1. IIT-JEE Syllabus

Periodic properties of elements: classification of elements into s,p, d and f blcok; periodicity in properties with respect to atomic and ionic radii, ionisation energy, electron affinity electronegativity, oxidation state, metallic and non-metallic character and trends in reactivity.

2. Introduction

Periodic table helps us to undergo a systematic study of the various elements found in nature without which it would have been impossible for us to study all the elements. By classifying the elements into various groups and periods a comparative study of the elements and their compounds can be done. It also help us to analyse the periodic trend in various properties such as ionisation potential, electron affinity, electronegativity etc.

3. Evolution of Modern Periodic Table

a) Dobereiner's Triads, 1829: Although atomic weights were not available for all elements, John Wolfgang Dobereiner in 1829 tried to classify the elements with similar properties in the groups of three elements (Triads). He could succeed in making only a few triads. In the triads of elements the atomic weight of the middle element was the arithmatic mean of the atomic weights of the other two. Some of the triads are as under.

Li	**Na**	**K**	**Ca**	**Sr**	**Ba**
7	23	39	40	88	137
P	As	Sb	Cl	Br	I
31	75	120	35.5	80	123

b) The Telluric Helix: It was in 1862, that a periodic classification of the elements was developed that approached the idea we have today. At that time A.E. de Chancourtois,a professor of Geology at the Ecole des Mines in Paris presented an account of his telluric helix in which he indicated the relative properties of elements and their atomic weights.

He used a vertical cylinder with 16 equidistant lines on its surface, the lines lying parallel to the axes. Then he drew a helix at 45 degree to the axis and arranged the elements on the spiral in the order of their increasing atomic weights. In this manner, elements that differed from each other in atomic weight by 16 or multiples of 16 fell very nearly on the same vertical line. In addition to the 16 vertical lines, de Chancourtois felt that other connecting lines could be drawn, and that all elements lying on such lines were related in some manner. His arrangement resulted in the proposal by de Chancourtois that the properties of the elements are the properties of numbers.

c) Newland’s Octet Law, 1864: Very shortly after the discovery of telluric helix. John Alexander Reina Newland in England made the first attempt to correlate the chemical properties of the elements with their atomic weights. According to him

i) If the elements are arranged in order of their increasing atomic weights, every eighth element had similar properties to first one like the first and eighth note in music. For example

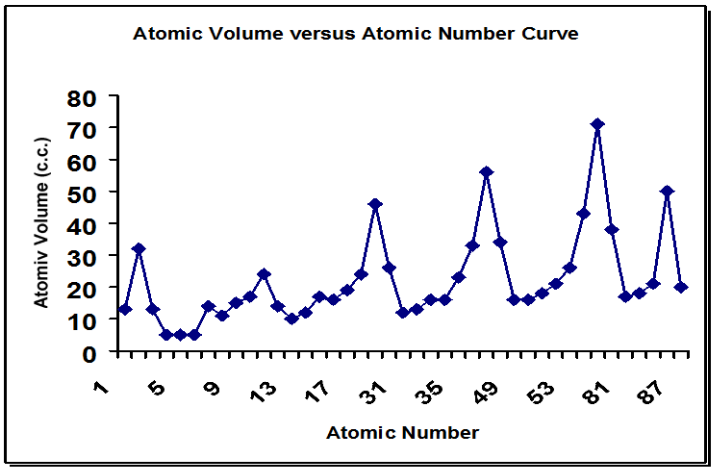
sa	**re**	**ga**	**ma**	**pa**	**dha**	**ni**	**sa**
Li	Be	B	C	N	O	F	Na
Na	Mg	Al	Si	P	S	Cl	K

ii) Inert gases were not discovered till then.

iii) All the elements could not be classified on this basis

d) Lothar Meyer's Atomic Volume Curve 1869

i) Lothar Meyer plotted a graph between atomic weight and atomic volume (i.e. atomic weight in solid state/density)



ii) Elements with similar properties occupied the similar positions on the graph

iii) Strong electropositive elements of IA except Li, all others Na, K, Rb, Cs etc. occupied the top position on the graph.

iv) IIA group elements Be, Mg, Ca, Sr, Ba etc. occupied the positions on the ascending part of the graph

v) Inert gases except He occupied the positions on the descending part of the graph

vi) Halogens also occupied the descending part of the graph.

e) Mendeleef's Periodic law: In spite of the importance of the earlier contributions the major portion of the credit for the development of the periodic table must go to the Russian Chemist, Dmitrii Ivanovich Mendeleef, who proposed

i) The physical and chemical properties of elements are periodic functions of their atomic weights.

ii) If the elements are arranged in the order of their increasing atomic weights, after a regular interval elements with similar properties are repeated.

4. Mendeleef's Periodic Table

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

4.1 Characteristics of Periods

i) First period is called shortest period and contains only two elements. Second and third periods are called short periods containing eight elements each. Fourth and fifth periods are long periods containing eighteen elements each. Sixth period is longest period with thirty-two elements. Seventh period is an incomplete period containing nineteen elements. Numbers 2, 8, 18, 32 are called magic numbers.

ii) Lanthanide and actinide series containing 14 elements each are placed separately under the main periodic table. These are related to sixth and seventh periods of III group respectively.

iii) Elements of third period from sodium (Na) to Chlorine (Cl) are called representative or typical elements.

iv) Valency of an element in a period increases from 1 to 7 with respect to oxygen.

Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl_2O
1	2	3	4	5	6	7

v) From left to right in a period generally

a) Atomic weight, effective nuclear charge, ionisation potential, electronegativity and electron affinity of an element increase.

b) Atomic radius, electropositive character and metallic character of an element decrease.

vi) Diagonal relationship — Elements of second period Li, Be and B resemble closely with the elements Mg, Al and Si of third period in the next higher group.

Second Period	Li	Be	B	C
Third Period	Na	Mg	Al	Si

viii) Elements of second period are called bridge elements.

4.2 Characteristics of groups

i) Mendeleef's periodic table contains nine groups. These are represented by Roman numerals I, II, III, IV, V, VI, VII, VIII and zero,. Groups I to VII are divided into two subgroups A and B, Group VIII consists of three sets, each one containing three elements.

ii) Inert gases are present in zero group. These were not discovered till that time.

iii) The valency of an element in a group is equal to the group number.

iv) There is no resemblance in the elements of subgroups A and B of same group, except valency

v) The elements of the groups which resemble with typical elements are called normal elements. For example IA, IIA, IIIA, IVA, VA, VIA, VIIA group elements are normal elements

PERIODIC CLASSIFICATION OF ELEMENTS

s-block; (Transition Elements) d-block; p-block; (Inner Transition Elements) f-block

GROUP	I-A	II-A	III-B	IV-B	V-B	VI-B	VII-B	VII			I-B	II-B	III-A	IV-A	V-A	VI-A	VII-A	INERT GASES	PERIOD
	1 H																	2 He	1
	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne	2
	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar	3
	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr	4
	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe	5
	55 Cs	56 Ba	57 • La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn	6
	87 Fr	88 Ra	89 •• Ac	104 Unq	105 Unp	106 Unh	107 Uns												7
• Lanthanide Series					58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	6
•• Actinide Series					90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Li	7

. vi) Those elements of the groups which do not resemble with typical elments are called transition elements. For example- IB, IIB, IIIB, IVB, VB, VIB, VIIB, and VIII group elements are transition elements.

vii) Hydrogen can be placed in both IA and VIIA groups.

viii) In a group, from top to bottom in general

a) Atomic weight, atomic size, electropositive character and metallic character of an element increase.

b) Ionisation potential, electron affinity and electronegativity of an element decrease.

4.3 Uses of Mendeleef's periodic table

i) Atomic weights of elements were determined with the help of periodic table Atomic weight = Valency × Equivalent weight = Group number × Equivalent weight.

ii) Atomic weight of elements were corrected. Atomic weight of Be was calculated to be 3 × 4.5 = 13.5 by considering its valency 3. Mendeleef calculated it 2 × 4.5 = 9.

iii) Discovery of new elements – In Mendeleef's periodic table two consecutive members differ by two or three units in the atomic weight. Where this gap was more, the gaps were left in the periodic table.

4.4 Defects of Mendeleef's periodic table

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

ii) No separate positions were given to isotopes.

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

iv) Although there is no resemblance except valency of subgroups A and B, they have been put in the same group.

v) Order of increasing atomic weights is not strictly followed in the arrangement of elements in the periodic table. For e.g. – Co (At.wt. 58.9) is placed before I (127) and Ar (39.9) before K (39).

5. Long form of the Periodic Table or Moseley's Periodic Table

i) Moseley (1909) studied the frequency of X-rays produced by the bombardment of a strong beam of electrons on a metal target. He found that the square root of the frequency of X-rays $\left(\sqrt{\nu}\right)$ is directly proportional to the total nuclear charge (z) of metal. $\sqrt{\nu} = a\ (Z - b)$ where a and b are constants. Nuclear charge of metal is equal to the atomic number. So Moseley related the properties of elements with their atomic number and gave the new periodic law.

ii) Moseley's Periodic Law or Modern Periodic Law: Physical and chemical properties of elements are the periodic functions of their atomic number. If the elements are arranged in order of their increasing atomic number, after a regular interval, element with similar properties are repeated.

5.1 Long form of the Periodic Table and Electronic Configuration of elements

Many different forms of a periodic classification of the elements have appeared since the 1871 table by Mandeleef. Each table was designed to point up the various trends and relationship which its author considered most significant. From the literally hundreds of tables which have been proposed,perhaps the most popular and easily reproduced periodic table is the conventional extended or long form, which is shown in table.

i) Each period starts with an alkali metal whose outermost electronic configuration is ns^1.

ii) Each period ends with a noble gas of outermost electronic configuration ns^2np^6 except He. The electronic configuration of He is $1s^2$.

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

v) The number of elements in each period may be determined by the number of electrons in a stable configuration as under

Periods	Stable electronic configuration	Number of electrons
First	$1s^2$	2
Second	$2s^2 2p^6$	8
Third	$3s^2 3p^6$	8
Fourth	$4s^2 3d^{10} 4p^6$	18
Fifth	$5s^2 4d^{10} 5p^6$	18
Sixth	$6s^2 4f^{14} 5d^{10} 6p^6$	32
Seventh		

5.2 Electronic basis for the periodic classification

With a better understanding of the part that the electron plays great role in the properties of the elements, a corresponding understanding of the periodic system came about.

On the basis of electronic configuration, the elements may be divided into four groups.

i) s-Block elements

a) These are present in the left part of the periodic table.

b) These are IA and IIA i.e. 1 and 2 group elements.

c) These are metals.

d) In these elements last electron fills in the s-orbital.

e) Electronic configuration of valence shell is $ns^{1\text{-}2}$ (n = 1 to 7).

ii) p – block elements

a) These are present in right part of the periodic table.

b) These constitute the groups IIIA to VIIA and zero groups i.e. groups 13 to 18 of the periodic table.

c) Most of these elements are metalloids and non metals but some of them are metals also.

d) The last electron fills in p-orbital of valence shell.

e) The electronic configuration of valence shell is $ns^2np^{1\text{-}6}$ (n = 2 to 7).

f) $ns^2np^6$is stable noble gas configuration. The electronic configuration of He $1s^2$.

iii) d-Block elements

a) These are present in the middle part of the periodic table (between s & p block elements.

b) These constitute IIIB to VIIB, VIII, IB and IIB i.e, 3 to 12 groups of the periodic table.

c) All are metals.

d) The last electrons fill in (n – 1)d orbital.

e) The outermost electronic configuration is $(n\text{-}1)d^{1\text{-}10}\ ns^{1\text{-}2}$ (n = 4 to 7).

f) There are three series of d-block elements as under:
3d series – Sc(21) to Zn (30)
4d series – Y (39) to Cd (48)
5d series – La (57), Hf (72) to Hg (80)

iv) f-Block elements

a) These are placed separately below the main periodic table.

b) These are mainly related to IIIB i.e. group 3 of the periodic table.

c) There are two series of f-block elements as under:
4f series – Lanthanides – 14 Elements from Ce (58) to Lu (71)
5f series – Actinides – 14 Elements from Th (90) to Lw (103)

d) The last electron fills in (n – 2) f-orbital

e) Their outermost electronic configuration is $(n\text{-}2)f^{1\text{-}14}\ (n\text{-}1)s^2\ (n\text{-}1)p^6\ (n\text{-}1)d^{0\text{-}1}ns^2$ (n = 6 and 7).

6. The Types of Elements

Using electronic configuration as the criterion, we ordinarily recognize four general type of elements; the inert gas elements, the representative elements, the transition elements, and the inner transition elements. The classification of the elements into these groups is dependent on the extent to which the s, p, d and f orbitals are filled.

i) Inert gases

a) s- and p-orbitals of the outer most shell of these elements are completely filled. The outermost electronic configuration is ns^2np^6.

b) Helium is also inert gas but its electronic configuration is $1s^2$.

ii) Representative or Normal Elements

a) Outermost shell of these elements is incomplete. The number of electrons in the outermost shell is less than eight.

b) Inner shells are complete.

c) s-and p-block elements except inert gases are called normal or representative elements.

iii) Transition Elements

a) Last two shells of these elements namely outermost and penultimate shells are incomplete.

b) The last shell contains one or two electrons and the penultimate shell may contain more than eight up to eighteen electrons.

c) Their outermost electronic configuration is similar to d-block elements i.e. $(n-1)d^{1-10}\ ns^{1-2}$.

d) According to latest definition of transition elements those elements which have partly filled d-orbitals in neutral state or in any stable oxidation state are called transition elements. According to this definition ***Zn, Cd and Hg (IIB group) are d-block elements but not transition elements because these elements have d^{10} configuration in neutral as well as in stable +2 oxidation state***.

e) Because of the extra stability which is associated with empty, half-filled, and filled subshells, there are some apparent anomalies in electronic arrangements in the transition series. This empirical rule is illustrated by the chromium and copper configuration in the first d series of elements:

	Sc	**Ti**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**
3d	1	2	3	5	5	6	7	8	10	10
4s	2	2	2	1	2	2	2	2	1	2

iv) Inner Transition Elements

a) In these elements last three shells i.e. last, penultimate and prepenultimate shells are incomplete.

b) These are related to IIIB i.e. group 3.

c) The last shell contains two electrons. Penultimate shell may contain eight or nine electrons and pre-penultimate shell contains more than 18 up to32 electrons.

d) Their outermost electronic configuration is similar to f-block element i.e. $(n-2)f^{1-14}(n-1)s^2\ (n-1)p^6\ (n-1)d^{0-1}ns^2$

v) Elements of the seventh period after atomic number 93 (i.e. actinides) are synthetic elements and are called transuranium elements.

7. Periodic Properties

From the discussion of the periodic table, it is evident that those properties which depend upon the electron configuration of an atom will vary periodically with atomic number. On the other hand, those properties which depend upon the total number of electrons will show no such variations. Some of the more common properties which depend upon electronic configurations are:

7.1 Atomic Radius

i) The radius of an atom may be taken as the distance between atomic nucleus and the outermost shell containing electrons of the atom.

ii) According to the Heisenberg's uncertainty principle the position of a moving electron can not be accurately determined. So the distance between the nucleus and the outermost electron is uncertain.

iii) Atomic radius can be determined indirectly from the inter nuclear distance between the two atoms in a gaseous diatomic molecule. This internuclear distance between the two atoms is called bond length.

iv) The inter nuclear distance between the two atoms can be measured by X – ray diffraction or spectroscopic studies.

v) **Covalent radius –** One half of the distance between the nuclei (internuclear distance) of two covalently bonded atoms in a homodiatomic molecule is called the covalent radius of that atom. The covalent bond must be single covalent bond. The covalent radius (r_A) of atom A in a molecule A_2 may be given as:

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

i.e. the distance between nuclei of two single covalently bonded atoms in a homodiatomic molecule is equal to the sum of covalent radii of both the atoms.

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

In a heterodiatomic molecule AB where the electronegativity of atoms A and B are different, the experimental values of internuclear distance d_{A-B} is less than the theoretical values $(r_A + r_B)$. According to Schomaker and Stevenson (1941) –

$$D_{A-B} = r_A + r_B – 0.09\ \Delta_x$$

Where Δ_x is the difference of electronegativities of the atoms A and B.

According to Pauling – If the electronegativities of the two atoms A and B are x_A and x_B respectively then

$$D_{A-B} = r_A + r_B – (C_1x_A – C_2x_B)$$

C_1 and C_2 are the Stevenson's coefficients for atoms A and B respectively.

7.2 Metallic Radius

Metal atoms are assumed to be closely packed spheres in the metallic crystal. These metal atom spheres are considered to touch one another in the crystal. One half of the internuclear distance between the two closest metal atoms in the metallic crystal is called metallic radius.

Metallic radius > Covalent radius

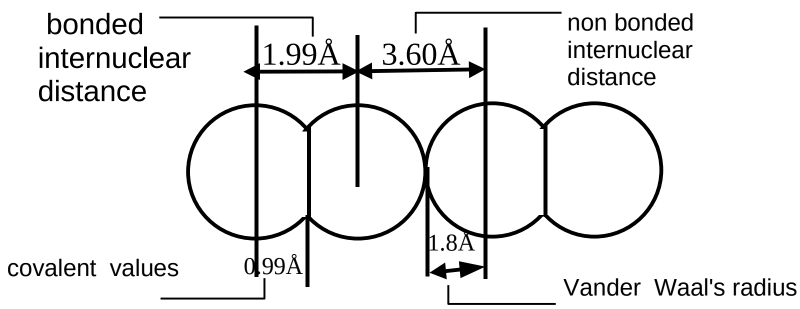
For example – Metallic radius and covalent radius of potassium are 2.3 Å and 2.03Å respectively.

7.3 Van der Waal's Radius or Collision radius

The molecules of non metal atoms are generally gases. On cooling, the gaseous state changes to solid state.

In the solid state, the non metallic elements usually exist as aggregations of molecules are held together by Van der Waal forces. **One half of the distance between the nuclei of two adjacent atoms belonging to two neighbouring molecules of a compound in the solid state is called Van der Waal's radius.**

It may also be defined as half of the inter nuclear distance of two non bonded neighbouring atoms of two adjacent molecules.



Vander Waal's radius > Metallic radius> Covalent radius

The Vander Waal's radius and Covalent radius of Chlorine atom are 1.80Å and 0.99Å respectively

7.4 Ionic Radius

A neutral atom changes to a cation by the loss of one or more electrons and to an anion by the gain of one or more electrons. The number of charge on cation and anion is equal to the number of electrons lost or gained respectively. The ionic radii of the ions present in an ionic crystal may be calculated from the internuclear distance between the two ions

i) **Radius of a Cation:** Radius of a cation is invariably smaller than that of the corresponding neutral atom

	Na	**Na^+**
Number of e^- =	11	10
Number of p =	11	11
	$1s^2 2s^2 2p^6 3s^1$	$1s^2 2s^2 2p^6$

Reasons

a) The effective nuclear charge increases. For example in Na atom 11 electrons are attracted by 11 protons and in Na^+, 10 electrons are attracted by 11 protons. Thus in the formation of cation number of electrons decreases and nuclear charge remains the same.

b) Generally the formation of cation results in the removal of the whole outer shell.

c) Interelectronic repulsion decreases. The interelectronic repulsion in Na is among $11e^-$ and in Na^+ among $10e^-$.

ii) **Radius of an anion:** Radius of an anion is invariably bigger than that of the corresponding atom.

	Cl	**Cl^-**
Number of e^- =	17	18
Number of p =	17	17

Reasons

a) The effective nuclear charge decrease in the formation of anion. Thus the electrostatic force of attraction between the nucleus and the outer electrons decreases as the size of the anion increases.

b) Interelectronic repulsion increases.

iii) **Isoelectronic series:** A series of atoms, ions and molecules in which each species contains same number of electrons but different nuclear charge is called isoelectronic series

	N^{3-}	**O^{2-}**	**F^-**	**Ne**	**Na^+**	**Mg^{2+}**
Number of e^-	10	10	10	10	10	10
Number of p	7	8	9	10	11	12

$\longrightarrow$

a) Number of electrons is same.

b) Number of protons is increasing

c) So the effective nuclear charge is increasing and atomic size is decreasing. In an isoelectronic series atomic size decreases with the increase of charge.

Some of the examples of isoelectronic series are as under

i) $S^{2-}, Cl^-, K^+, Ca^{2+}, Sc^{3+}$

ii) SO_2, NO_3^-, CO_3^{2-}

iii) N_2, CO, CN^-

iv) NH_3, H_3O^+

Periodicity in atomic radius and ionic radius

1. **For normal elements**

a) In a period from left to right effective nuclear charge increases because the next electron fills in the same shell. So the atomic size decreases. For example the covalent radii of second period elements in Å are as follows –

Li	Be	B	C	N	O	F
1.23	0.89	0.80	0.77	0.74	0.73	0.72

b) In a group moving from top to bottom the number of shells increases. So the atomic size increases. Although the effective nuclear charge increases but its effect is negligible in comparison to the effect of increasing number of shells. For example the covalent radii of IA group elements in Å are as follows –

Li	Na	K	Rb	Cs
1.23	1.57	2.03	2.16	2.35

2. **For inert gases:** The atomic radius of inert gas (zero group) is shown largest in a period because of its Vander Waal's radius which is generally larger than the covalent radius. The vander Waal's radius of inert gases also increases in moving from top to bottom in a group.

3. **For transition elements:** There are three series of transition elements –

3d – Sc (21) to Zn (30)

4d – Y (39) to Cd (48)

5d – La (57), Hf (72) to Hg (80)

a) From left to right in a period

i) The atomic size decreases due to the increase in effective nuclear charge.

ii) In transition elements, electrons are filled in the (n-1)d orbitals. These (n-1)d electrons screen the *ns* electrons from the nucleus. So the force of attraction between the *ns* electrons and the nucleus decreases.

This effect of (n-1)d electrons over *ns* electrons is called shielding effect or screening effect. The atomic size increases due to shielding effect and balance the decrease in size due to increase in nuclear charge to about 80%.

iii) Thus moving from left to right in a period, there is a very small decrease in size and it may be considered that size almost remains the same.

iv) In the first transition series the atomic size slightly decreases from Sc to Mn because effect of effective nuclear charge is stronger than the shielding effect. The atomic size from the Fe to Ni almost remains the same because both the effects balance each other. The atomic size from Cu to Zn slightly increases because shielding effect is more than effective nuclear charge due to d^{10} structure of Cu and Zn. The atomic radii of the elements of 3d transition series are as under.

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
1.44	1.32	1.22	1.18	1.17	1.17	1.16	1.15	1.17	1.25

4. **Inner transition elements:** As we move along the lanthanide series, there is a decrease in atomic as well as ionic radius. The decrease in size is regular in ions but not so regular in atoms. This is called lanthanide contraction. The atomic radii in Å are as under:

La	Ce	Pr	Nd	Pm	Sm	Eu	Gd
1.88	1.82	1.83	1.82	1.81	1.80	2.04	1.80
Tb	**Dy**	**Ho**	**Er**	**Yb**	**Lu**		
1.78	1.77	1.76	1.75	1.94	1.73		

There are two peaks one at Eu (63) and other at Yb (70). This is due to the difference in metallic bonding. Except Eu and Yb other lanthanides contribute three elctrons in metallic bond formation. These two atoms contribute two electrons in the bond formation leaving behind half filled and completely filled $4f$-orbitals respectively.

Cause of Lanthanide contraction – In lanthanides the additional electron enters into (n-2)f orbital. The mutual shielding effect of (n-2)f electrons is very little because the shape of f-subshell is very much diffused. Thus the effective nuclear charge increases in comparison to the mutual shielding effect of (n-2) f electrons. The outer electrons are attracted more by the nucleus. Consequently the atomic and ionic radii decreases from La (57) to Lu (71)

This type of contraction also occurs in actinides. The jump in contraction between the consecutive elements in the actinides is greater than lanthanides. This is due to the lesser shielding of $5f$-electrons which are therefore pulled more strongly by the nucleus.

In a group

i) The atomic radius of elements increases moving from first transition series (3d) to second transition series (4d). This is due to the increase in number of shells with the increase in atomic number.

ii) The atomic radii of second (4d) and third (5d) transition series in a group is almost same except Y(39) and La (57)

In third transition series, there are fourteen lanthanides in between La (57) of III B and Hf (72) of IV B groups, so the atomic radius of Hf(72) decreases much due to lanthanide contraction in lanthanides. The difference in the nuclear charge in the elements of a group in first and second transition series is + 18 units while this difference in second and third transition series is + 32 units except Y (39)$\rightarrow$ La(57). Due to the increase of + 32 units in the nuclear charge there is a sizable decrease in the atomic radius which balances the increase in size due to the increase in number of shells.

So in a group moving from second to third transition series, the atomic radii of the elements almost remain the same except IIIB. The difference is about 0.02Å.

Illustration 1: ***The radii of Ar is greater than the radii of chlorine***

Solution: In chlorine, the radii means the atomic or covalent radii which are actually half the inter–nuclear distance between 2 atoms whereas in Argon the radii means the Vander Waal's radii as Argon is not a diatomic molecule.

Vander Waal's radii is actually half the distance between adjacent molecule. So Vander Waal's radii being larger than atomic radii, Argon, has got a larger radii than chlorine

Illustration 2: ***Berilium and Al are placed in different periods and groups but they show the similar properties.***

Solution: On moving across a period the charge on the ions increases and the size decreases, causing the polarising power to increase. On moving down a group the size increases and polarising power decreases. On moving diagonally i.e., from Be to Al these two effects partly cancel each other and so there is no marked change in properties.

7.5 Ionisation potential or Ionisation Energy

i) The amount of energy required to remove the most loosely bound electron of the outermost shell (i.e. the outermost electron) from one mole of an isolated gaseous atom of an element in its ground state to produce a cation is known as ionisation energy of that element.

ii) Because ionisation energy is generally expressed in electron volts, so it is also known as ionisation potential.

iii) Energy required for the removal of first, second and third electron from the gaseous atom is called first, second and third ionisation energy respectively.

$$A_{(g)} + I_1 \rightarrow A_{(g)}^{+} + e^{-}$$

$$A^{+}_{(g)} + I_2 \rightarrow A_{(g)}^{2+} + e^{-}$$

$$A_{(g)}^{2+} + I_3 \rightarrow A_{(g)}^{3+} + e^{-}$$

iv) The order of first, second and third ionisation energies may be given as

$$I_1 < I_2 < I_3$$

This is because second and third electron is removed from monopositive and dipositive cations respectively. Effective nuclear charge increase with the increase of positive charge. So the attraction between the nucleus and the outermost electron increases and more energy is required for the removal of electron.

1. **Factors affecting ionisation potential**

   i) ***Atomic radius:*** The values of *ionisation* potential of an element decreases as its atomic radius increases. This is because the elecrostatic force of attraction between the nucleus and the outermost electron decreases as the distance between them increases. So the energy required for the removal of electron will comparatively be less

$$\text{Ionisation potential } \alpha \frac{1}{\text{Atomic radius}}$$

ii) ***Effective nuclear charge:*** The greater the effective charge on the nucleus of an atom, the more difficult it would be to remove an electron from the atom because electrostatic force of attraction between the nucleus and the outermost electron increases. So the greater energy will be required to remove the electron.

Ionisation potential α Effective nuclear charge (Z_{eff})

iii) ***Penetration effect of orbitals:*** The order of energy required to remove electron from s,p,d-and$f$-orbitals of a shell is s>p>d>f because the distance of the electron from the nucleus increases. For example – The value of ionisation potential of Be(Z=4, $Is^2 2s^2$) and Mg(Z=12, $1s^2 2s^2 2p^6 3s^2$) are more than the I.P.s of B (Z=5, $1s^2 2s^2 2p^1{}_x$) and Al (Z= 13, $1s^2 2s^2 2p^6 3s^2 3p^1{}_x$) because the penetration power of 2s and 3s electrons is more than 2*p and 3*p orbitals respectively. More energy will be required to separate the electrons from 2s and 3s orbitals.

iv) ***Shielding or screening effect:*** The shielding or screening effect increases if the number of electrons in the inner shells between the nucleus and the outermost electrons increases. This results in decrease of force of attraction between the nucleus and the outermost electron and lesser energy is required to separate the electron. Thus the value of I.P. decreases.

Ionisation potential $\alpha \dfrac{1}{\text{Shielding effect}}$

v) ***Stability of half-filled and fully-filled orbitals:*** According to Hund's rule the stability of half filled or completely filled degenerate orbitals is comparatively high. So comparatively more energy is required to separate the electron from such atoms.

For example

a) Removal of electron is comparatively difficult from the half filled configuration of N (Z=7, $Is^2 2s^2\, 2p_x^1 p_y^1 p_z^1$).

b) The ionisation potential of inert gases is very high due to most stable s^2p^6 electronic configurations.

2. **Periodicity in ionisation potential**

i) **For normal elements:** On moving from left to right in a period, value of ionisation potential of elements increases because effective nuclear charge also increases.

Exceptions

a) In a period, the ionisation energy of IIA group elements is more than the elements of IIIA because penetration power of s-orbitals electrons. The value of ionisation energy of Be($1s^2 2s^2$) is more than B ($1s^2 2s^2 p^1{}_x$) because the penetration power of 2s-electrons of Be is more than the $2p_{x-}$ electrons of B.

b) In a period, the ionisation energy of VA elements is more than the elements of VIA because the half filled p^3 configuration of VA elements is comparatively of higher stability. VIA group elements (p^4) have the tendency to acquire comparatively more stable (p^3) configuration by the loss of one electron. Ionisation energy N($Is^2 2s^2 2p^1_x p_y^1 pz^1$) $>$O $Is^2 2s^2 2p_x^2 p_y^1 p_z^1$

Thus P>S, As>Se.

But the value of I.P. of Sb (VA) & Te (VIA) and Bi (VA) & Po(VIA) are according to general rule i.e.

Sb (VA) <Te (VIA)

Bi (VA) < Po (VIA)

On moving from top to bottom in a group the value of I.P decreases because the atomic size increases.

Exceptions

a) In group IIIA the ionisation potential of Al (13) is equal to the ionisation potential of Ga(31). Before Ga (31) the electrons are filled in 3d – orbitals of ten transition elements. These 3d orbital electrons do not completely shield the 4P electron. So the increase of +18 units in nuclear charge results in the greater increase of effective nuclear charge. Due to increase in nuclear charge the I.P. increases which counter balance the decrease in I.P. due to the increase in number of shells.

b) The values of I.P. of Tl (81) and Pb (82) of sixth period is more than that I.P. values of In (49) and Sn (50) of same groups in period fifth. This is because of the electrons are filled in $4f$-orbitals before Tl (81) and Pb (82) which do not completely shield the outer electrons. Thus increase in + 32 units in nuclear charge results in the increase of ionisation potential values.

ii) ***For transition elements:*** On moving from left to right in a transition series

a) As the atomic number increases the effective nuclear charge also increases. Hence the I.P. increases.

b) The shielding effect of (n – 1)d electrons over ns electrons increases with the addition of electron in (n-1)d orbitals. Hence the I.P. decreases.

c) The increased values of I.P due to the increase of effective nuclear charge almost balances the decreased value of I.P. due to increase in shielding effect. There is a very small increase in the values of I.P. or it may be said that I.P. almost remains the same.

d) In first transition series from Sc to Cr the value of I.P. increases because effect of increase in effective nuclear charge is more than the shielding effect. I.P. values of Fe, Co, Ni and Cu are almost same. Due to $d^{10}s^2$ configuration of Zn, the first I.P. increases.

On moving from top to bottom in a group in transition series

a) In a group on moving from first to second transition series, the values of I.P. decreases because atomic size increases.

b) In moving from second to third transition series the value of I.P some what increases except IIIB group [Y(39) $\rightarrow$ La(57)]. This is because of 14 electrons are filled in $4f$-orbitals of lanthanides which do not shield the 5d electrons effectively. Thus the increase in +32 units in nuclear charge results in the increase of I.P., on moving from left to right this effect decreases and becomes negligible in the later part.

3. Applications of ionisation potential

i) Metallic or electropositive character of elements increases as the value of ionisation potential decreases. So in a group moving from top to bottom metallic or electropositive character increases because I.P. value decreases. In a period moving from left to right the values of I.P. increases so metallic or electropositive character decreases. Non metallic character increases.

ii) The relative reactivity of the metals increases with the decrease in I.P. values. The I.P. values of IA and IIA metals are comparatively low. So they are comparatively more reactive. The I.P. values of inert gases are very high. So they are almost unreactive.

In a group moving from top to bottom the reactivity of metal atoms increases because their I.P. value decreases.

iii) The reducing power of elements increases as the values of I.P. decreases because tendency to lose the electron increases. The reducing power increases going down a group because the I.P. value decreases. Li is exception in IA group. The reducing power of Li is highest in its own group. The order of reducing Power of IA elements is as under

Li > Cs > Rb > K > Na

iv) Determination of oxidation state or valency electrons of an element –

a) If the difference of two consecutive I.P.'s of an element is 16 eV or more, the lower oxidation state is stable. For e.g. the difference of first and second I.P. of Na is 42.4 eV which is more than 16 eV. So Na^+ will be stable. It can also be explained from its electronic configuration

Na (11) = $1s^2 2s^2 2p^6 3s^1$

Na^+ = $1s^2 2s^2 2p^6$

Neutral Na atom has the tendency to acquire the stable s^2p^6 configuration by the loss of one electron. Due to s^2p^6 configuration of Na^+, the further separation of electron is difficult. So IA group metals form monopositive ions.

b) If the difference of two consecutive I.P.s. of an element is 11.0 eV or less, the higher oxidation state is stable. For e.g. the difference of first and second I.P. of Mg is 7.4 eV which is less than 11.0 eV. So Mg^{2+} will be stable. It can also be explained on the basis of its electronic configuration.

The electronic configuration of Mg^{2+} is stable s^2p^6 configuration

$Mg^{2+} = 1s^2 2s^2 2p^6$

So IIA group elements form dipositive ions.

c) The difference of first and third I.P. of Al is 12.8 eV which is more than 11eV. Therefore first oxidation state of Al i.e. Al^+ must be stable. In gaseous state Al^+ is stable. This is due to the proportionate distribution of lattice energy and the difference of second and third I.P.s 9.6eV<11 eV.

Illustration 3: ***The first I.P. of nitrogen is greater than oxygen while the reverse is true for their second I.P. values.***

Solution: The first I.P corresponds to the removal of first electron. Since nitrogen is already half filled. So more energy is required to remove the electron. But once the electron is removed from oxygen it gains half filled stability and therefore the 2^{nd} I.P. becomes high.

Illustration 4: ***The ionisation energy of the coinage metals fall in the order Cu $>$ Ag $<$ Au.***

Solution: In all the 3 cases an s-electron in the unpaired state is to be removed. In the case of Cu a 4s electron is to be removed which is closer to the nucleus than the 5s electron of Ag. So I.P. decreases from Cu to Ag. However from Ag to Au the 14 f electrons are added which provide very poor shielding effect. The nuclear charge is thus enhanced and therefore the outer electron of Au is more tightly held and so the IP is high.

7.6 Electron affinity

i) The amount of energy released when an electron is added to the outermost shell of one mole of an isolated gaseous atom in its lower energy state.

ii) Electron affinity just defined is actually first electron affinity since it corresponds to the addition of one electron only. In the process of adding further electron, the second electron will be added to gaseous anion against the electrostatic repulsion between the electron being added and the gaseous anion. Sometimes energy instead of being released is supplied for the addition of an electron to an anion.

$A_{(g)} + e^- \rightarrow A_{(g)}^- + E_1$

$A_{(g)}^- + e^- + \text{Energy supplied} \rightarrow A_{(g)}^{2-}$

1. **Factors affecting the magnitude of electron affinity**

i) ***Atomic size:*** In general electron affinity value decreases with the increasing atomic radius because electrostatic force of attraction decreases between the electron being added and the atomic nucleus due to increase of distance between them.

$$\text{Electron affinity } \alpha \frac{1}{\text{Atomic size}}$$

ii) ***Effective nuclear charge:*** Electron affinity value of the element increase as the effective nuclear charge on the atomic nucleus increases because electrostatic force of attraction between the electron being added and the nucleus increases. As the electrostatic force of attraction increases, amount of energy released is more.

Electron affinity α Effective nuclear charge (Z_{eff})

iii) ***Screening or Shielding effect:*** Electron affinity value of the elements decreases with the increasing shielding or screening effect. The shielding effect between the outer electrons and the nucleus increases as the number of electrons increases in the inner shells.

Electron affinity $\alpha \dfrac{1}{\text{Shielding effect}}$

iv) ***Stability of half filled and completely filled orbitals:*** The stability of half filled and completely filled degenerate orbitals of a sub shell is comparatively more, so it is difficult to add electron in such orbitals and lesser energy is released on addition of electron hence the electron affinity value will decrease.

2. **Periodicity in electron affinity**

i) In general electron affinity value increases in moving from left to right in a period because effective nuclear charge increases.

Exceptions

a) The electron affinity value of alkaline earth metals of IIA group is zero.

b) Electron affinity value of alkali metals of IA group is also approximately zero because these elements have the tendency of losing the electron instead of gaining the electron.

c) Electron affinity values of nitrogen and phosphorous (VA) are lesser than the electron affinity values of carbon and silicon respectively. It is due to the comparatively stable half filled configuration (np^3) of nitrogen and phosphorus and the tendency to acquire the stable np^3 configuration by the gain of one electron in carbon and silicon $(np)^2$.

d) The theoretical value of the electron affinity of zero group inert gas elements is zero due to stable s^2p^6 configuration.

ii) In a group moving from top to bottom the electron affinity value of elements decreases because the atomic size increases

Exceptions

a) Electron affinity values of second period elements are smaller than the electron affinity values of third period elements. This unexpected behaviour can be explained by the very much high value of charge densities, of second period elements due to much smaller size. The electron being added experiences comparatively more repulsion and the electron affinity value decreases.

b) The electron affinity of fluorine (Second period) is less than the electron affinity of chlorine (third period). 2p-orbitals in fluorine are much more compact than 3p-orbitals of chlorine. So the electron being added in 2p-orbitals experiences comparatively more repulsion and the electron affinity value decreases.

Illustration 5: ***Electron affinity of SF_5 is among the highest known but that of SF_6 is quite modest.***

Solution: Sulfur in SF_6 is saturated in terms of maximum covalency and maximum co-ordination number and so it has very little tendency to attract electron. In SF_5 which is actually a free radical so it has got a very strong tendency to attract an electron to fulfill its covalency and co-ordination number. There fore the electron affinity of SF_5 is high.

7.7 Electronegativity

i) It may be defined as the tendency of an atom to attract shared pair of electrons towards itself in a covalently bonded molecules.

ii) The numerical value of the electronegativity of an element depends upon its ionisation potential and electron affinity values. Higher ionisation potential and higher electron affinity values implies higher electronegativity value.

1. **Electronegativity scale:** Some arbitrary scales for the quantitative measurement of electronegativities are as under

   i) ***Pauling's scale:*** Pauling related the resonance energy(Δ_{AB}) of a molecule AB with the electronegativities of the atoms A and B. If x_A and x_B are the electronegativities of atoms A and B respectivey then

   $0.208\sqrt{\Delta_{AB}} = x_A - x_B$ if $x_A > x_B$

   or $\Delta_{AB} = 23.06\,(x_A - x_B)^2$

   $\Delta_{AB} = E_{A\text{-}B(experimental)} - E_{A\text{-}B(theoretical)}$ where $E_{A\text{-}B}$ is the energy of A-B bond. In a purely covalent molecule, AB, the experimental and theoretical values of bond energy A-B are equal.

   So $\Delta_{AB} = 0$

   or $0 = 23.06\,(x_A - x_B)^2$

   or $x_A = x_B$

   In an ionic molecule AB, $E_{A\text{-}B(experimental)}$ is more than $E_{A\text{-}B(Theoretical)}$.

   Pauling assumed the electronegativity value of fluorine 4 and calculated the electronegativity values of other elements from this value.

ii) ***Mulliken's electronegativity:*** According to Mulliken, the electronegativity of an element is the average value of its ionisation potential and electron affinity.

or Electro-negativity $= \frac{\text{Electron affinity} + \text{Ionisation potential}}{2}$

$$= \frac{\text{Electron affinity} + \text{Ionisation potential}}{5.6} \text{ (on pauling scale)}$$

When both are expressed in electron volt

iii) ***Alred Rochow's electronegativity:*** The electronegativity of an element is the electrostatic force of attraction between the electron present on the circumference of the outermost shell of this atom and the atomic nucleus. If the distance between the circumference of outermost shell and the nucleus is *r* and the effective nuclear charge Z_{eff} then –

Electro-negativity $= \frac{Z_{eff}e^2}{r^2} = \frac{0.359Z_{eff}}{r^2} + 0.744$

$Z_{eff} = Z - \sigma$

Z = The actual number of charge present in the nucleus i.e number of protons and σ = Shielding constant

2. **Factors affecting the magnitude of electronegativity**

i) ***Atomic radius:*** As the atomic radius of the element increases the electronegativity value decreases.

$$\text{Electronegativity} \, \alpha \, \frac{1}{\text{Atomic radius}}$$

iii) ***Effective nuclear charge:*** The electronegativity value increases as the effective nuclear charge on the atomic nucleus increases.

Electronegativity α Effective nuclear charge (Z_{eff})

iii) ***Oxidation state of the atom:*** The electronegativity value increases as the oxidation state (i.e. the number of positive charge) of the atom increases.

iv) ***Hybridisation state of an atom in a molecule:*** If the s- character in the hybridisation state of the atom increases electronegativity increases because s-electrons are comparatively nearer to the nucleus. For example the electronegativity values of C-atom in various hybridisation states are as under:

Hybridisation states	sp^3	sp^2	sp
s-Character	25%	33.33%	50%
Electronegativity	2.48	2.75	3.25

$\longrightarrow$

s-character is increasing

So the electronegativity value is increasing

Exercise 1 : ***i) NaOH behaves as a base while $Zn(OH)_2$ is amphoteric why?***

ii) Among fluorine – fluorine bond and chlorine – chlorine bond, which is more stronger and why?

3. **Periodicity in Electronegativity**

i) In a period moving from left to right, the electronegativity increases due to the increase in effective nuclear charge.

ii) In a period the electronegativity value of IA alkali metal is minimum and that of VIIA halogen is maximum.

iii) In a group moving from top to bottom, the electronegativity decreases because atomic radius increases.

iv) The electronegtivity value of F is maximum and that of Cs is minimum in the periodic table.

v) The electronegativity of Cs(55) should be more than Fr(87) but it is less. This is due to the increase of +32 units in nuclear charge of Fr which makes the effective nuclear charge comparatively high.

vi) On moving from second to third transition series in a group [except Y(39) $\rightarrow$ La (57)] electronegativity increases due to the increase of +18 units in nuclear charge.

vii) The electronegativity of inert gas elements of zero group is zero due to stable s^2p^6 configuration. Inert gases are monoatomic molecules and the electronegativity is of bonded atoms.

4. **Applications of electronegativity**

i) ***Partial ionic character in covalent Bond:*** The ionic character of a covalent bond increases as the electronegativity difference of bonded atoms increases. According to Haney and Smith if the electronegativity difference of bonded atoms is Δx then percentage ionic character of the bond $= 16\Delta x + 3.5\Delta x^2$

If the value of Δx is 2.1 then ionic character percentage is about 50. For example the order of ionic character in H–X bond is as follows–

H–F>H–Cl>H–Br>H–I

Because the electronegtivity difference of bonded atoms (Δx) decreases.

ii) ***Bond strength:*** If the electronegativity difference of covalently bonded atoms (Δx) increases, the bond energy of the covalent bond also increases. For example – the order of the H–X bond strength is –

H – F > H – Cl > H – Br > H – I

As the bond strength is decreasing the acid strength is increasing. So order of increasing acid strength is

HF < HCl < HBr < HI

iii) ***Acidic and basic nature of oxides of normal elements in a period:*** The acidic nature of the oxides of normal elements increases as we move from left to right in a period. In a period from left to right the electronegativity of the elements increases. So the difference of the electronegativities of oxygen and the elements ($x_O - x_E$) decreases. If the ($x_O - x_E$) values is about 2.3 or more then oxide will be basic. If ($x_0 - x_E$) values is less than 2.3 the oxide will be acidic. The oxides of the IIIA elements are amphoteric.

The order of acidic or basic nature of the oxides of third period elements may be given as under:

Na_2O MgO SiO_2 P_2O_5 SO_3 Cl_2O_7

$\longrightarrow$

The value of $x_O - x_E$ is decreasing

Basic nature is decreasing

Acidic nature is increasing

iv) ***Metallic and non metallic properties of elements:***

a) The metallic character decreases as the electronegativity of the element increases.

b) On moving from left to right in a periods, the electronegativity of the elements increases. So the metallic character decreases.

c) On moving down a group, the electronegativity of the elements decreases. So the metallic character increases.

v) ***Basic nature of the hydroxides of elements:*** A hydroxide MOH of an element M may ionise in two ways in water.

$$M{-}O{-}H + H_2O \rightleftharpoons MO^- + H_3O^+ \quad \ldots(1)$$

$$M{-}O{-}H + H_2O \rightleftharpoons MOH_2^+ + OH^- \quad \ldots(2)$$

If the ionisation is according to eqn (1) then it is acidic. It is possible when ionic character of O–H bonds is more than the ionic character of M-O bond i.e. ($x_O - x_H$) > ($x_O - x_M$) where x_0, x_H and x_M are the electronegativities of oxygen, hydrogen and element respectively.

If the ionisation is according to eqn. (2) then it is basic. This is only possible when ionic character of O –H bond is less than M–O bond i.e ($x_O - x_H$) < ($x_O - x_M$)

Exercise 2:

i) In alkali metal group which is the strongest reducing agent and why?

ii) Although Aluminium is above hydrogen in the electrochemical series, it is stable in air and water. Explain.

8. Effective Nuclear Charge and Shielding Effect

i) In a multielectron atom, the effect of nuclear charge experienced by the outermost electron is less than the theoretical value of the nuclear charge (Z).

ii) If the nuclear charge of an atom is Z, effective nuclear charge Z_{eff} and shielding constant is σ then according to Slater

$Z_{eff} = Z - \sigma$

Exercise 3: ***Predict and explain the reactions:***

a) $KI + Cl_2 \rightarrow$

b) $KClO_3 + I_2 \rightarrow$

9. Solution to Exercises

Exercise 1:

i) In NaOH the bond electronegativity difference between Na and oxygen is greater than between H and O and therefore it is the Na–O bond that breaks releasing OH^-. But in case of Zn—O—H bond the difference of electronegativity of Zn—O and O—H are almost same. So there is equal probability that the bond breaks in both ways leading to an amphoteric behaviour

ii) In Cl—Cl bond, a filled p-orbital of chlorine can overlap with a suitable vacant d-orbital of adjacent chlorine thereby introducing some double bond character. Thus the bond strength increases. This is not possible in fluorine as it has got no vacant d-orbital.

Exercise 2:

i) Li is the strongest reducing agent. Since I.P. decreases down the group we would expect that Li will have the lowest reducing power in that group. But since it's hydration energy is very high and which in fact decreases down the group, Li will have highest reducing power.

ii) Due to the formation of protective oxide layer on its surface.

Exercise 3:

$2KI + Cl_2 \rightarrow 2KCl + I_2$

$KClO_3 + I_2 \rightarrow KIO_3 + Cl_2$

Because in the first case Cl_2 is more powerful oxidising agent than I_2 and in second case ClO_3^- is more powerful oxidising agent than IO_3^- [Cl^{5+}] being reduced to Cl^0 and I^0 being oxidised to I^{5+}]

10. Solved Problems

Problem 1: ***Calculate the dipole moment of HBr molecule if the bond length is 1.2476.***

Solution: μ = q.r. = $(1.6023 \times 10^{-19}\text{C})\ (1.2476 \times 10^{10}\ \text{m})$

$= 1.99 \times 10^{-29}$ cm

$= \dfrac{1.99 \times 10^{-29}}{3.336 \times 10^{-30}} = 5.99$ D

Problem 2: ***HBr molecule has internuclear distance of 1.27×10^{-10} m. The electronic charge is 4.8×10^{-10} esu. Observed dipole moment is 1.03 D. find % ionic character of the bond.***

Solution: % ionic character = $\dfrac{\mu_{(\text{observed})}}{\mu_{(\text{Theo})}} \times 100$

$= \dfrac{1.03 \times 100}{\left(\dfrac{2.035 \times 10^{-29}}{3.33 \times 10^{-30}}\right)} = 16.80$

Problem 3: ***The electronegativity of H, N are 2.1, 3.0 respectively. Calculate percentage ionic character of H – N bond.***

Solution: % Ionic character = $16\ (x_A - x_B) + 3.5\ (x_A - x_B)^2$

$x_A = 3.0,\ x_B = 2.1$

$\therefore$ % IC = $16 \times 0.9 + 3.5 \times 0.81$

= 17.24

Problem 4: ***Calculate effective nuclear charge on a valence electron in a nitrogen atom $N = 1s^2\ 2s^2\ 2p^3$.***

Solution: $= 4 \times 0.35 + 2 \times$grouping of orbitals as $(1s)^2$, $(2s, 2p)^5$

= 3.1

$= Z^* = Z - 6 = 7 - 3.1 = 3.9$

Problem 5: ***Calculate Alred Rochow electronegativity in F using Slater rule, r_F = 5.413Å.***

Solution: $X = \dfrac{0.359}{r^2} Z^* + 0.744$

$= 0.359 \times \dfrac{(0.35 \times 7 + 0.85 \times 2)}{(0.7065)^2} + 0.744 = 4.23$

Problem 6: ***The electron affinity of sulfur is greater than oxygen. Why?***

Solution: This is because of smaller size of oxygen due to which it has got higher change density and thus electronic repulsion increases as it takes electron. So its E.A. is less than sulphur.