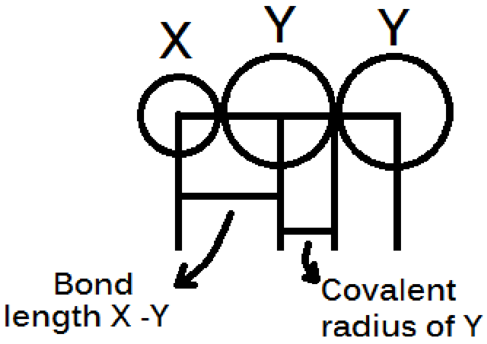
r = 1/2 (bond length) , e.g. the internuclear distance between two chlorine atoms in Cl2 molecule is 1.96 A°. Thus the covalent atomic radius of a chlorine atom is 1.96/2 = 0.98 A°.

- **Covalent Single Bond Radius For Heteronuclear Molecules where the electronegativity difference of corresponding bonded atoms is not so high:**

The covalent single bond radius of an atom X in a heteronuclear molecule is defined as the difference between the single bond length X - Y and the covalent radius of other single bonded atom, Y.

Covalent radius of X in the single bond X - Y = Bond length of X -Y - Covalent radius of Y in X - Y

For example, the bond length of Si - C bond (d Si - C) is 193 pm and covalent radius of carbon atom (r C) is 77 pm. Thus the covalent single bond radius of Si = (d Si - C) - r C = 193 - 77 = 116 pm



- **Covalent Single Bond Radius For Heteronuclear Molecules where the electronegativity difference is high**:

When there is a large difference in the electronegativity of two bonded atoms X and Y, the bond length will be shorter than expected and will have some ionic character of the bond. In this case the following relationship may be used:

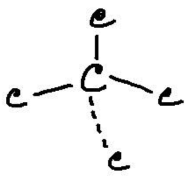
d X-Y = r A + r B - 0.09 (X A - X B),

where d X - Y is the bond length of X - Y and r A and r B are the covalent radius of A and B and X A and the X B are the electronegativities of A and B respectively.

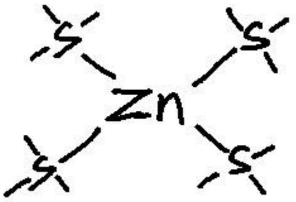
Covalent radii can further be studied as <u>Tetrahedral covalent radii</u> and <u>Octahedral covalent radii.</u>

- **Tetrahedral Covalent Radii:** Crystals having arrangement of lattice points similar to either diamond or sphalerite (ZnS called Zinc blende having cubic structure) or wurzite (Sulphide of Zn having hexagonal structure) give rise to covalent radii.

  In each of the arrangement where one atom is surrounded by four other atoms (similar or dissimilar atoms) tetrahedrally gives the covalent radius.



The central 'c' atom
Surrounded by 4 atoms
as in diamond



Tetrahedral
arrangement
in Sphalerite

Elements like C, Si, Ge, Sn have diamond like arrangement. All other elements which show tetrahedral arrangement are similar to either sphalerite (Cubic type structure) or wurzite (hexagonal structure).

- **Octahedral Covalent Radii:** Crystals having arrangement of lattice points similar to pyrite (FeS_2) structure fall into this category. Arrangement of lattice points where one atom is surrounded by 6 other atoms (similar or dissimilar atoms) octahedrally give rise to octahedral radii.
  In FeS_2 each S atom is surrounded by 4 atoms tetrahedral and each Fe atom is surrounded by six S atoms octahedrally.
  Thus we can find the internuclear distance of Fe - S which is 227 pm. subtracting the tetrahedral radius of S from 227 pm we get the octahedral radius of Fe = 227 - 104 = 123 pm.

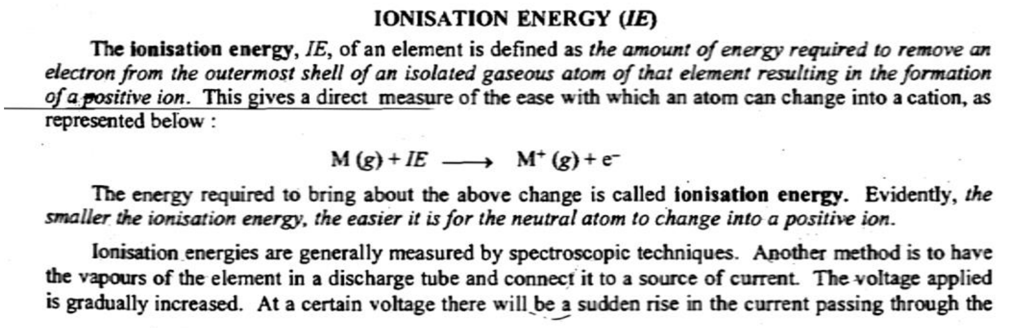
The magnitude of various atomic radii is in the order as follows:

Van der Waal's > metallic > covalent

Trends of Atomic Radius:

(a) Along the period: On moving across a period, atomic radii decreases because effective nuclear charge increases.

(b) Down the group: On moving down a group, atomic radii increases, because number of orbits increases.



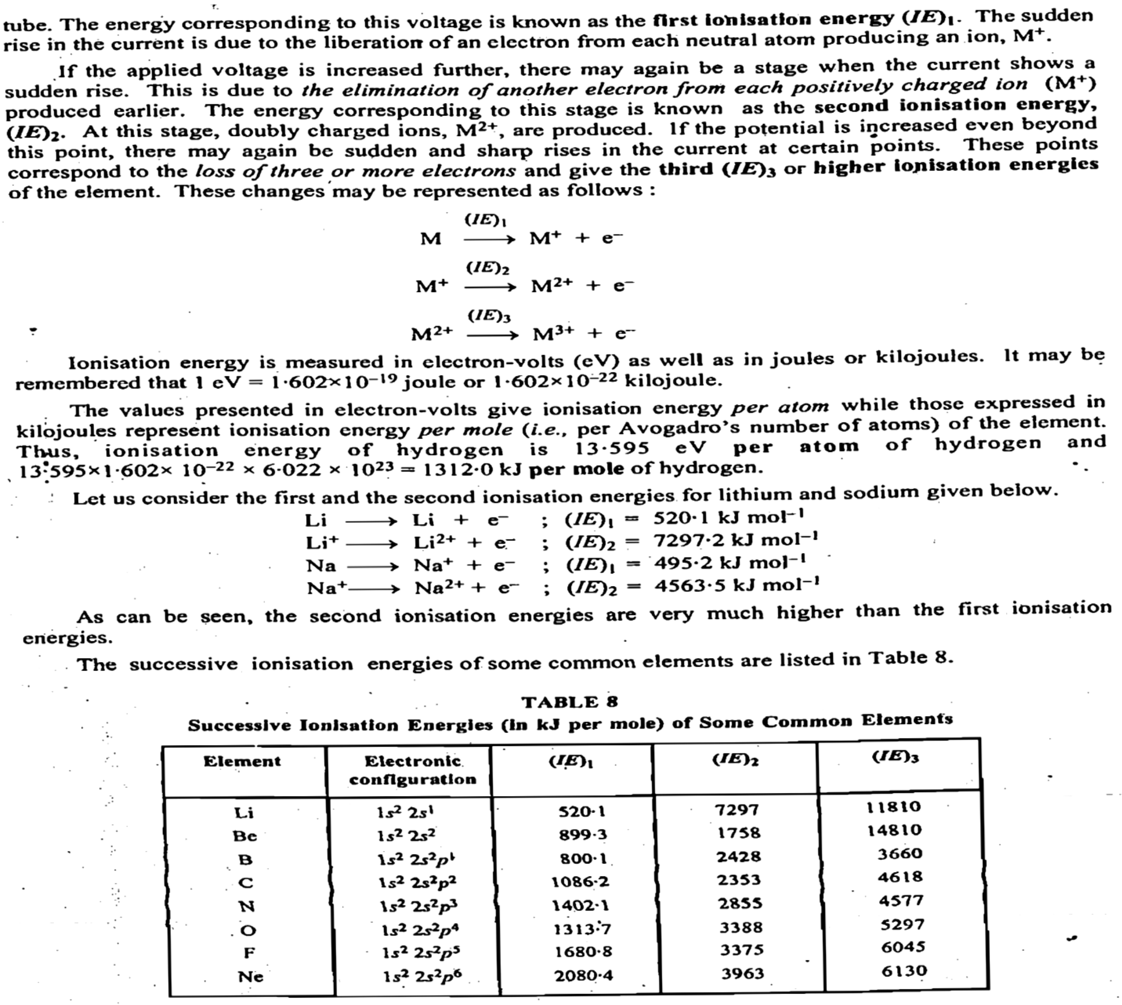
IONISATION ENERGY (*IE*)

The **ionisation energy**, *IE*, of an element is defined as *the amount of energy required to remove an electron from the outermost shell of an isolated gaseous atom of that element resulting in the formation of a positive ion*. This gives a direct measure of the ease with which an atom can change into a cation, as represented below :

$$M(g) + IE \longrightarrow M^+(g) + e^-$$

The energy required to bring about the above change is called **ionisation energy**. Evidently, *the smaller the ionisation energy, the easier it is for the neutral atom to change into a positive ion.*

Ionisation energies are generally measured by spectroscopic techniques. Another method is to have the vapours of the element in a discharge tube and connect it to a source of current. The voltage applied is gradually increased. At a certain voltage there will be a sudden rise in the current passing through the



tube. The energy corresponding to this voltage is known as the **first ionisation energy** $(IE)_1$. The sudden rise in the current is due to the liberation of an electron from each neutral atom producing an ion, M^+.

If the applied voltage is increased further, there may again be a stage when the current shows a sudden rise. This is due to *the elimination of another electron from each positively charged ion* (M^+) produced earlier. The energy corresponding to this stage is known as the **second ionisation energy, $(IE)_2$**. At this stage, doubly charged ions, M^{2+}, are produced. If the potential is increased even beyond this point, there may again be sudden and sharp rises in the current at certain points. These points correspond to the *loss of three or more electrons* and give the **third $(IE)_3$** or **higher ionisation energies** of the element. These changes may be represented as follows :

$$M \xrightarrow{(IE)_1} M^+ + e^-$$

$$M^+ \xrightarrow{(IE)_2} M^{2+} + e^-$$

$$M^{2+} \xrightarrow{(IE)_3} M^{3+} + e^-$$

Ionisation energy is measured in electron-volts (eV) as well as in joules or kilojoules. It may be remembered that $1 \text{ eV} = 1\cdot602 \times 10^{-19}$ joule or $1\cdot602 \times 10^{-22}$ kilojoule.

The values presented in electron-volts give ionisation energy *per atom* while those expressed in kilojoules represent ionisation energy *per mole* (*i.e.*, per Avogadro's number of atoms) of the element. Thus, ionisation energy of hydrogen is 13·595 eV **per atom** of hydrogen and $13\cdot595 \times 1\cdot602 \times 10^{-22} \times 6\cdot022 \times 10^{23} = 1312\cdot0$ kJ **per mole** of hydrogen.

Let us consider the first and the second ionisation energies for lithium and sodium given below.

$$Li \longrightarrow Li^+ + e^- \quad ; \quad (IE)_1 = 520\cdot1 \text{ kJ mol}^{-1}$$

$$Li^+ \longrightarrow Li^{2+} + e^- \quad ; \quad (IE)_2 = 7297\cdot2 \text{ kJ mol}^{-1}$$

$$Na \longrightarrow Na^+ + e^- \quad ; \quad (IE)_1 = 495\cdot2 \text{ kJ mol}^{-1}$$

$$Na^+ \longrightarrow Na^{2+} + e^- \quad ; \quad (IE)_2 = 4563\cdot5 \text{ kJ mol}^{-1}$$

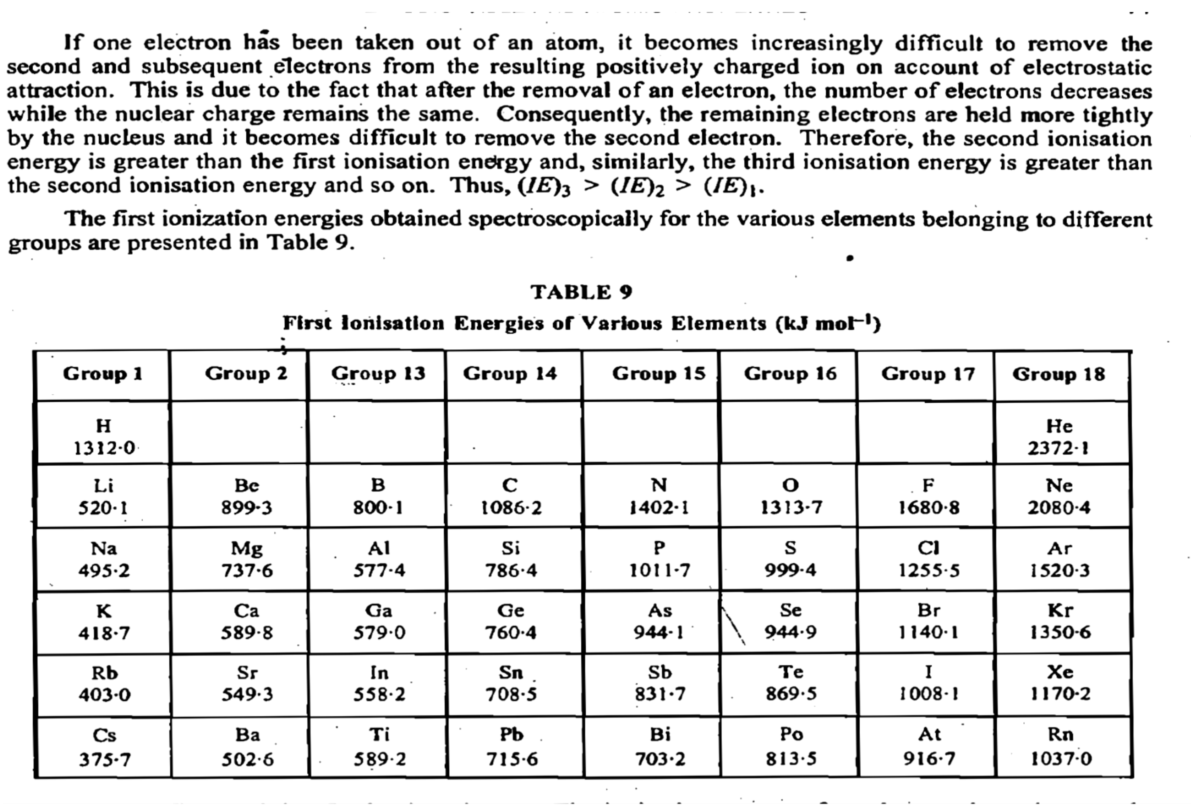
As can be seen, the second ionisation energies are very much higher than the first ionisation energies.

The successive ionisation energies of some common elements are listed in Table 8.

TABLE 8

Successive Ionisation Energies (in kJ per mole) of Some Common Elements

Element	Electronic configuration	$(IE)_1$	$(IE)_2$	$(IE)_3$
Li	$1s^2\,2s^1$	520·1	7297	11810
Be	$1s^2\,2s^2$	899·3	1758	14810
B	$1s^2\,2s^2p^1$	800·1	2428	3660
C	$1s^2\,2s^2p^2$	1086·2	2353	4618
N	$1s^2\,2s^2p^3$	1402·1	2855	4577
O	$1s^2\,2s^2p^4$	1313·7	3388	5297
F	$1s^2\,2s^2p^5$	1680·8	3375	6045
Ne	$1s^2\,2s^2p^6$	2080·4	3963	6130



If one electron has been taken out of an atom, it becomes increasingly difficult to remove the second and subsequent electrons from the resulting positively charged ion on account of electrostatic attraction. This is due to the fact that after the removal of an electron, the number of electrons decreases while the nuclear charge remains the same. Consequently, the remaining electrons are held more tightly by the nucleus and it becomes difficult to remove the second electron. Therefore, the second ionisation energy is greater than the first ionisation energy and, similarly, the third ionisation energy is greater than the second ionisation energy and so on. Thus, $(IE)_3 > (IE)_2 > (IE)_1$.

The first ionization energies obtained spectroscopically for the various elements belonging to different groups are presented in Table 9.

TABLE 9

First Ionisation Energies of Various Elements (kJ mol^{-1})

Group 1	Group 2	Group 13	Group 14	Group 15	Group 16	Group 17	Group 18
H 1312·0							He 2372·1
Li 520·1	Be 899·3	B 800·1	C 1086·2	N 1402·1	O 1313·7	F 1680·8	Ne 2080·4
Na 495·2	Mg 737·6	Al 577·4	Si 786·4	P 1011·7	S 999·4	Cl 1255·5	Ar 1520·3
K 418·7	Ca 589·8	Ga 579·0	Ge 760·4	As 944·1	Se 944·9	Br 1140·1	Kr 1350·6
Rb 403·0	Sr 549·3	In 558·2	Sn 708·5	Sb 831·7	Te 869·5	I 1008·1	Xe 1170·2
Cs 375·7	Ba 502·6	Ti 589·2	Pb 715·6	Bi 703·2	Po 813·5	At 916·7	Rn 1037·0

Factors affecting Ionisation Potential

(a) Number of shells: With the increase in the number of shells, the atomic radius increases i.e. the distance of outermost shell electron from the nucleus increases and hence the ionization potential decreases.

(b) Effective Nuclear Charge: Atomic size decreases with the increase in effective nuclear charge because, higher the effective nuclear charge, stronger will be the attraction of the nucleus towards the electron of the outermost orbit and higher will be the ionization potential.

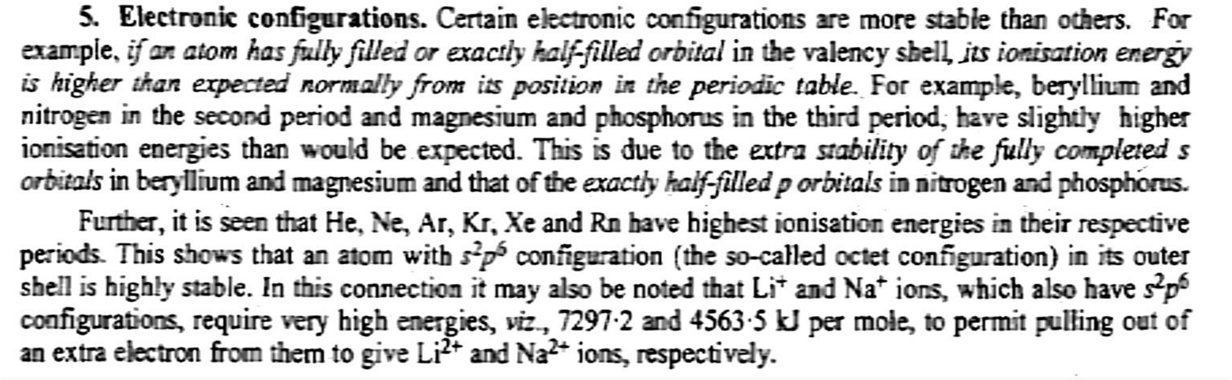
(c) Shielding Effect: The electrons of the inner orbits repel the electrons of the outermost orbit due to which the attraction of the nucleus towards the electrons of the outermost orbit decreases and thus the atomic size increases and the value of ionization potential decreases.

(d) Stability of half-filled and fully filled orbitals: The atoms whose orbitals are half-filled (p^3 ,d^5 ,f^7) or fully filled (s^2 ,p^6 ,d^{10} ,f^{14}) have greater stability than the other. Therefore, they require greater energy to remove an electron. However, stability of fully filled orbitals is greater than that of the half-filled orbitals.

(e) Penetration power: In any atom, the s-orbital is nearer to the nucleus in comparison to p, and f orbitals.

Therefore, greater energy is required to remove an electron from s-orbital than from p, d and f orbitals. The order is as follows-

s > p > d > f



5. Electronic configurations. Certain electronic configurations are more stable than others. For example, *if an atom has fully filled or exactly half-filled orbital* in the valency shell, *its ionisation energy is higher than expected normally from its position in the periodic table*. For example, beryllium and nitrogen in the second period and magnesium and phosphorus in the third period, have slightly higher ionisation energies than would be expected. This is due to the *extra stability of the fully completed s orbitals* in beryllium and magnesium and that of the *exactly half-filled p orbitals* in nitrogen and phosphorus.

Further, it is seen that He, Ne, Ar, Kr, Xe and Rn have highest ionisation energies in their respective periods. This shows that an atom with s^2p^6 configuration (the so-called octet configuration) in its outer shell is highly stable. In this connection it may also be noted that Li^+ and Na^+ ions, which also have s^2p^6 configurations, require very high energies, *viz.*, 7297·2 and 4563·5 kJ per mole, to permit pulling out of an extra electron from them to give Li^{2+} and Na^{2+} ions, respectively.

Periodic Trends in Ionisation Potential

In a Period: The value of ionization potential normally increase across a period, because effective nuclear charge increases and the atomic size decreases.

Exceptions: In the second period, ionization potential of Be is greater than that of B, and in the third period, ionization potential of Mg is greater than that of Al due to the high stability of fully filled orbitals. In the second period, ionization potential of N is greater than O and in the third period, ionization potential of P is greater than that of S, due to the stability of half-filled orbitals.

In a Group: The value of ionization potential normally decreases down the group because both, atomic size and shielding effect increase.

Exception: The value of ionization potential remains almost constant from Al to Ga in the III A group. (B > Al, Ga > In).

In IV B group i.e. Ti, Zr and Hf, the I.P. of Hf is higher than that of Zr due to Lanthanide contraction. Thus the I.P. of

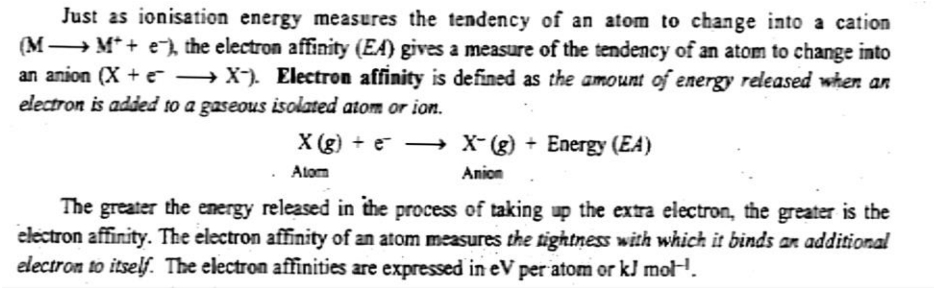
IV B group varies as Ti > Zr < Hf.

Applications of Ionization Enthalpy

Ionization enthalpy plays a vital role in various fields of science. In analytical chemistry, it is used to identify the presence of elements in a sample. The ionization energy of an element can be used to distinguish it from other elements in the sample. In addition, ionization enthalpy is used in the design of electronic devices such as transistors and diodes. It is also an essential parameter in studying chemical reactions and bonding.

Electron gain enthalpy:

Electron gain enthalpy is sometimes also referred to as Electron affinity although there is a minute difference between them. Electron gain enthalpy is defined as the amount of energy released when an electron is added to an isolated gaseous atom. During the addition of an electron, energy can either be released or absorbed.



Just as ionisation energy measures the tendency of an atom to change into a cation ($M \longrightarrow M^+ + e^-$), the electron affinity (*EA*) gives a measure of the tendency of an atom to change into an anion ($X + e^- \longrightarrow X^-$). **Electron affinity** is defined as *the amount of energy released when an electron is added to a gaseous isolated atom or ion.*

$$\underset{\text{Atom}}{X(g)} + e^- \longrightarrow \underset{\text{Anion}}{X^-(g)} + \text{Energy }(EA)$$

The greater the energy released in the process of taking up the extra electron, the greater is the electron affinity. The electron affinity of an atom measures *the tightness with which it binds an additional electron to itself.* The electron affinities are expressed in eV per atom or kJ mol^{-1}.

For example,

$O(g) + e^- \rightarrow O^-(g)$; $EA_1 = +\,141$ kJ mol^{-1} $\Delta H_{EA1} = -141$ kJ/mol

$O^-(g) + e^- \rightarrow O^{2-(}g)$; $EA_2 = -\,780$ kJ mol^{-1} $\Delta H_{EA2} = +780$ kJ/mol

Factors Affecting Electron Affinity

- **Atomic size or atomic radius:** When the atomic size/radius increases, the electrons entering the outermost orbit is more weakly attracted by the nucleus and the value of electron affinity is lower.
- **Effective Nuclear charge:** When effective nuclear charge is more, then, the atomic size is less. Then, the atom can easily gain an electron and possess a higher value of electron affinity.
- **Stability of Fully-Filled and Half-Filled orbitals:** The stability of the configuration having fully-filled orbitals (p^6, d^{10} f^{14}) and half—filled orbitals (p^3, d^5, f^7) is relatively higher than that of other configurations. Hence, such type of atoms have a lesser tendency to gain an electron, therefore, their electron affinity values will be very low or zero.

Trends in Electron Affinity: In a period, atomic size decreases with the increase in effective nuclear charge and hence, increases the electron affinity.

Exception:

(a) Ongoing from C6 to N7 in the second period, the values of electron affinity decrease instead of increasing. This is because there are half-filled (2p3) orbitals in the outermost orbit of N, which are more stable. On the other hand, the outermost orbit in C has a 2p2 configuration.

(b) In the third period, the value of electron affinity of Si is greater than that of P. This is because the electronic configuration of the outermost orbit in P atom is 3p3, which being half-filled, is relatively more stable. The values of electron affinity of inert gases are zero, because their outermost orbit has fully-filled p orbitals.

(c) In a period, the value of electron affinity goes on decreasing on going from group IA to group IIA. The value of electron affinity of the elements of group IIA is zero because ns orbitals are fully-filled and such orbitals have no tendency to accept electrons.

In a Group: The values of electron affinity normally decrease down a group because the atomic size increases, decreasing the actual attractive force of the nucleus.

Exceptions:

- **(a)** The value of the electron affinity of F is lower than that of Cl, because the size of F is very small and compact and the charge density is high on the surface. Therefore, the incoming electron/s experience more repulsion in comparison to Cl accounting for the highest value of Cl in the periodic table.
- **(b)** The values of electron affinity of alkali metals and alkaline earth metals can be regarded as zero, because they do not have the tendency to form anions by accepting electron/s.

Electronegativity, Pauling's/ Mulliken's/ Allred Rachow's/ and Mulliken-Jaffé's electronegativity scales. Variation of electronegativity with bond order, partial charge, hybridization, group electronegativity. Sanderson's electron density ratio.

Electronegativity: The tendency of an atom to attract the shared pair of electrons of the covalent bond towards itself is called electronegativity of that atom.

Factors Affecting Electronegativity

Atomic size: Electronegativity of a bonded atom decreases with increase in size since the attractive force on the valence electrons decreases and hence electronegativity decreases.

Hybridisation state of atom: Electronegativity increases with increase in the s-character of the hybrid orbital. This is because, the s-orbital is nearer to the nucleus and thus, suffers greater attraction leading to increased electronegativity.
The number of covalent bonds present between two bonded atoms is known as its bond order. With increase in the bond order, the bond distance decreases, effective nuclear charge increases and thus electronegativity increases.

I**ncreasing order of electronegativity is as follows: C – C < C = C < C ≡ C.**
When effective nuclear charge is high, the nucleus will attract the shared electrons with greater strength to give high electronegativity.

Oxidation number: The electronegativity value increases with the increase in oxidation number since the radius decreases with the increase in oxidation number.
The increasing order of electronegativity is as follows: $Fe < Fe^{+2} < Fe^{+3}$
Electronegativity does not depend on stability of fully-filled or half-filled orbitals because it is simply the capacity of the nucleus to attract a bonded pair of electrons.

Trends in Electronegativity: Atomic size decreases across a period. Thus, electronegativity increases. Atomic size increases down a group decreasing the electronegativity.
F has maximum electronegativity value in the periodic table, while Cs has minimum.

According to the Pauling scale, the electronegativity value of F is 4.0, O is 3.5 N is 3.0 and Cl is 3.1

Exceptions

(a) The elements of group IIB i.e. Zn, Cd and Hg show increase in electronegativity value down the group.

(b) The elements of group IIIA, i.e Al to Ga show increase in electronegativity value down the group.

(c) The elements of group IVA, Si onwards, show no change in electronegativity value down the group.

Measurement of Electronegativity:

Pauling's Approach. Pauling defined **electronegativity** *as the power of an atom in a molecule to attract electrons to itself.* He calculated electronegativities of different elements from thermodynamic data. He considered that in a reaction of the type

$$1/2\,(A - A) + 1/2\,(B - B) \longrightarrow A - B \qquad \text{...(2)}$$

the bond dissociation energy of *A* – *B* is higher than the mean of the bond dissociation energies of A – A and (B – B) bonds and that their difference (Δ) is related to the difference in the electronegativities of A and B according to the following empirical equation :

$$\Delta = E_A - E_B - 1/2(E_{A-A} + E_{B-B}) = 23(\chi_A - \chi_B)^2 \qquad \text{...(3)}$$

where E_{A-B}, E_{A-A} and E_{B-B} represent the bond dissociation energies of A – B, A – A, and B – B bonds, respectively and χ_A and χ_B denote the electronegativities of A and B, respectively. Thus,

$$\Delta = 23(\chi_A - \chi_B)^2 \qquad \text{...(4)}$$

or

$$0{\cdot}208\sqrt{\Delta} = \chi_A - \chi_B \qquad \text{...(5)}$$

Pauling later took the geometric mean instead of the arithmetic mean of E_{A-A} and E_{B-B} and suggested the following empirical correlation :

$$E_{A-B} - (E_{A-A} \times E_{B-B})^{1/2} = \Delta' = 30\,(\chi_A - \chi_B)^2 \qquad \text{...(6)}$$

or

$$0{\cdot}182\sqrt{\Delta'} = \chi_A - \chi_B \qquad \text{...(7)}$$

In Pauling's equations, the dissociation energies are taken *in kcal* (and not in kJ) per mole.

Example 1. Calculate the electronegativity of fluorine from the following data : $E_{H-H} = 104{\cdot}2$ kcal mol^{-1}, $E_{F-F} = 36{\cdot}6$ kcal mol^{-1}, $E_{H-F} = 134{\cdot}6$ kcal mol^{-1}.

Solution : According to Eq. 6,

$$\Delta = E_{H-F} - (E_{H-H} \times E_{F-F})^{1/2} = 134{\cdot}6 - (104{\cdot}2 \times 36{\cdot}6)^{1/2} = 72{\cdot}85 \text{ kcal}$$

According to Eq. 7,

$$\chi_F - \chi_H = (0{\cdot}182)\,(72{\cdot}85)^{1/2} = 1{\cdot}55$$

$$\chi_F = 1{\cdot}55 + \chi_H = 1{\cdot}55 + 2{\cdot}1 = \mathbf{3{\cdot}65}$$

Example 2. Calculate the electronegativity of carbon from the following data : $E_{H-H} = 104{\cdot}2$ kcal mol^{-1}, $E_{C-C} = 83{\cdot}1$ kcal mol^{-1}, $E_{C-H} = 98{\cdot}8$ kcal mol^{-1}.

Solution : According to Eq. 6,

$$\Delta = E_{C-H} - (E_{H-H} \times E_{C-C})^{1/2} = 98{\cdot}8 - (104{\cdot}2 \times 83{\cdot}1)^{1/2} = 5{\cdot}75 \text{ kcal}$$

According to Eq. 7,

$$\chi_C - \chi_H = 0{\cdot}182\,(5{\cdot}75)^{1/2} = 0{\cdot}44$$

$$\chi_C = 0{\cdot}44 + \chi_H = 0{\cdot}44 + 2{\cdot}1 = \mathbf{2{\cdot}54}$$

Allred and Rochow's Approach. Allred and Rochow defined **electronegativity** *as the electrostatic force of attraction exerted by the nucleus of an atom on the valency electrons.* Making use of the effective nuclear charge at the periphery of the atom, Z_{eff}, as calculated by Slater's rules, they proposed the following empirical relation for calculating the electronegativity :

$$\chi = 0{\cdot}359 \times Z_{eff}/r^2 + 0{\cdot}744 \qquad ...(8)$$

where χ is the electronegativity and r is the covalent radius of the atom in angstrom units. The electronegativities as calculated with the help of Eq. 8 are found to be remarkably close to those reported by Pauling.

Example 3. Calculate the electronegativity of carbon atom following Allred-Rochow's approach. The covalent radius of carbon atom is 0·77 Å.

Solution : According to Slater's rules (Chapter 1),

Z_{eff} at the periphery of C atom $= Z_{actual} - S = 6 - (0{\cdot}35 \times 4 + 0{\cdot}85 \times 2) = 2{\cdot}90$

According to Eq. 8, $\chi_C = 0{\cdot}359 \times 2{\cdot}90\,(0{\cdot}77)^2 + 0{\cdot}744 = \mathbf{2{\cdot}50}$

Example 4. Calculate the electronegativity of silicon following Allred-Rochow approach. Covalent radius of Si = 1·175 Å.

Solution : Electronic configuration of Si is $1s^2\,2s^2p^6\,3s^2p^2$

According to Slater's rules (Chapter 1),

$$Z_{eff} = Z_{actual} - S = 14 - (0{\cdot}35 \times 4 + 0{\cdot}85 \times 8 + 1{\cdot}0 \times 2) = 3{\cdot}80$$

According to Eq. 8, $\chi_{Si} = 0{\cdot}359 \times 3{\cdot}80/(1{\cdot}175)^2 + 0{\cdot}744 = \mathbf{2{\cdot}50}$

Mulliken's Approach. Mulliken suggested that *the average of the ionization energy (IE) and electron affinity (EA) of an atom should be a measure of the* **electronegativity** *(χ_M) of the atom*, that is,

$$\chi_M = 1/2(IE + EA) \qquad ...(9)$$

However, the ionisation energy and the electron affinity of an atom in Mulliken's definition are not the experimentally observed values for the isolated gaseous atom in its ground state. These are instead the calculated values for the atom in its valence state, *i.e.*, when the atom forms a part of a molecule.

For instance, in BeF_2, the ionisation energy of Be atom used in Mulliken's formula is not the one which is experimentally observed for an isolated Be atom having $1s^2\,2s^2$ configuration but is the *hypothetical* energy required to remove an electron from an *sp* hybrid orbital of Be atom. In other words, it is the average of energies *IE(s)* and *IE(p)* required to remove 2*s* and 2*p* electrons from the promoted valence state of Be atom in BeF_2 molecule :

$$\begin{tikzcd} 1s^2\,2s^2 \arrow[r] & 1s^2\,2s^1\,2p^1 \arrow[r, "IE\,(s)"] \arrow[dr, "IE\,(p)"] & 1s^2\,2s^0\,2p^1 \\ \text{(ground state of Be)} & \text{(promoted valence state)} & 1s^2 2s^1 2p^0 \end{tikzcd}$$

The *IE* and *EA* used in Mulliken's formula can be calculated by a complicated mathematical procedure which does not concern us here.

Several empirical equations have been proposed by chemists to bring Mulliken's values at par with the values of χ on Pauling's scale. But no such equation gives satisfactory results for all the elements. One such equation which attempts to give χ_M nearly at par with the value of χ on Pauling's scale is :

$$\chi_M = 0{\cdot}336\left[\frac{IE+EA}{2} - 0{\cdot}615\right] \qquad ...(10)$$

In this equation, *IE* and *EA* are in electron volts.

Factors Influencing Electronegativity. Although the electronegativity of an element is conventionally assigned a definite value, yet it may differ from one molecule to another. The ability of an atom in a molecule to attract electrons towards itself depends upon its environment in the molecule. The electronegativity of an atom would thus depend upon the nature of the other atom with which it is attached in the molecule. The factors which largely determine the electronegativity of an atom are as follows.

Charge on the atom. An atom which acquires a positive charge, either integral or partial, would tend to attract electrons more strongly than a neutral atom. Thus, a cation will be more electronegative than the parent atom which, in turn, would be more electronegative than its anion. Also, the higher the positive oxidation state of an atom in a species, the greater would be its electron-attracting power and hence the greater would be its electronegativity. For example, the oxidation state of central chlorine atom is +1 in HClO and +5 in $HClO_3$. Hence, the chlorine atom will be more electronegative in $HClO_3$ than in HClO. Accordingly, the release of hydrogen as H^+ ion in $HClO_3$ would be much easier than a similar change in HClO. In other words, $HClO_3$ *behaves as a stronger acid than* HClO.

Hybridisation. We know that *s* electrons are more penetrating than the *p* electrons. Therefore, if an atom has hybrid orbitals with a greater *s* character, the electronic charge in such orbitals would remain closer to the nucleus of that atom. This means that *the electronegativity of the atom would increase with increase in s character of its hybrid orbitals.*. For example, in methane, the carbon atom involves sp^3 hybridisation of its orbitals so that the hybrid orbitals have 25% *s* character. In ethylene, the carbon atom involves sp^2 hybridisation of its orbitals and consequently the *s* character of hybrid orbitals increases to 33%. In acetylene, the carbon atom involves *sp* hybridisation of its orbitals and, therefore, the *s* character of hybrid orbitals increases to 50%. Accordingly, the electronegativity of carbon atom increases as we move from CH_4 to C_2H_4 and to C_2H_2. Due to greater electronegativity of carbon atom in ethylene and acetylene, the electron pair of C – H bond is pulled more towards the carbon atom thereby facilitating the release of H atom as H^+ion. Thus, while methane is neutral, ethylene is slightly acidic while acetylene is considerably acidic.

Similarly, the *basicity of amines* also varies with the type of the hybridisation of the orbitals of the nitrogen atom. The higher the *s* character of the hybrid orbitals, the greater would be the electronegativity and the lower would be the electron-donating power of the nitrogen atom and hence the lower would be the basicity of the amine. For example, the molecules RCN, C_5H_5N (pyridine) and $C_6H_5NH_2$, involve, respectively, *sp*, sp^2 and sp^3 hybridisation of the orbitals of the nitrogen atom. Accordingly, the *s* character of the hybrid orbitals of nitrogen atom is 50% in RCN, 33% in pyridine and 25% in aniline. Accordingly, aniline is a stronger base than pyridine which, in turn, is a stronger base than RCN.

Effect of substituents. The electronegativity of an atom depends considerably upon the nature of the substituents attached to that atom. For example, the carbon atom in CF_3I acquires a greater positive charge than in CH_3I. Hence, the carbon atom in CF_3I is more electronegative (*i.e.*, more electron pulling) than in CH_3I. The difference in the electronegativities of an atom caused by the substituents results in different chemical behaviour of that atom. For instance, CF_3I and CH_3I yield different products on hydrolysis :

$$CF_3I + OH^- \longrightarrow CF_3H + IO^-$$

$$CH_3I + OH^- \longrightarrow CH_3OH + I^-$$

Role of ionization energies and electron affinities. According to Mulliken, electronegativity is related to the average of the ionization energy and electron affinity of the atom (Eq. 9). Evidently, the higher the ionization energy and electron affinity, the greater would be the electronegativity of the atom.

Effective nuclear charge. Variation of electronegativity in the periodic table. Allred and Rochow reasoned that the electron attracting power of an atom in a molecule is proportional to the effective nuclear charge, Z_{eff}. Thus, any factor which increases Z_{eff}, should also increase the electronegativity of the atom. For example, Z_{eff} decreases as we go down a group in the periodic table. This is because with increase in atomic number within a group, the atomic size increases. Hence, *electronegativity decreases as we move down a* **group**. Thus, the electronegativity of the halogens *decreases* in the order :

$$F\,(4{\cdot}0) > Cl\,(3{\cdot}1) > Br\,(2{\cdot}9) > I\,(2{\cdot}6).$$

Z_{eff} increases with decrease in size of the atom and the size of the atom decreases as move along a period from left to right in the periodic table. Accordingly, *electronegativity goes on increasing with increase in atomic number as we move along a* **period**. Thus, electronegativities of the elements of the second period *increase* in the order :

$$Li\,(1{\cdot}0) < Be\,(1{\cdot}5) < B\,(2{\cdot}0) < C\,(2{\cdot}5) < N\,(3{\cdot}0) < O\,(3{\cdot}5) < F\,(4{\cdot}0)$$

Z_{eff} also depends upon the number of inner electrons which screen the last electron. The larger the number of inner electrons, the greater would be the screening and the lesser would be the effective nuclear charge. Thus, electronegativity would *decrease* with increase in the number of inner electrons in atoms of the elements in the same group. This is an additional reason why the electronegativity of alkali metals *decreases* in the order :

$$Li\,(1{\cdot}0) > Na\,(0{\cdot}9) > K\,(0{\cdot}8) > Rb\,(0{\cdot}8) > Cs\,(0{\cdot}7)$$

Sanderson Electronegativities:

The ability of an atom or ion to attract electrons to itself is dependent upon the effective nuclear charge felt by the outermost valence electrons.

As the effective nuclear charge increases the size of the atom decreases.

The Sanderson electronegativity **S** is proportional to the compactness of an atom:

$$\mathbf{S} \approx \frac{Z}{\frac{4}{3}\pi r^3} \approx \frac{D}{D_0}$$

D is the electron density of an atom (its atomic number divided by its atomic volume (covalent radius cubed)) and D_0 is the expected electron density of an atom, calculated from extrapolation between the noble gas elements.

$$\sqrt{\chi_P} = a \times S + b$$