B.Sc. (Semester-I)
General Chemistry – I
(US01CCHE21)
UNIT - II PERIODIC PROPERTIES

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Brief Introduction of Periodic Table:

Mendeleeff's Periodic Law and Periodic Table:

"*The properties of elements are a periodic function of their atomic weight*". That is if elements are arranged in the increasing order of their atomic weight, the properties of elements repeated after definite regular intervals or period. Mendeleeff arranged the elements in the increasing order of their atomic weights, in the form of a table, which is known as Mendeleeff's Periodic Table. In this the elements are arranged in groups (or columns) and periods (or rows).

Defects of Mendeleeff's Periodic Table

(1) Anomalous position of hydrogen:

Mendeleeff has placed hydrogen in group IA, alongwith alkali metals, but at the same time, hydrogen also resembles halogens. Thus, the position of hydrogen is still a matter of dispute.

(2) Similar pairs of elements, placed in different groups, while dissimilar elements placed in the same group:

Many pairs of elements, which have similar properties with each other, have been placed in different groups. Examples are: Cu (IB)-Hg (IIB), Ag (IB-TI(IIIA), Ba (IIA)-Pb (IVA) etc. Many elements, which have dissimilar properties have been placed in the same group, e.g., coinage metals (IB: Cu, Ag and Au) have been placed along with alkali metals (IA). Similarly, Mn (VIIB) has been placed with halogens (VIIA).

(3) Position of lanthanides and actinides:

Lanthanides and actinides elements have not been placed in the main body of the Periodic Table. Rather these have been given a separate place at the bottom of the Periodic Table.

(4) Reversible order in position of four pairs of elements:

Mendeleeff's periodic table contains four pairs of elements, in which element with lower atomic weight has been placed after the element with higher atomic weight. These pairs are: Ar-K, Co-Ni, Te-I and Th-Pa.

(5) Position of isotopes:

If the elements are arranged in the order of their increasing atomic weights, it is not possible to accommodate the large number of isotopes in the periodic table.

(6) Group does not represent valency:

Excepting Osmium, elements placed in group eight do not show a valency of 8. Also, the elements lying in the middle of long periods show two or more valences e.g. Cr, Mn etc.

Mosely's Periodic Law (Modern Periodic Law):

"***The properties of elements are a periodic function of their atomic number***". It means if the elements are arranged in the increasing order of their atomic numbers, the properties of the elements are repeated after definite regular intervals or periods.

Long form of Periodic Table or Modern Periodic Table:

In this table, the arrangement of elements has been made in accordance with Mosley’s periodic law, i.e. the elements have been grouped in the increasing order of their atomic number.

Groups: There are 18 vertical columns in the long form of the periodic table are called groups or families. The outer-most electronic configurations of the elements in the same group are similar. The groups are numbered according to IUPAC as1 to 18 while according to another system, the groups are named as IA (for 1), IIA (2), IIIB (3) to VIIB (7), VIIIB (8, 9, 10), IB (11), IIB (12), IIIA (13) to VIIA (17), VIIIA or Zero (18).

The elements of group IA and IIA are called **s-block elements** and those of groups IIIA to VIIIA are called **p-block elements**, *s- and p-block elements together are called* ***main group elements.*** The elements of groups IA to VIIA are called **representative elements** and those of group VIIIA (zero group) are called **noble gases**. The elements belonging to groups IIIB to VIIIB, IB and IIB are called **d-block or transition elements**. There are two rows of elements placed separately at the bottom of the periodic table called **f-block elements or inner-transition elements or rare earth metals.**

LONG FORM OF THE PERIODIC TABLE

	Representative Elements		Transition Elements										Representative Elements					Noble gases
	←s-Block→		←d-Block→										←p-Block→					
GROUPS→	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
	(IA)	(IIA)	(IIIB)	(IVB)	(VA)	(VIB)	(VIIB)	← VIII →			(IB)	(IIB)	(IIIA)	(IVA)	(VA)	(VIA)	(VIIA)	(0)
PERIODS ↓	(ns^1)	(ns^2)	$(n-1)\ d^{1-10}\ ns^{1-2}$										(ns^2np^1)	(ns^2np^2)	(ns^2np^3)	(ns^2np^4)	(ns^2np^5)	(ns^2np^6)
1 (1 s)	1 H																	2 He
2 (2s 2p)	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3 (3s 3p)	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4 (4s 3d 4p)	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
5 (5s 4d 5p)	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
6 (6s 4f 5d 6p)	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
7 (7s 5f 6d 7p)	88 Fr	88 Ra	89 Ac**	104 Ku/Rf	105 Ha	106 Unh	107 Ns	108 Hs	109 Mt	110 Unm								

← Metals → ←Metalloids→ ←Non metals →

Inner Transition Elements or *f*-Block Elements
$[(n-2)\ f^{1-14}\ (n-1)^{0-1}\ ns^2]$

LANTHANIDES* ($4f^{1-14}5d^{0-1}6s^2$)	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
ACTINIDES** ($5f^{1-14}6d^{0-1}7s^2$)	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 Lr

Table 2.1 : Long form of the periodic table

Periods: There are seven horizontal rows are called periods, 1st, 2nd and 3rd periods which contain 2, 8 and 8 elements respectively are called ***short periods*** while 4th, 5th and 6th periods which contain 18, 18 and 32 elements are called ***long periods***. 7th period is an incomplete period, since it contains only 20 elements and is expected to contain 32 elements, first element of each period is an alkali metal and the last element is a noble gas.

1st period (short period) consists of two elements, i.e. H $_1$ and He $_2$.

2nd period (short period) contains 8 elements namely Li $_3$ to Ne $_{10}$.

3rd period (short period) also contains 8 elements namely Na $_{11}$ to Ar $_{18.}$

4th period (long period) has 18 elements which are K $_{19}$ to Kr $_{36}$.

5th period (long period) also has 18 elements which are Rb $_{37}$ to Xe $_{54.}$

6th period (long period) contains 32 elements which are Cs $_{55}$ to Rn $_{86}$.

7th period (incomplete) contains 20 elements which are Fr $_{87}$ to Unh $_{106}$.

Superiority of long form of periodic table over Mendeleeff's table or Merits of the long form of Modern periodic table:

(1) The arrangement of elements in long form of periodic table has been made on the basis of atomic number of the elements, which is a more fundamental property of the elements.

(2) The elements having the same valence shell configurations have been placed in the same group.

(3) The elements of the two sub-group have been placed separately and thus dissimilar elements do not fall together.

(4) This periodic table is easier to remember, understand and reproduce.

Defects of Long form of periodic table:

(1) The problem of the position of hydrogen still remains unsolved.

(2) Like Mendeleeff's table, it fails to accommodate the lanthanides and actinides in the main body of the table.

Types of Elements:

On the basis of electronic configuration, we recognize four basic types of elements:

(1) Inert gas elements:

Atoms of these elements have all the sets of *s*, *p*, *d* and *f* orbitals which have closed shell configuration. Except Helium having $\mathbf{1s^2}$ electronic configuration, the characteristic outer electronic structure of all the other elements is $\mathbf{ns^2np^6}$. All atoms have spherically symmetrical electron distributions and **1*s*** ground states.

These elements are highly stable and are highly unreactive.

(2) The representative elements (*s* - *p* block) (Main group elements):

These are also known as main group elements. These form the largest groups IA, IIA (*s*-block) and IIIA to VIIIA (*p*-block). Atoms of these elements have only outermost electron shell incomplete. Their valance electron configurations range from $\mathbf{ns^1}$ to $\mathbf{ns^2\ np^5}$. The chemical behaviour of these elements is governed by the tendency of their atoms to gain, lose or share their valance electrons so as to achieve the stable inert gas type configuration. There are 44 representative elements.

(3) The transition elements (d - block):

These elements form groups IIIB to IB. The outermost electron shells are incomplete. Their outer electronic structure ranges from (n - 1) d^1 to (n - 1) d^9. There are 4 such series. One each in 4th, 5th,6th and 7thlong periods corresponding to 3d, 4d, 5d and 6d orbitals. The incomplete d-sub shell confers many interesting physical and chemical properties. 1st, 2nd and 3rd series contains 10 elements each whereas 4th series is incomplete.

The most characteristic of these being:

- formation of coloured and paramagnetic ions
- existence of several oxidation states and
- ability to form large number of complexes

(4) The inner transition elements (f - block):

These forms two series, lanthanides and actinides in 6th and 7th long period by filing 4f and 5f orbitals respectively. The atoms of these elements have outermost 3-electron shells incomplete. Their general configuration is (n - 2) f^{1-14} (n - 1) s^2 $p^6d^{0 \text{ or } 1}$ ns^2. The similarity of the outer most electron configuration causes the inner transition series elements to have very closely similar properties.

Shielding (or Screening) Effect and Effective Nuclear Charge, Z* or Z_{eff} :

The electrons present in the shells between the nucleus and outer shell (valence shell) are called ***intervening electrons***. Because of presence of intervening electrons, the force of attraction between nucleus and the outermost electron is reduced. The reduction (decrease) in the force of attraction because of presence of intervening electrons is called ***shielding effect or screening effect***. Thus, the actual nuclear charge (Z) acting on the outermost electron is less than the nuclear charge which is equal to the atomic number of atom (Z). The symbol for effective nuclear charge is Z* or $Z_{eff.}$ The decrease or reduction in the actual charge is called ***screening constant or shielding constant*** (σ). Thus, the effective nuclear charge (Z_{eff} can be calculated using the following equation.

$Z_{eff} = Z - \sigma$

Factors affecting shielding constant (σ) and effective nuclear charge (Z_{eff}):

(1) Number of intervening electrons:

As number of intervening electrons increases, the value of σ increases and as value of σ increases the effective nuclear charge decreases. Thus, as number of intervening electrons increases effective nuclear charge (Z_{eff}) decreases.

When we move down the group in the periodic table, number of intervening electrons increases. As number of intervening electrons increases shielding effect also increases and hence effective nuclear charge (Z_{eff}) decreases. Thus, in any group downward effective nuclear charge decreases.

(2) Size of the atom:
As size of atom increases, force of attraction by nucleus for outermost electron or shell decreases. Thus, with increase in size, effective nuclear charge (Z_{eff}) decreases. When we move down the group in the periodic table, atomic size increases and hence effective nuclear charge (Z_{eff}) decreases. As we move from left to right across the period, size of atom decreases and hence, effective nuclear charge increases. Thus, across the period as atomic number increases, effective nuclear charge increases.

Slater's rules:
The screening or shielding constant (σ) can be calculated using the following Slater's rules.

(1) The electrons in ion or atom are rearranged according to following order of groups.

(1s) (2s2p) (3s3p) (3d) (4s4p) (4d) (4f) (5s5p)

(2) Electrons in a group beyond that of electron under consideration, contributes nothing to screening or shielding constant (σ).

(3) For the electron in (ns np) group, σ is calculated by the following contributions of other electrons.

- 0.35 of each electron in a same group.
- 0.85 of each electron in (n - 1) shell.
- 1.00 of each electron in an inner shell

(4) For the electron in (nd) or (nf) group, σ is calculated by the following contributions of other electrons.

- 0.35 of each electron in same group.
- 1.00 of each electron in lower group.

(5) For one of the two electrons present in 1s orbital of any atom, the contribution of other electron is 0.3

Note: To calculate the effective nuclear charge felt at the periphery (surface or boundary) of an atom or ion, all the electrons present in an atom or ion are considered and contributes for calculating screening constant or shielding constant.

<u>Example:</u> Calculate the screening constant and effective nuclear charge on 4s electron of (i) Mn (Z = 25), (ii) Cu (Z = 29) (iii) K (Z = 19),

<u>Solution:</u>

(i) For Mn-atom:

Electron configuration of Mn (Z = 25) is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^5$

Calculating σ by applying Slater's rule,

$$\text{Mn (Z=25): } \underbrace{(1s^2)\ (2s^2\ 2p^6)}_{1.0 \times 10}\ \ \underbrace{(3s^2\ 3p^6)\ \ (3d^5)}_{0.85 \times 13}\ \ \underbrace{(4s^2\ 4p^0)}_{0.35 \times 1}$$

$\sigma = (1.0 \times 10) + (0.85 \times 13) + (0.35 \times 1)$
$= 10 + 11.05 + 0.35$
$= 21.40$

Now,

$Z_{eff} = Z - \sigma$
$= 25 - 21.40$
$= 3.6$

(ii) For Cu-atom:

Electron configuration of Cu (Z = 29) is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1\ 3d^{10}$
Calculating σ by applying Slater's rule,

$$\text{Cu (Z=29): } \underbrace{(1s^2)\ (2s^2\ 2p^6)}_{1.0 \times 10}\ \ \underbrace{(3s^2\ 3p^6)\ (3d^{10})}_{0.85 \times 18}\ \ \underbrace{(4s^1\ 4p^0)}_{0.35 \times 0}$$

$\sigma = (1.0 \times 10) + (0.85 \times 18) + (0.35 \times 0)$
$= 25.30$

Now,

$Z_{eff} = Z - \sigma$
$= 29 - 25.30$
$= 3.70$

(iii) For K-atom:

Electron configuration of K (Z = 19) is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$
Calculating σ by applying Slater's rule,

$$\text{Cu (Z=29): } \underbrace{(1s^2)\ (2s^2\ 2p^6)}_{1.0 \times 10}\ \ \underbrace{(3s^2\ 3p^6)\ (3d^{10})}_{0.85 \times 18}\ \ \underbrace{(4s^1\ 4p^0)}_{0.35 \times 0}$$

$\sigma = (1.0 \times 10) + (0.85 \times 8) + (0.35 \times 0)$
$= 16.80$

Now,

$Z_{eff} = Z - \sigma$
$= 19 – 16.80$
$= 2.20$

<u>Example</u>: Calculate Z_{eff} for the last electron in (i) CI-atom (Z= 17) and (ii) Cl^- ion.

<u>Solution:</u>

(i) For Cl-atom:

Electron configuration of Cl (Z = 17) is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$

Calculating σ for last electron (i.e. 3p electron) by applying Slater's rule,

$$\text{Cl } (Z = 17): \underbrace{(1s^2)}_{1.0 \times 2}\quad \underbrace{(2s^2\ 2p^6)}_{0.85 \times 8}\quad \underbrace{(3s^2\ 3p^5)}_{0.35 \times 6}$$

$\sigma = (1.0 \times 2) + (0.85 \times 8) + (0.35 \times 6)$

$= 2 + 6.80 + 2.1$

$= 10.9$

$Zeff = Z - \sigma$

$= 17 - 10.9$

$= 6.1$

(ii) For Cl^- ion:

Electron configuration of Cl (Z = 17) is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$

Electron configuration of Cl^- ion is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$

Calculating σ for last electron (i.e. 3p electron) by applying Slater's rule,

$$\text{Cl}^- (Z = 17): \underbrace{(1s^2)}_{1.0 \times 2}\quad \underbrace{(2s^2\ 2p^6)}_{0.85 \times 8}\quad \underbrace{(3s^2\ 3p^6)}_{0.35 \times 7}$$

$\sigma = (1.0 \times 2) + (0.85 \times 8) + (0.35 \times 7)$

$= 2 + 6.80 + 2.45$

$= 11.25$

$Zeff = Z - \sigma$

$= 17 - 11.25$

$= 5.75$

<u>Example:</u> Calculate Z_{eff} for the last electron in (i) Na atom (Z = 11) and (ii) Na^+ ion.

<u>Solution:</u>

(i) For Na-atom:

Electron configuration of Na (Z = 11) is $1s^2\ 2s^2\ 2p^6\ 3s^1$

Calculating σ for last electron (i.e. 2p electron) by applying Slater's rule,

$$\text{Na } (Z = 11): \underbrace{(1s^2)}_{1.0 \times 2}\quad \underbrace{(2s^2\ 2p^6)}_{0.85 \times 8}\quad \underbrace{(3s^1)}_{0.35 \times 0}$$

$\sigma = (1.0 \times 2) + (0.38 \times 8) + (0.35 \times 0)$

$= 8.80$

Now,

$Z_{eff} = Z - \sigma$
$= 11 - 8.80$
$= 2.20$

(ii) For Na^+ ion:

Electron configuration of Na (Z = 11) is $1s^2\ 2s^2\ 2p^6\ 3s^1$
Electron configuration of Na^+ ion is $1s^2\ 2s^2\ 2p^6$
Calculating σ for last electron (i.e. 2p electron) by applying Slater's rule,

$$Na^+ (Z = 11) : \underbrace{(1s^2)}_{0.85 \times 2}\quad \underbrace{(2s^2\ 2p^6)}_{0.35 \times 7}$$

$\sigma = (0.85 \times 2) + (0.35 \times 7)$
$= 1.7 + 2.45$
$= 4.15$

Now,

$Z_{eff} = Z - \sigma$
$= 11 - 4.15$
$= 6.85$

<u>Example</u>: Calculate σ and Z_{eff} for 3d electron in (i) Mn (Z 25) and (ii) Cu (Z = 29).

<u>Solution:</u>

(i) For Mn-atom:

Electron configuration of Mn (Z = 25) is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^5$
Calculating σ by applying Slater's rule,

$$Mn (Z=25): \underbrace{(1s^2)\ (2s^2\ 2p^6)\ (3s^2\ 3p^6)}_{1.0 \times 18}\quad \underbrace{(3d^5)}_{0.35 \times 4}\quad \underbrace{(4s^2\ 4p^0)}_{\text{not contribute}}$$

$\sigma = (1.0 \times 18) + (0.35 \times 4)$
$= 19.40$

Now,

$Z_{eff} = Z - \sigma$
$= 25 - 19.40$
$= 5.60$

(ii) For Cu-atom:

Electron configuration of Cu (Z = 29) is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1\ 3d^{10}$
Calculating σ by applying Slater's rule,

$$Cu (Z = 29): \underbrace{(1s^2)\ (2s^2\ 2p^6)\ (3s^2\ 3p^6)}_{1.0 \times 18}\quad \underbrace{(3d^{10})}_{0.35 \times 9}\quad \underbrace{(4s^1 4p^0)}_{\text{not contribute}}$$

$\sigma = (1.0 \times 18) + (0.35 \times 9)$
$= 18 + 3.15 = 21.15$

Now,

Z_{eff} = Z – σ
= 29 - 21.15
= 7.85

<u>Example</u>: Calculate Z_{eff} experienced by an electron residing in K and L shell in Li_3, Be_4, B_5, C_6, N_7, O_8, F_9 and Ne_{10} atoms.

(Answer: Li_3 : For L shell: σ = 1.7, Z_{eff} =1.3, for K shell: σ = 0.3, Z_{eff} = 2.7, Be_4: For L shell: σ 2.05, Z_{eff} = 1.95, for K shell: σ = 0.3, Z_{eff} = 3.7, B_5: For L shell: σ = 2.4, Z_{eff} = 2.6, for K shell: σ = 0.3, Z_{eff} = 4.7, N_7: For L shell: σ = 3.1, Z_{eff} = 3.9, for K shell: σ = 0.3, Z_{eff} = 6.7, O_8: For L shell: σ = 3.45, Z_{eff} = 4.55, for K shell: σ = 0.3, Z_{eff} = 7.7, F_9: For L shell: σ = 3.8, Z_{eff} =5.2, for K shell: σ = 0.3, Z_{eff} = 8.7, Ne_{10}: For L shell: σ = 4.15, Z_{eff} = 5.85, for K shell: σ = 0.3, Zeff = 9.7.)

<u>Solution</u>: For C_6 atom:
For L shell: Calculating σ for L shell- electron (i.e. 2p electron) by applying Slater's rule,

C (Z = 6): $(1s^2)$ $(2s^2\ 2p^2)$
------- -----------
0.85 x 2 0.35 x 3

σ = (0.85 x 2) + (0.35 x 3)
= 1.7 + 1.05 = 2.75
Now,
Z_{eff} = Z – σ
= 6 - 2.75 = 3.25
For K shell : Calculating σ for K shell electron (i.e. 1s electron) by applying Slater's rule,
C (Z = 6): $(1s^2)$ $(2s^2\ 2p^2)$
------- -----------
0.3 x 1 not contribute
σ = (0.3 x 1) = 0.3
Now,
Z_{eff} = Z – σ
= 6 – 0.3 = 5.7

<u>Example:</u> Calculate effective nuclear charge Z* at the periphery of (i) N-atom (Z = 7), (ii) Cr atom (Z= 24) and (iii) O^{2-} ion (Z=8).
(Answers: For N-atom : σ = 3.45, Z_{eff} = 3.55 (ii) For K^+ ion : σ = 11.6, Z_{eff} = 7.4)
(**Note:** To calculate screening constant (σ) at periphery of any atoms or ions, consider all electrons for contribution.)
<u>Solution :</u>
(i) For N atom :
Electron configuration of N (Z = 7) is $1s^2\ 2s^2\ 2p^3$

Calculating σ for all the electrons present (i.e. at periphery) by applying Slater's rule,

$$\text{N } (Z = 7)\text{: } \underbrace{(1s^2)}_{0.85 \times 2} \quad \underbrace{(2s^2\ 2p^3)}_{0.35 \times 5}$$

$\sigma = (0.85 \times 2) + (0.35 \times 5)$

$= 1.7 + 1.75 = 3.45$

Now,

$Z_{eff} = Z - \sigma$

$= 7 - 3.45$

$= 3.55$

(ii) For Cr atom :

Electron configuration of Cr (Z=24) is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1\ 3d^5$

Calculating σ for all the electrons present (1.e. at periphery) by applying Slater's rule,

$$\text{Cr } (Z=24)\text{: } \underbrace{(1s^2)\ (2s^2\ 2p^6)}_{1.0 \times 10} \quad \underbrace{(3s^2\ 3p^6)\ (3d^5)}_{0.85 \times 13} \quad \underbrace{(4s^1\ 4p^0)}_{0.35 \times 1}$$

$\sigma = (1.0 \times 10) + (0.85 \times 13) + (0.35 \times 1)$

$= 10 + 11.05 + 0.35 = 21.40$

Now,

$Z_{eff} = Z - \sigma$

$= 24 - 21.40$

$= 2.6$

(iii) For O^{2-} ion:

Electron configuration of O (Z= 8) is $1s^2\ 2s^2\ 2p^4$

Electron configuration of O^{2-} ion is $1s^2\ 2s^2\ 2p^6$

Calculating σ for all the electrons present (i.e. at periphery) by applying Slater's rule,

$$O^{2-}\ (Z=8)\text{: } \underbrace{(1s^2)}_{0.85 \times 2} \quad \underbrace{(2s^2\ 2p^6)}_{0.35 \times 8}$$

$\sigma = (0.85 \times 2) + (0.35 \times 8)$

$= 1.7 + 2.8$

$= 4.5$

Now,

$Z_{eff} = Z - \sigma$

$= 8 - 4.5$

$= 3.5$

<u>Example</u>: Calculate σ and effective nuclear charge (Z_{eff}) for 1s electron in (i) Nitrogen atom (Z = 7) and (ii) Helium atom (Z = 2)). (Answers: (ii) For He-atom: σ = 0.3, Z_{eff} = 1.7)

<u>Solution:</u>

(i) For N-atom:

Electron configuration of N (Z=7) is $1s^2\ 2s^2\ 2p^3$

Calculating σ by applying Slater's rule,

(According to Slater's rule number 5)

N(Z=7):	($1s^2$)	($2s^2\ 2p^3$)
	---------	--
	0.3 x1	not contribute (according to Slater's rule no. 5)

$\sigma = 0.3 \times 1$

$= 0.3$

Now,

$Z_{eff} = Z - \sigma$

$= 7 - 0.3$

$= 6.7$

Ionization Energy:

The amount of energy required to remove an electron from the valence-shell of the isolated gaseous atom of the element to convert the atom into the gaseous cation is called ionization energy (IE). Thus:

$M_{(g)} - e^- \rightarrow M^+_{(g)}$ ΔH= Energy required----(i)

=IE of M atom

(Endothermic reaction)

Since IE is the energy required, it is represented with a positive sign. The removal of an electron from a gaseous atom is an endothermic process, since it requires energy.

IE values are expressed in electron volts per atom (eV/ atom), kilo calories per mole (kcal/mole) or Kilo joules per mole (kJ/ mole). These energy units are related as:

1 eV/ atom=96.4705kJ/ mole=23.06 Kcal/mole

*** Successive ionization energies:**

IE defined by equation (i) is called first ionization energy (IE_I), since it corresponds to the removal of one electron only. IE_2 is the amount of energy required to remove an electron from $M^+_{(g)}$ ion, IE_3 is the energy required to remove an electron from $M^{2+}_{(g)}$ ion. In this way IE_4, IE_5, etc. can also be defined. Thus:

$M_{(g)} - e^- \rightarrow M^+_{(g)}$, $\Delta H = +IE_1$

$M^+_{(g)} - e^- \rightarrow M^{2+}_{(g)}$, $\Delta H = +IE_2$

$M^{2+}_{(g)} - e^- \rightarrow M^{3+}_{(g)}$, $\Delta H = +IE_3$

IE_2, IE_3, IE_4 etc. are called successive ionization energies of the neutral gaseous atom. It has Been observed that for a given element $M_{(g)}$, the magnitude of successive ionization energies are in the increasing order: $IE_1 < IE_2 < IE_3 <$……. .

The above order of successive ionization energies can be explained as follows:

(i) Explanation based on the size of the atom or cation:

The magnitude of ionization energy increases with the decrease in the size of the atom or cation from which the electron is being removed. Thus , since the size of $M^+_{(g)}$, $M^{2+}_{(g)}$, $M^{3+}_{(g)}$………….decreases in the order $M_{(g)} > M_{(g)}^{+1} > M_{(g)}^{+2} > M_{(g)}^{+3} >$-------------**,** the successive I.E. increase in the order $IE_1 < IE_2 < IE_3 < IE_4 <$---------------

(ii) Explanation based on the effective nuclear charge experienced by the electron to be removed:

Effective nuclear charge (Z_{eff}) increases as an electron is removed from a gaseous atom or a gaseous cation. For Example, the values of Z_{eff} experienced by $2p^1$ electron in N ($N = 2s^2 2p^3$), N^+($N^+ = 2s^2 2p^2$) and N^{2+}($N^{2+} = 2s^2 2p^1$) are in the increasing order (N=3.9, N^+ = 4.25, N^{+2} = 4.60). With the increase in the value of Z_{eff} from $N \rightarrow N^+ \rightarrow N^{2+}$, the value of successive ionization energies also increases

For example

$Li_{(g)} - e^-$ ----------> $Li_{(g)}^+$, IE_1= 520.3 kJ/mole

$Li_{(g)}^+ - e^-$-----------> $Li_{(g)}^{2+}$, IE_2 = 7298.1 kJ/mole

$Li_{(g)}^{2+} - e^-$-----------> $Li_{(g)}^{3+}$, IE_3 = 11814.9 kJ/mole

In above reaction, the successive ionization energy is always higher than the preceding one (i.e.$IE_1 < IE_2 < IE_3 < IE_4 <$ …………). Since, the constant nuclear charge acts on successive decreasing the number of electrons resulting in successive reduction in their electronic repulsion and increase in average nuclear attraction. So, the electron cloud remaining on the cation becomes more compact and more strongly bound and thus for the removal of successive electrons more energy is required. Therefore, successive ionization energy is always higher than preceding one.

Factors affecting the magnitude of ionization energy:

Following are the important factors which affect the magnitude of ionization energy of the elements:

(1) Nuclear charge: For the species having different charges the force of attraction between the nucleus and the outer most valence shell electron increases with the increase of nuclear charge and hence more energy is required to remove the outer most valance shell electron from the atom. Thus, with the increase of nuclear charge ionization energy increases.

Ionization energy of Li^+ ion ($1s^2$) is greater than that of He atom ($1s^2$). The I.E. of Li^+=7298.1 kJ/mole and He = 2372.3 kJ/mole. Both the species have different nuclear charges (Li^+ = 3, He = 2), but the number of electrons in both the species is the same (Li^+ =3-1=2, He =2). Due to greater nuclear charge on Li^{+2}ion, the force of attraction between the nucleus and the outer most shell electron cloud increases and hence the value of ionization energy also increases. Therefore, ionization energy of Li^+ ion is greater than that of He-atom.

(2) Size of the atom or ion: Greater is the size of the atom or ion, more far is the outer most valance shell electron from the nucleus and hence lesser is the force of attraction between the nucleus and outer most valence shell electron and lesser the amount of energy will be required to remove the outer most valence shell electron. So lesser will be the ionization energy of the atoms or its ion. Thus, the magnitude of ionization energy of an atom or ion is inversely proportional to its size. Thus, the size of atom or ion is $M_{(g)} > M^+_{(g)} > M^{+2}_{(g)}$, so $IE_1 < IE_2 < IE_3$.

e.g. Li → r = 1.23 Å, IE = 520.3 KJ/mole

Li^+ → r =0.68 Å, IE = 7298.1 KJ/mole

(3) Principal quantum number (n): The principal quantum number determines the distance of electron from nucleus. As the value of principal quantum number increases the distance of an electron from nucleus increases and hence attraction of nucleus to outermost valence shell electron decreases, as the attraction decreases the ionization energy decreases. Thus, the large value of principal quantum number n, the lower is the ionization energy.

e.g. for Mg-atom ($1s^2\ 2s^2\ 2p^6\ 3s^2$) the value of IE_3 is much greater than that of IE_1 and IE_2. (IE_1= 737.7, IE_2 =1450.7, IE_3 =7732.8 KJ/mole). Here, IE_1 and IE_2 are due to removal of electron from 2p-orbital, where n=2.Therefore, with the decrease in the value of principal quantum number, the value of I.E. increases.

IE_3 value for Be-atom ($1s^2\ 2s^2$) is much greater than IE_3 value of B-atom ($1s^2\ 2s^2\ 2p^1$). (IE_3 for Be =14848.7 KJ/mole, IE_3 for B-atom =3659.8 KJ/mole) IE_3 for Be-atom is the energy required to remove an electron from 1s-orbital which has a lower value of n (=1) while IE_3 for B-atom is the energy required to remove an electron from 2s orbital which has a higher value of n (=2). With the increase of the value of n of the orbital from which the electron is to be removed, the value of IE_3 decreases. Thus, IE_3 for B-atom is much lower than IE_3 for Be-atom.

(4) Shielding effect or screening effect: The valence shell electrons in a multi electron atom is attracted by nucleus and repelled by the electron of inner shells. The combine effect of this attractive and repulsive force acting on the valence shell electron is that valence shell electron suffers less attraction from nucleus. This is known as screening effect or shielding effect. Due to shielding effect produced by inner shell electron, the force of attraction, between nucleus and outer most valence shell electron decreases and hence I.E. decreases. Thus, with increase of shielding effect the magnitude of I.E. decreases.

(5) Energy of the orbital from which the electron is to be removed: The relative order of energy of s, p, d and f orbital of a given nth shell is as ns < np < nd < nf. This order shows that the electron residing in these orbital's can be removed will be as ns < np < nd < nf. This order clearly indicates that to remove an electron from f-orbital of a given shell will be the easiest while to remove the same from s-orbital belonging to the same shell will be the most difficult. i.e. the amount of energy required to remove an electron from f-orbital is minimum while that required to remove an electron from s-orbital is maximum. Thus the I.E. of an electron in s, p, d and f-orbital are in the order: ns > np > nd > nf.

(6) Half- filled and completely filled orbital: According to Hund's rules, atoms with Half-filled or completely filled shells are more stable and hence more energy is needed to remove an electron from such orbital. This means that I.E. of an atom having half-filled or completely filled orbital is higher than expected. The three elements of group VA (N, P and As) having greater I.E. than VIA group (O, S and Se) lying in the same group.

N (Z=7) :$1s^2\ 2s^2\ 2p^3$ Half-filled shell, IE= 1402.3 KJ/mole
Ne (Z=10) : $1s^2\ 2s^2\ 2p^6$ completely filled shell, IE =2080.3 KJ/mole

Variation of IE values in main group elements:

(a) Variation in a period: On going from left to right, in a period of main group elements of the periodic table, the nuclear charge increases by +1 at each next element. The increase in nuclear charge increases the electrostatic force of attraction between the Nucleus and the valence shell electron and hence the magnitude of IE increases. Thus, ongoing from left to right the IE values increases with the successive increase in the magnitude of nuclear charge. Consequently, if we consider the IE values of the elements of 2nd period, the completely filled 2s orbital in Be-atom (Be=$2s^2$) is more stable than $2s^2\ 2p^1$ configuration of the next element. B-atom (B=$2s^1\ 2p^1$) and half-filled 2p orbital of N-atom (N=$2s^2\ 2p^3$) are more stable than $2s^2\ 2p^4$ configuration of next element O-atom (O=$2s^2\ 2p^4$), both these elements (i.e. Be and N) have greater IE values than B and O-atoms respectively. Thus, the actual order of IE values of the elements of 2nd period becomes Li < B < Be < C < O < N < F < Ne. Similarly, the actual order of IE values of the elements of 3rdperiod is: Na < Al < Mg < Si < S < P < Cl < Ar. It may be seen that in each period, alkali metals have the lowest IE values while the noble gases have the highest IE values. The highest values for noble gases can be explained on the basis of the fact that greater amount of energy is required to remove an electron from the highly stable8-electron configuration ($ns^2\ np^6$).

(b) Variation in a group: On descending a group IE values of the elements go on decreasing. The following two explanation have been suggested:

(i) On proceeding down the group, the size of the atoms and nuclear charge, both increase simultaneously. The increase in size of the atoms tends to decrease the magnitude of ionization energies, while the increase in nuclear charge tends to increase the magnitude of ionization energies. Thus, the increase in the size of atoms dominates the increase in the nuclear charge and hence IE values of the elements gradually go on decreasing down the group.

(ii) As we move down a group, the number of inner-shell electrons (i.e. intervening electrons) increases and hence the magnitude of shielding effect caused by these electrons on the valence shell electron increases. With the increase of the magnitude of shielding effect, the ionization energy decreases.

Variation of ionization energy of the elements of the elements of different groups :

The variation of ionization energy of the elements of main group elements, belonging to IA to VIIA groups and noble gases is discussed below:

Group IA elements (Alkali metals): Atoms of these elements have largest radii in their respective periods and have the lowest value of ionization energy. Ongoing down, the group from Li to Cs the ionization energy decreases.

Due to lowest ionization energy of alkali metals, these metals can easily lose their ns^1 electron and can thus form M^+ ions quite easily. Since M^+ ion has stable noble gas configuration viz. ns^2(for Li^+) or ns^2 np^6 (for Na^+, K^+, Rb^+, Cs^+) in the valence shell, the energy required to pull out an electron from M^+ ion to converted this ion into M^{2+} ion is very high and hence ordinary M^+ ion is not convert in to M^{+2} ion. Consequently, the chemistry of alkali metals is the chemistry of M^+ ions and these metals from ionic compounds which contain alkali metals as M^+ ions.

Group IIA elements (alkaline earth metals):

The first and second ionization energy values decrease on going from Be to Ra.

Elements:	Be	Mg	Ca	Sr	Ba	Ra
1st I.E.(KJ/mole)	899.5	737.7	589.8	549.5	502.9	509.0
2nd I.E.(KJ/mole)	1757.1	1450.7	1146.0	1064.0	965.0	979.0

The ionization energies of alkaline earth metals are low. They should lose one electron from ns orbital easily and hence form M^+ ions. However, these metals prefer to form M^{+2} ions and not M^+ ions. This abnormal behavior of the metals can be explained by studying the energy change involved in the conversion of $CaCl_{(s)}$ to $CaCl_{2(s)}$.

$$2\,CaCl_{(s)} \rightarrow CaCl_{2(s)} + Ca_{(s)}$$

In this conversion heat equal to (-160+ S) $KJmol^{-1}$ is released. Here, S=heat of sublimation of calcium. Since the energy is a negative quantity, the conversion of $CaCl_{(s)}$ to $CaCl_{2(s)}$ is spontaneous. i.e. Ca prefer to form Ca^{+2} ion and not ca^{+} ion. The greater stability of $CaCl_2$ over CaCl is also confirmed by the fact that the lattice energy of $CaCl_2$ (=2200 $KJmol^{-1}$) is greater than that of CaCl (=720 $KJmol^{-1}$). The metal of these group never forms M^{3+}cations, since the value of 3rd ionization potential is very high as third electron has to be removed from a highly stable ns^2 or ns^2 np^6 configuration of M^{2+}cation.

Since the 2nd ionization energy of Be-atom is the highest (=1757.1 $KJmol^{-1}$), it does not lose the two electrons from ns orbital readily to form Be^{+2} ion, Accordingly, Be does not form ionic compounds readily. Rather, its compounds with O_2 , Cl_2 , N_2 , S etc. are more covalent in nature than the corresponding compounds of Mg, Ca, Sr and Ba .

Elements of group IIIA:

IE values of the elements of Group IIIA are as B =880.6, Al=577.6, Ga=578.8, In= 558.3 and Tl=589.3 KJ/mole. The IE of B is highest in the group , since its atomic radius is the smallest (B=0.85 Å, Al=1.43 Å, Ga=1.35 Å, In = 1.67 Å ,Tl=1.70 Å) and the shielding of the nuclear charge by the intervening $1s^2$ electrons is the lowest (B=$1s^2$ $2s^2$ $2p^1$).The sharp decrease from B to Al is due to an appreciable increase in atomic radius and effective shielding of the nuclear charge by the intervening $2s^2$ and $2p^2$ electrons (A1 = 2,$2s^2p^6$,$3s^2p^1$). In case of Ga, there are ten 3d electrons in its inner shell viz. 3rd shell (Ga = 2,8,$3s^2p^6d^{10}$,$4s^2p^1$). Since d-electrons shield the nuclear charge less effectively than the s- and p-electrons, the outer electron i.e. ($4p^1$ electron) in Ga is held fairly strongly by the nucleus. Consequently, the IE value of Ga remains almost the same as that of Al. In case of In, since the number of d-electron viz., 4d electrons (In = 2,8,18,$4s^2p^6d^{10}$,$5s^2p^1$) is the same as in 3d orbitals of Ga, their screening effect also remains same. However, since the size increases as we move from Ga to In, the IE value decreases from Ga to In. The last element viz. Tl has fourteen 4f-electrons (Tl = 2,8,18,$4s^2p^6d^{10}f^{14}$,$5s^2p^6d^{10}$,$6s^2p^1$). Since the shielding effect of f-electrons is much smaller than that of d-electrons, and also since there is only a slight increase in atomic size from In to Tl, the outer electrons in Tl are held quite firmly and hence the value of IE shows a marginal increase, when we go from In to Tl.

Although the nuclear charge of elements is larger and their size is smaller than that of the elements of group II-A, the first ionization energies of these elements are lower than those of the elements of Group II-A. This is due to the fact that the p-electrons (Group III-A) are less penetrating and more shielded than s-electrons (Group II-A), i.e. p-electrons, are at a greater distance from the nucleus of the s-electrons and held less tightly with the nucleus, they can be removed more easily than the s-electrons.

In this group, the IE_1, IE_2 and $IE_3$is very high for Boron. Hence, boron is notable to exist as B^{+3}ionin its compounds. This is because of its extremely small size and because of the fact that its valance electrons are not effectively shielded from the nuclear charge by the intervening electrons.

Due to smaller value of IE_3 for Al, Ga and In, 2723, 2942 and 2682 KJ/mole respectively, these elements have relatively higher tendency to give M^{+3} ions under suitable conditions. Thus Al, Ga and in prefer to form ionic compounds in which these elements are present as Al^{+3}, Ga^{+3} and In^{+3}respectively.

Elements of group IV-A: In this group the values of IE of C, Si, Ge and Sn shows regular decrease from C to Sn, but the value of IE for Pb shows a marginal increase. This marginal increase is because of following two factors:

(i) Fourteen 4f-electrons present in the inner configuration of Pb (Pb= 2,8,18,$4s^2p^6d^{10}f^{14}$,$5s^2p^6d^{10}$,$6s^2p^2$) shield the nuclear charge less effectively than the 5d-electrons.

(ii) There is only a marginal increase in the atomic radius as we move from Sn to Pb (Sn = 1.4 A^0, Pb = 1.47 A^0).

Elements of group V-A: The ionization energy values of these elements decreases as we move down the group from N to Bi (N = 1402.3 KJ/mole, P = 1011.8, As = 944.0 Sb = 831.6, Bi = 703.3).

Elements of group VI-A: In this group IE values decreases as we move down the group from O to Po (O = 1314.0, S = 999.62, Se = 940.9, Te = 869.3, Po = 812.0 KJ/mole).

Elements of group VII-A (Halogens): The atoms of these elements have smallest radii in their respective periods. Therefore, these elements have the largest values of their ionization energy.

Noble gases: The ionization energy of noble gases is very high. These values are higher than even those of halogens. Their high values are due to the presence of stable ns^2np^6 configuration in their valence shell. These values decrease with the increase in Vander walls radii of the atoms of these elements when we move down the group from, He to Rn.

Ionization energies of iso-electronic species:

We know that:

(i) The size (r) of iso-electronic species decrease with increase of their atomic number (Z). i.e. $r \propto 1/Z$ or $Z \propto 1/r$.

(ii) The magnitude of ionization energy (IE) of an atom decreases with the increase of its size (r), i.e. $IE \propto 1/r$.

On combining these two relations, we can write $IE \propto Z$. i.e. the ionization energies of isoelectronic species increase with the increase of an atomic number. For example, the IE of iso-electronic species viz. Ca^{+2} (Z = 20), Cl^- (Z = 17), K^+ (Z = 19) and S^{2-} (Z = 16) are in the order: $S^{2-} < Cl^- < K^+ < Ca^{2+}$. All these species contain 18 electrons.

To find out the order of the second IE values of the elements of 2nd period:

The successive increase in the magnitude of the nuclear charge from Li to Ne increases the second or first IE values of the elements of 2nd period. The order for M^+ (g) cation is i.e. $Li^+ < Be^+ < B^+ < C^+ < N^+ < O^+ < F^+ < Ne^+$.

The experimental values for $M^+ (g) \rightarrow M^{2+}(g)$, process in KJ/mole is Li = 7298.1, Be^+ = 1757.1, B^+ = 2427.0, C^+ = 2352.6, N^+ = 2856.1, O^+ = 3388.2, F^+ = 3374.2 and Ne^+ = 3952.3. However, suggest that the actual order is $Be^+ < C^+ < B^+ < N^+ < F^+ < O^+ < Ne^+ < Li^+$.

This can be explained by considering the valance-shell configurations of M^+ cations given as: Li^+, $1s^2$, $Be^+ = 2s^1$, $B = 2s^2$, $C = 2s^2 2p^1$, $N^+ = 2s^2 2p^2$, O^+ = 2s22p3, $F^+ = 2s^2 2p^4$ and $Ne^+ = 2s^2 2p^5$.

Since the value of principal quantum number for the 1st orbital in Li^+ ion is minimum (=1) maximum amount of energy is required to remove an electron from this ion. i.e. IE value for Li^+ ion is the highest. Due to the extra stability associated with the completely filled 2s-orbital in B^+ ion ($2s^2$) and half-filled 2p orbital in O^+ ion ($2s^2 2p^3$), these two ions have higher IE values than the next ions, namely C^+ ($2s^2 2p^1$) and F^+ ($2s^2 2p^4$) ions respectively. Thus, order of IE values is well explained.

Difference between ionization potential and electrode potential of a metal:

Main Difference between these two properties of the metal is that ionization potential is concerned with the formation of a gaseous metal ion from the metal atom in the solid state.

$$M_{(s)} - e^- \rightarrow M^+_{(g)}$$

On the other hand, the electrode potential is concerned with the formation of a hydrated metal ion from the metal atom in the solid state.

Electron Affinity (EA):

Definition: Electron affinity is defined as the amount of energy released when an extra electron is added to isolated gaseous atom or ion in its lowest energy state to produce an anion is called its ***electron affinity*** (EA).

$$X^o_{(g)} + e^- \rightarrow X^-_{(g)}, \qquad \Delta H = \text{Energy released}$$

$$= \text{EA of X-atom}$$

(Exothermic process)

The addition of an electron to an atom is exothermic process. Since, EA is energy involved in adding an electron to an atom, it is also called enthalpy of electron attachment. ***Again since, energy is released, it should be represented with negative (-) sign, but unfortunately it is represented with positive (+) sign.***

The addition of first electron is called first electron affinity, EA_1. It represents energy released. So, it is called exothermic electron affinity. Just as I.E. is measure of the tendency of an atom to change into an anion. Greater is the amount of energy released; greater is the electron affinity of an atom. e.g. consider the electron affinity of Cl-atom it is 348.8 KJ/mole in the gaseous state it is defined as,

$Cl_{(g)} + e^- \rightarrow Cl^-_{(g)}$, ΔH =Electron affinity of $Cl_{(g)}$
= Energy released
= +348.8 KJ/mole

Relation between EA of $X_{(g)}$ atom and IE of $X^-_{(g)}$ ion:

EA of $X^-_{(g)}$ - atom is defined by the exothermic process,

$X^0_{(g)} + e^- \rightarrow X^-_{(g)}$, ΔH = energy released = EA of $X_{(g)}$ atom

While IE of $X^-_{(g)}$ ion is defined by the endothermic process,

$X^-_{(g)} \rightarrow X_{(g)} + e^-$, ΔH = energy required = IE of $X^-_{(g)}$, ion.

These two equations show that:

-EA of $X_{(g)}$ atom = IE of $X^-_{(g)}$ ion

Since these reactions are opposite to each other the magnitude of EA of $X_{(g)}$ and IE of $X^-_{(g)}$ ion are same, but have opposite signs, because in one energy is released while in another energy is required.

Second electron affinity: EA_2

Second electron affinity, EA_2 of a gaseous element $M_{(g)}$ is the amount of energy required to add an electron to the uninegative gaseous ion of that element, ($M^+_{(g)}$ ion). Thus:

$M_{(g)} + e^- \rightarrow M^-_{(g)}$, ΔH = energy released = $+EA_1$

$M^-_{(g)} + e^- \rightarrow M^{2-}_{(g)}$, ΔH = energy required = $-EA_2$

Since EA_1 (energy released) is shown with +ve sign, EA_2 (energy required) is shown with a –ve sign. Thus, EA_1 is exothermic process, while EA_2 is endothermic process.

EA_2 represents energy required. Why?

When an electron is added to an $M^-_{(g)}$ energy is required, since electron being added against the electrostatic force of repulsion, existing between –ve charge on $M^-_{(g)}$ ion. Thus, in the process of adding one electron to $M^-_{(g)}$ ion, energy is required and not released, as in case of adding one mole electron in $M_{(g)}$ atom. So EA_2 is endothermic process.

Example: Calculate the magnitude of energy involved in the conversion of (a) $O_{(g)}$ atom to $O^{2-}{}_{(g)}$ ion (b) $S_{(g)}$ atom to $S^{2-}{}_{(g)}$ ion. Predict whether the given conversion is an endothermic process.

Solution: (a): The conversion of $O_{(g)}$ atom to $O^{2-}{}_{(g)}$ ion can be shown as:

$$O_{(g)} + 2e^- \rightarrow O^{2-}{}_{(g)}$$

The above reaction actually takes place through the following two steps:

$$O_{(g)} + e^- \rightarrow O^-{}_{(g)}, \quad EA_1 = +141.1 \text{ KJ/mole}$$

$$\underline{O^-{}_{(g)} + e^- \rightarrow O^{2-}{}_{(g)}, \quad EA_2 = -844.0 \text{ KJ/mol}}$$

$$O_{(g)} + 2e^- \rightarrow O^{2-}{}_{(g)}, \Delta H = EA_1 + EA_2 = (+141.1-844.0)\text{KJ/mole}$$

$$=-702.9 \text{ KJ/mole}$$

Since ΔH has –ve sign, the conversion of $O_{(g)}$ to $O^{2-}{}_{(g)}$ requires energy equal to702.9 KJ/mole. It is endothermic process.

(b) The conversion of $S_{(g)}$ atom to $S^{-2}{}_{(g)}$ ion can be shown as

$$S_{(g)} + 2e- \rightarrow S^{2-}{}_{(g)}$$

The above reaction actually takes place in two steps:

$$S_{(g)} + e- \rightarrow S^-{}_{(g)}, EA_1 = +200.43 \text{ KJ/mole}$$

$$S^-{}_{(g)} + e- \rightarrow S^{2-}{}_{(g)}, EA2 = -338.00 \text{ KJ/mole}$$

$$S_{(g)} + 2e- \rightarrow S^{2-}{}_{(g)}, \quad \Delta H = + EA_1+(- EA_2) = (+200.43-338.0)\text{KJ/mole}$$

$$= -132.57 \text{ KJ/mole}$$

So, this conversion also requires energy. Therefore, it is endothermic process.

Example: The amount of energy released when one million of atoms of iodine in vapor state are converted to iodine ion, $I^-{}_{(g)}$ is 4.9×10^{-13} J, according to the reaction

$$I_{(g)} + e- \rightarrow I^-{}_{(g)}$$

Express the electron affinity of iodine in terms of KJ/mole and eV/atom. ($Z = 6.02 \times10^{23}$ gm/mole)

Solution: EA of iodine is the amount of energy released when one mole or 6.02×10^{23} atoms of iodine in the gaseous state are converted into $I^-{}_{(g)}$ ions. Thus:

Amount of energy released when 1 million or 10^6 atoms of iodine are converted into $I^-{}_{(g)} = 4.9\times 10^{-13}$J

Amount of energy released, when one mole of iodine or 6.02×10^{23} atoms are converted to $I^-{}_{(g)}$ ions.

10^6 atoms of iodine required = 4.9×10^{-13}J

6.02×10^{23} atoms required =?

$$\frac{6.02 \times10^{23}\times4.9\times 10^{-13}}{10^6} = 29.5\times10^4 \text{ J} = 295 \text{ KJ/mole}$$

Now since 96.3 KJ/mole =1eV/atom

295 KJ/mole=?

1X295/96.3 = 3.06 eV/atom

Example: The electron affinity of chlorine is 349 KJ/mole. How much energy in KJ is released when 1 gm of chlorine is converted completely into $Cl^{-}_{(g)}$ ions?

Solution: Electron affinity of chlorine is the amount of energy released when 1 mole or 35.5 gm of chlorine in the gaseous state are converted into $Cl^{-}_{(g)}$ ions.

Thus:

Amount of energy released when 35.5 gm of chlorine are converted into $Cl^{-}_{(g)}$ = 349 KJ/mole.

Amount of energy released when 1 gm of chlorine is converted into $Cl^{-}_{(g)}$ ions =349/35.5 KJ/mole=9.83 KJ/mole

Important note: when two atoms of an elements, in the gaseous state ($2X_{(g)}$), gain two electrons, to from two monovalent anions ($2X_{(g)}$), the energy released in this process is equal to the double of the electron affinity energy of that element. For example, in the process,

$$2\,Cl_{(g)} + 2e^{-} \rightarrow 2\,Cl^{-}_{(g)}$$

Energy released = -2× EA of Cl-atom

= -2× 349 KJ/mole = -698 KJ/mole

Here, (-) sign indicates the release of energy in the above process.

Factors affecting the magnitude of electron affinity:

The factors affecting the magnitude of electron affinity are discussed below:

(1) **Size of the atom**: In case of smaller atoms, the attraction of the nucleus for the electron to be added is stronger. Thus, smaller is the size of atom, greater is electron affinity.

(2) **Nuclear charge**: Greater is the magnitude of nuclear charge of elements (along a period) stronger is the attraction of its nucleus for the electron to be added. Thus, with the increase in the magnitude of nuclear charge, electron affinity also increases.

(3) **Electronic configuration of the atom**: The elements of group IIA and IIB either do not accept the electron being added to them or have a very little tendency to accept electron. So, they show zero EA values even if they accept the electron, they do not liberate energy; rather they absorb some energy in the process of adding the electron to them. i.e. they have negative (endothermic) values of EA.

EA values of N and P atoms are very low. This is because of the presence of half-filled np orbital's in their valence shell ($N=2s^2\ 2p^2$, $P=3s^2\ 3p^3$), these half-filled orbitals, being very stable, have very little tendency to accept any extra electron to be added to them. Thus, EA values of N and P are very small.

Noble gases have stable $ns^2\ np^6$ configuration (except Helium, $He=1s^2$ configuration) and hence the atom of these gases, either don't accept any extra electron or have a little tendency to accept the electron. Thus, these elements have nearly zero or slightly negative EA values.

Variation of electron affinity in main group elements of the periodic table:

(a) **Variation in a period**: On moving from alkali metals to halogens in a period, the size of the atoms decrease and the nuclear charge increase both these factors increase the force of attraction between the nucleus and the electron being added and hence the atom has a greater tendency to attract the electron toward itself. Thus, the electron affinity values go on increase when we move from alkali metals to halogens.

(b) **Variation in a group:** On moving down a group, both the size of the atom and the nuclear charge increase. The increase in atomic size tends to decrease the EA values, while the increase in nuclear charge tends to increase the EA values. The net result is that the effect produced by outweighs the effect produced by the progressive increase in nuclear charge and thus the EA goes on decrease as +Ve move from top to bottom in a group.

The electron affinity of O and F are less than those of S and Cl respectively. Due to small size of O and F atoms, as compared to the size of S and Cl atoms respectively, the addition of an extra electron to O and F atom produce high electron density round them. The high electron density produced screens the nucleus and hence nuclear charge is decreased. i.e. the repulsion between the electrons already present in the relatively compact 2p-orbitals of the valence-shell of these atoms [4 in O-atom (O= $2s^2$ $2p^4$) and S in F-atom (F=$2s^2$ $2p^5$)] and the extra electron being added to these atoms to get O^- and F^- ions increase. Due to the strong electron – electron repulsion, O and F atoms show lesser tendency to attract an electron towards them to from O^- and F^- ions respectively and hence the electron affinity values of these elements become less than those of S and Cl atoms respectively.

Variation of electron affinity values of elements of different group:

The variation of EA values of elements of groups IA, IIA, IIB, IIIA, IVA, VIIA and noble is discussed below:

Elements of group IA (alkali metals): Since the atomic radii of the atoms of alkali metals increase as we more down the group, the EA values of these elements decrease in same direction.

Elements of group IIA and IIB: The atom of the elements of both these group, either do not accept the electron being added to them or have a very little tendency to accept the electron. When they do not accept the electron, they show zero EA value.

Element of IIIA and IVA: EA value the element these groups do not show the expected decreasing trend, as we more down the group.

Element of group VA: EA values of these elements do not show a regular trend. EA value of N and P are very law. This is because of the presence of half-filled orbital in their valence-shell.

Element of group VIA: EA values decreases gradually down the group from S to Po. EA value of O- atom is lower than that of S- atom although it is expected to be higher. This because of small size of O–atom compared to S-atom and decrease in nuclear charge is due to addition of extra electron to O-atom as electron density increases.

Element of group VIIA: Since the atomic radii of the atom of halogens are the smallest in each period, the element has maximum tendency to give an electron to form X^-_g ion. Thus, halogens have highest EA values. EA values of F are lower than that of Cl. This is because small size of F compared to Cl and high electron density due to addition of extra electron and decrease in nuclear charge

Noble gases: Noble gases have stable ns^2np^6 configuration. Therefore, they have either close to zero or slightly negative EA values.

Electronegativity:

Different definitions and methods for its calculation are given below:

(i) Pauling's approach (1932):

Definition: Electronegativity of an atom of an element in a molecule is its relative tendency to attract the shared electron pair towards itself. The electronegativity of atom is represented by χ.

Pauling calculated the value of electronegativity of the element by the method in which, he considered the AB covalent molecule formed from A_2 and B_2 covalent molecules, Thus,

$$½A_2 + ½B_2 \rightarrow AB \text{ ---- ----- ------ (I)}$$

It is also represented as A-B, A-A and B-B bonds. The bond dissociation energy of A-B bond, $E_{A\text{-}B}$ is always greater than geometrical means of $E_{A\text{-}A}$ and $E_{B\text{-}B}$

$$\text{So, } E_{A\text{-}B} > (E_{A\text{-}A} \times E_{B\text{-}B})^{½}$$

The difference between $E_{A\text{-}B}$ and $(E_{A\text{-}A} \times E_{B\text{-}B})^{½}$ is called *ionic resonance energy* of A-B bond and it's shown as $\Delta_{A\text{-}B.}$

$$\Delta_{A\text{-}B} = E_{A\text{-}B} - (E_{A\text{-}A} \times E_{B\text{-}B})^{½} \text{ ---- ----- ----- (ii)}$$

Or

$$(\Delta_{A\text{-}B}) = [E_{A\text{-}B} - (E_{A\text{-}A} \times E_{B\text{-}B})^{½}]^{½} \text{ ---- ----- ---- (iii)}$$

Pauling further suggested that the square root of $\Delta_{B\text{-}B}$ is the measure of ionic character of A-B covalent bond, with increase of $(\Delta_{A\text{-}B})^{½}$, the amount of ionic character increases.

$$\therefore (\Delta_{A\text{-}B})^{½} \alpha \text{ Amount of ionic character in A-B bond ---- ---- ---- (iV)}$$

Now difference in electronegativity value of A and B atoms (i.e. χ_A-X_B, if $\chi_A > \chi_{B,}$) also increases the ionic character of A-B bond

$$\therefore (\chi_A\text{-}\chi_B) \alpha \text{ Amount of ionic character in A-B bond --- --- --- ---- (v)}$$

By comparing equation (iV) and (v), we get

$$(\chi_A\text{-}\chi_B) \alpha (\Delta_{A\text{-}B})^{½}$$

$$\therefore (\chi_A\text{-}\chi_B) = K (\Delta_{A\text{-}B})^{½} \text{.......... .... (vi)}$$

Where K is constant

Now substituting the value of $(\Delta_{A\text{-}B})^{½}$ from equation (iii), equation (vi) becomes:

$$\therefore (\chi_A\text{-}\chi_B) = K\ [E_{A\text{-}B}\text{-}(EA_{\text{-}A}\times E_{B\text{-}B})^{½}]^{½}$$

If bond dissociation energies are expressed in Kcal, the value of K =0.182 is found.

$$\therefore (\chi_A\text{-}\chi_B) = 0.182\ [E_{A\text{-}B}\text{-}(EA_{\text{-}A}\times E_{B\text{-}B})^{½}]^{½} \text{ ---- ---- ---- (Vii)}$$

This equation (Vii) is called Pauling's equation. Pauling assumed the Electronegativity of H-atom to be equal to 2.1 taking as standard and calculated the value of Electronegativity for other elements.

Example: Calculate the Electronegativity of carbon atom from the data given as $E_{H\text{-}H}$=104.2Kcal/mole, $E_{C\text{-}C}$= 83.1 Kcal/mole, $E_{C\text{-}H}$= 98.8 Kcal/mole and χ_H=2.1

Solution: We have equation:

$$(\chi_A\text{-}\chi_B) = 0.182\ [E_{A\text{-}B}\text{-}(EA_{\text{-}A}\times E_{B\text{-}B})^{½}]^{½}$$

$$(\chi_C\text{-}\chi_H) = 0.182\ [E_{C\text{-}H}\text{-}(EC_{\text{-}C}\times E_{H\text{-}H})^{½}]^{½}$$

$$\chi_C\text{-}2.1 = 0.182[98.8 - (83.1 \times 104.2)^{½}]^{½}$$

$$=0.182(98.8\text{-}93.05)^{½}$$

$$=0.43$$

$$\chi_C = 2.53$$

(2) Allred and Rochow's scale (1958): Allred and Rochow's suggested that Electronegativity of an element, A can be calculated with the help of the following equation:

$$(\chi_A)_{AR} = 0.359\times Z_{eff}/r^2 + 0.744$$

Where $(\chi_A)_{AR}$ = Electronegativity of atom A on Allred and Rochow's scale
Z_{eff} = effective nuclear charge on periphery
Z_{eff} = Z-σ, where Z = Atomic number
σ= Screening or shielding constant
Effective nuclear charge can be calculated by using Slater's rules. They are given below

(i) Write the electron configuration of the atom /ion and arranged the following groupings.
(1s) (2s2p) (3s3p) (3d) (4s4p) (4d) (4f) -----------------------

(2) The contribution for σ of ns np electrons,

(a) 0.35 For each electron in ns np grouping (except H-atom, it is 0.30).

(b) 0.85 For each electron in (n-1) and penultimate shell.

(c) 1.00 For each electron in (n-2) and lower all electrons.

Example: Calculate the electron affinity of Lead following Allred- Rochow procedure. Use the following data: Covalent radius of Lead = 1.53 Å and atomic number of Lead = 82.

Solution: We know that the electronic configuration of Pb (Z=82) is:

$$\underset{(60)}{\underline{1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14}}},\ \underset{(18)}{\underline{5s^2 5p^6 5d^{10}}},\ \underset{(4)}{\underline{6s^2 6p^2}}$$

According to Slater's rule:

σ for all the electrons present in the electronic configuration of

Pb-atom = (4X0.35) + (18X0.85) + (60X1.0)

= 76.70

Z_{eff} at the periphery of Pb-atom = Z- σ

= 82-76.70

= 5.30

$\chi_{Pb} = 0.359 \text{X} 5.30/ (1.53)^2 + 0.744$

$\chi_{Pb} = 1.55$

(i) Mulliken's Approach: According to Mulliken, the average of ionization energy and EA of an atom is the measure of electronegativity. He proposed that the Electronegativity of an atom can be calculated with the following equation:

$$\chi_A = 0.374\ [(IE)_A + (EA)_A/2] + 0.17$$

Or

$$\chi_A = 0.187\ [(IE)_A + (EA)_A] + 0.17$$

Where χ_A = electronegativity of atom A

$(IE)_A$ = Ionization energy of atom A

$(EA)_A$ = Electron affinity of atom A

This equation is used when IE and EA values are given in electron volt (eV).

Example: Calculate the electronegativity of fluorine atom, given that ionization energy of F-atom = 17.41 eV and electron affinity of F-atom = 3.45 eV.

Solution: According to Mulliken's method, equation for electronegativity is,

$\chi_A = 0.187\ [(IE)_A + (EA)_A] + 0.17$

$\chi_F = 0.187\ [(IE)_F + (EA)_F] + 0.17$

$\chi_F = 0.187\ [17.41+ 3.45] + 0.17$

$\chi_F = 4.07$

Example: Calculate the electronegativity of Cl- atom. Given that ionization energy of Cl-atom = 13.0 eV and electron affinity of Cl-atom = 4.0 eV.

Solution: By using Mullikan's method,

$$\chi_{Cl} = 0.187\,[(IE)_{Cl} + (EA)_{Cl}] + 0.17$$
$$= 0.187\,[13.0 + 4.0] + 0.17$$
$$= 3.35$$

Factors affecting the magnitude of electronegativity:

The factors affecting the magnitude of electronegativity are discussed below:

(1) **Size of the atom**: Smaller atom has greater tendency to attract two shared electron pair toward it and hence has greater electronegativity than a smaller atom.

(2) **Oxidation state of the element**: If an atom shows many positive oxidations states the size of the atom decreases with the increase in its oxidation state. Thus, the size of Fe, Fe^{+2} and Fe^{+3} is in the order: $Fe > Fe^{+2} > Fe^{+3}$. Now, if smaller is the size of an atom or ion greater is its electronegativity. Thus, the electronegativity of an element which shows many oxidation states is directly proportional to the magnitude of its positive oxidation state. Thus, the electronegativity of the Fe, Fe^{+2} and Fe^{+3} is in increasing order: Fe (= 1.80) < Fe^{+2}(= 1.83) <Fe^{+3}(= 1.96).

(3) **Effective nuclear charge of the element**: The electronegativity of an element is proportional tom the magnitude of effective nuclear charge at the periphery of the atom of that element. Thus, with increase in magnitude of effective nuclear charge of an element, the electronegativity of that element also increases.

(4) **Electropositive character of elements**: The elements which are highly electropositive have low values of electronegativity and the elements which have very weak electropositive character have very high values of electronegativity.

(5) **Ionization energy and electro affinity**: The average of ionization energy and electro affinity of an atom is the measure of its electronegativity. Thus, higher is the value of IE and EA of an atom; higher is the electronegativity of that atom.

If an atom has high IE then it is very difficult to remove most loosely bonded electron from that atom and it shows high EA. Thus, the atoms of the elements which have higher value of ionization energy (IE) and electron affinity (EA) also have higher values of electronegativity.

(6) **Type of hybridization undergone by the central atom**: The electronegativity of an atom having hybrid orbital with greater S-character would be high. E.g. the electronegativity of C-atom in methane (CH_4), Ethylene (C_2H_4) and acetylene (C_2H_2) varies with the change of the type of hybridization undergone by in this molecule. In these molecules C-atom is sp^3, sp^2 and sp-hybridized respectively. The S-character in sp, sp^2 and sp^3 hybrid orbital is 25%, 33% and 50% respectively. With increase in the percentage of S-character in hybrid orbital electronegativity of C-atom also increases. Thus, of C-atom in CH_4, C_2H_4 and C_2H_2 is in the increasing order as $CH_4 < C_2H_4 < C_2H_2$. With increase in the electronegativity of C-atom, the electron pair-accepting power of C-atom in these molecules also increases in the same direction. So acidic character of this molecule is in the order: $CH_4 < C_2H_4 < C_2H_2$.

In case of aniline (C_6H_5-NH_2), Pyridine (C_5H_5N) and R-C-N: molecules, N-atom in these molecules are SP^3, SP^2 and SP hybridized.

$C_6H_5NH_2$	C_5H_5N	R-C≡N:	
sp^3	sp^2	sp →	hybridization
25%	33%	50% →	S-character

With increase in S-character, the acidic character of above molecule increases. Therefore, we can say that with increase in S-character, the basic character of the molecules decreases. Thus, the basic character of molecules is in the order:$C_6H_5NH_2$ > C_5H_5N >R-C=N:

Variation of electronegativity in a group of s- and p- block elements:

The electronegativity values of an elements decrease as move down a group in s- and p- block elements. It can be explained by following facts:

(i) Smaller atoms have greater electronegativity because they have greater tendency to attract the shared electron pair towards itself. Thus, with increase in size of the atom down the group, the electronegativity of the elements decreases.

(ii) The number of electrons residing in the inner shells also increases. These elements screen the last electron. With the increase in the number of inner electrons the magnitude of screening constant (σ) increases and hence the magnitude of Z_{eff} decreases. (Z_{eff} = Z actual - σ). The decrease in the magnitude of Z_{eff} also decreases the electronegativity values.

(iii) In going down a group the electropositive character of the elements increases. This results in a decrease in the electronegativity values.

(iv) Ionization energy and electron affinity both decrease as the group is descended. With the decrease of these quantities, the electronegativity values also decrease.

Variation of electronegativity of the elements of different groups:

The variation of the electronegativity among the elements of groups belonging to main group elements is discussed below:

Group IA (Alkali Metals): Alkali metals have the lowest tendency to attract the electrons towards them because they have highest atomic size and lowest electronegativity in their respective periods. Cesium has the lowest electronegativity of all the elements in the periodic table. It is due to the lowest electronegativity values for alkali metals that when these elements combine with the elements having high electronegativity, ionic compounds are obtained.

Group II A: The element of group II A has low electronegativity. In going down a group, electronegativity value decreases.

Group III A: Due to smaller atomic size, the element of this group is more electronegative as compared to those of group II A element.

Group IV A: Electronegativity value of the elements of this group show irregular trends. There electronegative decreases from C to Si, increases from Si to Ge, again decrease from Ge to Sn and finally increases from Sn to Pb.

Group V A and VI A: On moving down the group. The electronegativity values of the elements of both the groups decreases gradually. This is because of the increases in atomic size of the elements which leads to the lesser attraction of the nucleus for the electrons. The gradual decrease in electronegativity value down the group indicates gradual change from non- metallic to metallic character of the element.

Group VII A (Halogens): The halogens have the maximum tendency to attract the electrons toward then because they have the least atomic size hence have maximum electronegativity in their respective periods. Fluorine has the maximum electronegativity (=4.0) of the entire element in the periodic table. It is due to the highest electronegativity value for halogens that when this element combines with the elements having low electronegative, ionic compounds are obtained. The gradual decrease down the group indicate a gradual decrease in the non-metallic character of halogens from F to I electronegativity values.

Noble gases: The valence-shell configuration of the atoms of noble gases is ns^2np^6 which is very stable and hence these atoms have no tendency to accommodate any electron consequently noble gases have been assigned zero electronegativity values.

Question: Explain why the electronegativity of Si is lower than that if Ge.

Answer: It has been observed that Ge-X bond (X= halogens atom) can easily be reduced to Ge-H by nascent hydrogen (Zn/HCl) but Si-x bon cannot be --reduced.

$$\text{Ge-X} + 2\text{H} \dashrightarrow \text{Ge–H} + \text{Hx}$$

This observation shows that Si-X bond is stronger than Ge-X bond. This means that Si – X bond is more polar than Ge-X bond. This is possible only when electronegativity difference between X and Si is more than that between X and Ge.

$[(\chi_X - \chi_{Si}) > (\chi_X - \chi_{Ge})]$ i.e. the electronegativity of Si is lower than that of Ge.

- **Variation of electronegativity in a period of s- and p- block elements:**

  In going from left to right in a period of s- and p- block elements (from alkali metals to halogens) electro negativity value increase with increase in atomic number, this can be explained on the basic of following facts:

  (i) In going from left to right in a period, effective nuclear change increase, thus, electronegativity values increase with the increase atomic number, as we more from left to right along a period.

  (ii) In going from left to right in a period, the electropositive character of the element goes on decreasing. this means that as we more from left to right in a period, the electronegativity value goes on increasing.

  (iii) In going from left to right in a period, there is decrease in the size of the atoms, thus, smaller atoms have higher electronegativity values.

  (iv) In going from left to right in a period, there is an increase of imitation energy and electron affinity of the element, thus, they have higher electronegativity.

Role of electronegativity in chemical behavior Or Applications of electronegativity:

Some important facts that can be explained on the basis of electronegativity are:

(1) Atoms of similar electronegativity form purely covalent bonds on combination. As electronegativity difference of both the atoms increases sharing becomes increasingly uneven and partial ionic character develops in the bond. Hannay and Smith gave following equation for calculating percent ionic character.

% ionic character = $[16(\chi_A-\chi_B) + 3.5 (\chi_A-\chi_B)^2]$ %

(2) The bond length and bond strength can be related to the electronegativity difference between the bonded atoms. Larger the value of $(\chi_A-\chi_B)$, more stable is bond A-B. For e.g.,

H-X (bond)	**$\chi_X-\chi_H$**	**Bond length (Å)**	**Bond energy (Kcal/mole)**
H-F	4.0 – 2.1 = 1.9	0.92	135
H-Cl	3.0 – 2.1 = 0.9	1.27	103
H-Br	2.8 -2.1 = 0.7	1.41	87.4
H-I	2.5 – 2.1 = 0.4	1.61	71.4

(3) On moving from left to right the acidic character of normal oxide of the element increases. Due to increase in electronegativity there is change from strongly basic to strongly acidic character and due to consequent decrease in χ_O - $\chi_{E.}$ Acidity of the oxide increases with increasing proportion of oxygen.

CrO basic, Cr_2O_3 amphoteric, CrO_3 acidic

(4) Chemical behavior of hydroxide of a general formula E-O-H is acidic or basic depending upon if it is the O-H bond or E-O bond which is readily broken. Since the bond length can be related to the difference in electronegativities of bonded atoms the acidic or basic nature of E-O-H will be determined by relative values of χ_O - χ_E and $\chi_O – \chi_{H.}$

If (χ_O - χ_E) > ($\chi_O – \chi_H$) the EOH is basic and if (χ_O - χ_E) < ($\chi_O – \chi_H$) it is acidic.

For example, Na-O-H $\chi_O – \chi_{Na} = 3.5 – 1.0 = 2.5$
$\chi_O – \chi_H = 3.5 – 2.1 = 1.4$
$(\chi_O – \chi_{Na}) > (\chi_O – \chi_H)$ Thus, NaOH is basic
Cl-O-H $\chi_O – \chi_{Cl} = 3.5 – 2.8 = 0.7$
$\chi_O – \chi_H = 3.5 – 2.1 = 1.4$
$(\chi_O – \chi_{Cl}) > (\chi_O – \chi_H)$ Thus, ClOH is acidic

(5) To predict the nature of bond: Non-polar covalent, polar covalent and ionic bond. With the help of electronegativity difference, (χ_A-χ_B), between two atoms A and B, we can predict whether A-B bond would be non-polar covalent bond, polar covalent bond or ionic bond.

a. When χ_A= χ_B or χ_A-χ_B is equal to zero, the bond is non-polar covalent bond. This bond exists between two identical or homonuclear diatomic molecules. i.e. H_2, O_2 etc.
b. When there is small difference between χ_A and χ_B (χ_A-χ_B), the bond is polar covalent bond. i.e. $\chi_A > \chi_B$. There is charge separation between atoms A and B, $A^{\delta-}$ - $B^{\delta+}$, i.e. $H^{\delta+}$ - $F^{\delta-}$
c. When (χ_A-χ_B) is very large, complete transfer of electron from atom B to atom A takes place. Hence bond is purely ionic. i.e. $Li^+ F^-$.

(6) To calculate the percentage of ionic character in A-B polar covalent bond in AB molecule:

Greater is the electronegativity difference between the bonded atoms, greater will be the magnitude of ionic character in polar covalent bond. Several empirical equations have been proposed to calculate the amount of ionic character in A-B bond. Here two equations are given:

(a) **Pauling equation**: According to Pauling, the amount of ionic character is given as,

$$= (1-e^{0.25(\chi_A-\chi_B)}) \%$$

With the help of this equation, Pauling gave following relation between (χ_A-χ_B) and % ionic character.

(χ_A-χ_B):	0.6	1.0	1.4	1.7	2.0	2.4	3.0	3.2
	9	22	39	51	63	76	91	92

Pauling also gave alternative empirical equation for calculating the ionic character in A-B Bond.

Ionic character in A-B bond = $[18(\chi_A-\chi_B)\ 1.4]$ %

<u>Example</u>: On the basis of Pauling equation, calculate the percentage of ionic character in HF molecule.

Given: $\chi_H = 2.2$, $X_F = 4.0$

<u>Solution:</u> χ_F-χ_H = (4.0-2.2) = 1.8

Ionic character in HF molecule = $[18(\chi_A-\chi_B)^{1.4}]$ %

= $(18X\ (1.8)^{1.4})$ %

= 44.12%

(b) **Hannay and Smith equation:** These two chemists proposed the following equation to calculate the ionic character.

Ionic character in A-B bond = $[16(\chi_A-\chi_B) + 3.5\ (\chi_A-\chi_B)^2]$ %

<u>Example</u>: On the basis of hannay and smith equation calculate the percentage ionic character in gaseous HF, HCl, HBr and HF molecules. (Given that $\chi_F = 4.0$, $\chi_{Cl} = 3.2$, $\chi_{Br} = 3.0$, $\chi_I = 2.7$ and $\chi_H = 2.1$).

<u>Solution:</u> In HF-molecule, H-F bond

χ_F-χ_H = (4.0-2.2) = 1.8

Ionic character of H-F bond in HF molecule

= $[16(\chi_A-\chi_B) + 3.5\ (\chi_A-\chi_B)^2]$ %

= $[16(1.8) + 3.5\ (1.8)^2]$ %= 40.14%

Similarly,

Ionic character of H-Cl bond in HCl molecule = $[16(1.0) + 3.5\ (1)^2]$ % = 19.5%

Ionic character of H-Br bond in HBr molecule = $[16(0.8) + 3.5\ (0.8)^2]$ % = 15.04%

Ionic character of H-I bond in HI molecule = $[16(0.5) + 3.5\ (0.5)^2]$ % = 8.875%

(7) Variation in bond angles:

The bond angle B-A-B of different molecules of the ABx type in an atom changes, but B remain constant.

In H_2O = 104.50, H_2S = 92.20

$\chi_0 = 3.5$ $\chi_S = 2.5$

As we move from H_2O to H_2S, since the electronegativity of O (3.5) is more than S (2.5). The bonding e- pair in the formation of O-H bond is shifted more toward more electronegative O-atom than bonding electron pair of S-H bond is shifted towards less electronegative atom.

Thus, the electron density on O-atom is more than that the on S-atom. Due to this b.p.-b.p. repulsion in H_2O molecule becomes greater than the bp-bp repulsion in H_2S molecule. So, in going from H_2O to H_2S molecule, bp-bp repulsion decreases. Due to decrease in bp-bp repulsion bond angle in SH_2 molecule also decreases. i.e. H-O-H angle in H_2O is 104^0 30' while H-S-H angle, 92^0 20'.

(8) Calculation of bond length d_{A-B} in a hetero-diatomic molecule AB type: If AB molecule has some ionic character and the radii and electronegativity of atom A and B are r_A , r_B and χ_A ,χ_B respectively, them d_{A-B} (in *pm* units) is given by **Schomaker and Stevenson's equation**,

$d_{A-B}= r_A + r_B - 9(\chi_A-\chi_B)$

If r_A and r_B are in Å, then d_{A-B} will be in Å and the above equation will be,

$d_{A-B}= r_A + r_B - 0.09(\chi_A-\chi_B)$

<u>Example</u>: **Calculate the H-F bond length in HF molecule using Schomaker and Stevenson equation. Given: $r_F= 0.72$ A^0, $r_H = 0.37$ A^0, $\chi_F = 4.0$ and $\chi_H = 2.2$**

<u>Solution:</u> The bond length d_{F-H} in HF molecule,

$d_{F-H}= R_F + r_H - 0.09(\chi_F-\chi_H)$

$= 0.72 + 0.37 - 0.09(4-2.2)$

$d_{F-H}= 0.828$ Å

<u>Example</u>: **Calculate the H-Cl bond length in HCl molecule**

Given: $r_{Cl} = 0.99$ Å, $r_H = 0.37$ Å, $\chi_{Cl} = 2.83$ and $\chi_H = 2.2$.

(9) Explanation of diagonal relationship: The elements of 2nd period show similarities in properties with the elements lying to their right in 3rd period. This is called diagonal relationship.

Elements of 2nd period: Li Be B C N O F

↘ ↘ ↘ ↘ ↘ ↘

Elements of 2nd period: Na Mg Al Si P S Cl

Electronegativity of elements increases on moving from left to right in a period and decreases down the group. These two variations are opposite to each other and hence cancel each other when move diagonally in the periodic table. Thus, results are that the diagonal pairs have almost similar electronegativity and hence show similar properties.

Thus since the elements of pairs, Li(1.0)-Mg(1.2) , Be(1.5)-Al(1.5) , B(2.0)- Si(1.8)…….. have similar values of electronegativity of two elements of each pair show similar properties. i.e. they show diagonal relationship.

(10) Calculation of enthalpy (heat) of formation of a molecule:

With the help of electronegativity values of the elements, we can calculate the heat of formation of a molecule. Pauling has suggested the following equation for calculating the heat of formation of a given molecule.

$\Delta H_f = 23\Sigma(\chi_A-\chi_B) 2-55.4n_N-26.0n_0$

Here, Σ = no. of bonds in molecule, χ_A and χ_B= electronegativities of atoms A and B. n_N = no. of N and atoms present in molecule. Values of ΔH_f obtained from Pauling's equation are only approximately and are in Kcal/mole.

Example: Using Pauling's equation, calculate the heat of formation of $BeCl_2$ molecule.
Given: $\chi_{Be} = 1.6$ and $\chi_{Cl} = 3.2$

Solution: Since $BeCl_2$ has two Be-Cl bonds, $\Sigma = 2$. Also, there are no nitrogen and oxygen atoms present in $BeCl_2$ molecule, so $n_N = 0$ and $n_o = 0$. Thus,

ΔH_f of $BeCl_2 = 23 \times 2(3.2-1.6)2-0-0$

$= 117.75$ Kcal/mole

Note: experimental values = 122.0 Kcal/mole

(11) To explain acidic and basic character:

(a) To explain the variation in the acidic character of the hydrides of elements of the same period.

Let us consider the acidity of CH_4, NH_3, H_2O and HF molecules-hydrides of 2nd period elements. It is observed that the acidity of the molecules increases from CH_4 to HF. As the electronegativity of the central atom increases, the acidity increases. So, order of acidity is $CH_4 < NH_3 < H_2O < HF$.

(b) To explain the variation in the acidic character of the oxyacid's of elements of the same group and in the same oxidation state.

Let us consider the perhelic acidity of Cl, Br and I. i.e. $HClO_4$, $HBrO_4$, HIO_4 molecules. The acidic strength of these acids decreases as the electronegativity of halogen atom decreases as we move from Cl to I.

(c) To predict the acidic/basic character of hydroxy compounds:

Explain: **Whether CsOH and IOH molecules will show acidic and basic character in aqueous solution.**

The values of electronegativity of different element present in these molecules and those of χ_O-χ_{Cs}, χ_O-χ_H and χ_O-χ_I are: Cs-O-H I-O-H. In Cs-O-H molecule, $(\chi_O-\chi_{Cs})$ (=2.6) > $(\chi_O-\chi_H)$(=1.2), Cs-O bond would be more polar than O-H bond and hence the ionization of CsOH in aqueous solution will take place at Cs – O bond in Cs – O – H and $[OH_{(aq)}]^-$ ion will be produced.

$Cs\text{-}O\text{-}H_{(aq)} \longrightarrow [Cs_{(aq)}]^+ + [OH_{(aq)}]^-$ ion due to the production of $[OH_{(aq)}]$ ions, CsOH molecule will show basic character in aqueous solution.

In I – O – H molecule, since $(\chi_o-\chi_H)$(=1.2) > $(\chi_o-\chi_I)$ (=0.7), O-H bond will be more polar than O – I bond, hence the ionization of IOH in aqueous solution will take place a O – H bond in I-O-H and $(H_{(aq)})$ ion will be obtained.

$$I\text{-}O\text{-}H_{(aq)} \longrightarrow [IO_{(aq)}]^- + [H_{(aq)}]^+$$

Due to production of $[H_{(aq)}]^+$ ions, IOH molecules will behave as an acid in aqueous solution.

QUESTION BANK

Multiple Choice Questions:

1. The position of ________ element in modern periodic table is still a matter of dispute.
   (a) Helium (b) Hydrogen (c) Lithium (d) Carbon
2. Which is the more fundamental property of the elements?
   (a) Atomic weight (b) Ionic radius (c) Atomic number (d) Ionization energy
3. A diagonal line drawn through periodic table from___________ separate metals and non-metals.
   (a) B, Si, As, Te, & At (b) Al, Ge, Sb, Po & At (c) B, C, As, Te & Al (d) C, P, Se, I & Al
4. For given value of 'n' the degree of penetration of electrons is least one for ____orbital.
   (a) d (b) p (c) s (d) f
5. _______element does not form ionic compound readily.
   (a) Be (b) Sr (c) Ca (d) Mg
6. In IIIrd-A group element _____________ has little tendency to form M^{3+}ion.
   (a) Al (b) Ga (c) I (d) B
7. _____ is not gas at room temperature.
   (a) H_2 (b) N_2 (c) Br_2 (d) Ne
8. _____ is not isoelectronic ion.
   (a) O^{2-} (b) Ca^{2+} (c) K^+ (d) S^{2-}
9. The electron affinity of ____________ elements is either close to zero or slightly –ve.
   (a) Alkali metals (b) Alkaline earth (c) Halogen (d) Nobel gases
10. Electronegativity of an element in a molecule is its ability to ___________.
    (a) attract electron pair toward itself (b) attract lone pair of electrons toward itself
    (c) attract the shared electron pair toward itself (d) attract electron toward itself
11. The actual order of electron affinity of halogen element is……………….
    (a) $F < Cl > Br > I$ (b) $F > Cl > Br > I$
    (b) $F < Cl < Br > I$ (d) $F > Cl < Br > I$
12. sp^3 hybridization orbital has _________ % s-character.
    (a) 75 (b) 50 (c) 25 (d) 0
13. Which of the following hybrid orbital has equal both s and p-character.
    (a) sp (b) sp^3 (c) sp^2 (d) dsp^2
14. Which of the following pair has not diagonal relationship?
    (a) Li-Mg (b) Be-Al (c) N-S (d) C-Si
15. _____________ metals have lowest tendency to attract electrons towards them.
    (a) Alkaline earth (b) Transition (c) P-block (d) Alkali
16. The correct order of acidic character of hydride of 2nd period is…………….
    (a) $H_2O < CH_4 < NH_3 < HF$ (b)$CH_4 < NH_3 < H_2O < HF$
    (b) $CH_4 > NH_3 < H_2O < HF$ (d) $CH_4 < NH_3 > H_2O < HF$

17. The square root of ionic resonance energy directly proportional to………………
    (a) Amount of ionic character in A-B bond
    (b) Amount of covalent character in A-B bond
    (c) Difference in bond dissociation energies of A-A and B-B bonds
    (d) Difference in electron affinity of A and B element
18. How many series of transition elements are there in periodic table.
    (a) three (b) two (c) five (d) four
19. No space was reserved for ____________ elements in Mendeleef's periodic table.
    (a) halogen (b) inner transition (c) Inert gases (d) chalcogen
20. The correct order of ionization energy values for the elements of 2nd period is…………
    (a) $Li < Be < B < C < N < O < F$ (b) $Li < Be > B < C < N > O < F$
    (c) $Li < Be < B < C < N > O < F$ (d) $Li > Be > B < C < N < O < F$
21. The classification of the elements in modern periodic table has been made on the basis of…………….
    (a) electronic configuration of the elements
    (b) electronic configuration of valance shell of the elements
    (c) atomic weight of the elements
    (d) atomic size of the elements

(**Ans : 1-b, 2-c, 3-a, 4-d, 5-a, 6-d, 7-c, 8-a, 9-d,10-c, 11-b, 12-c, 13-a, 14-d, 15-d, 16-b, 17-a, 18- d, 19-c, 20-c, 21-b**)

Objective Questions:

1. What is Mosely's periodic law or Modern periodic law?
2. Define ionization energy.
3. Name the factors affecting the magnitude of ionization energy.
4. What is shielding or screening effect?
5. What is the difference between ionization potential and electrode potential of a metal?
6. Define electron affinity?
7. Name the factors affecting the magnitude of electron affinity.
8. Give the Pauling's equation for electronegativity.
9. Give the Allred and Rochow's equation for electronegativity and also give the terms involved in it.
10. Give the Mulliken's equation for electronegativity.
11. Name the factors affecting the magnitude of electronegativity.
12. Give the Pauling's equation for calculating the heat of formation.
13. Give the Pauling's equation for calculating the %age ionic character of covalent bond.
14. Give the Hannay and Smith equation for calculating the %age ionic character of covalent bond.

15. What is Mendeleef's periodic law?
16. What are the defects of long form of periodic table?
17. Write increasing order of successive ionization energy.
18. Why alkali metals can not form M^{2+} ion?
19. Give the iso-electronic species of third period of Periodic Table.
20. Write equation for ionic resonance energy of A-B covalent bond.
21. Which group of periodic table has highest value of electronegativity?

Subjective Questions:

1. Discuss the long form of periodic table.
2. Discuss the classification of elements in periodic table.
3. Define ionization energy. Discuss the factors affecting the magnitude of ionization energy.
4. Discuss the variation of ionization energy values of elements of different groups.
5. Define electron affinity. Discuss the factors affecting the magnitude of electron affinity.
6. Discuss the variation of electron affinity in main group elements of periodic table.
7. Discuss the variation of electron affinity values of elements of different groups.
8. Define electronegativity. Discuss the factors affecting the magnitude of electronegativity.
9. Discuss the variation of electronegativity in a group of s and p-block elements.
10. Discuss the variation of electronegativity values of elements of different groups.
11. Discuss the variation of electronegativity in a period of s and p-block elements.
12. Discuss the applications of electronegativity.
13. Describe Pauling's method to determine the electronegativity of an atom.
14. Discuss the defects of Mendeleef's periodic table.
15. Give the merits of the long form of periodic table.
16. Describe the superiority of long form of Mendeleef's periodic table.

Explanations:

1. Successive ionization energy is always higher than preceding one.
2. Ionization energy of Li^+ ion is greater than that of He- atom.
3. Third ionization energy value for Be-atom is much greater than third ionization energy value of B-atom.
4. With increase of shielding effect, the magnitude of ionization energy decreases.
5. The magnitude of ionization energy of an atom or ion is inversely proportional to its size.
6. The ionization energy of N is higher than expected.
7. Ionization energy values of the elements gradually go on decreasing down the group.

8. First electron affinity is exothermic process while second electron affinity is endothermic process.
9. Electron affinity values of N and P are very low.
10. CsOH is basic while IOH is acidic.
11. H-O-H angle in H_2O is $104^03'$ while H-S-H angle in H_2S is $92^02'$.

Examples:

1. Calculate the magnitude of energy involved in the conversion of (a) $O_{(g)}$ atom to $O^{2-}_{(g)}$ ion (b) $s_{(g)}$ atom to $s^{2-}_{(g)}$ ion. Predict whether the given conversion is an endothermic process.
2. The amount of energy released when one million of atoms of iodine in vapor state are converted to iodine ion, $I^-_{(g)}$ is 4.9×10^{-13} J, according to the reaction:

   $I_{(g)} + e^- \rightarrow I^-_{(g)}$

   Express the electron affinity of iodine in terms of KJ/mole and eV/atom.

   ($Z = 6.02 \times 10^{23}$ gm/mole)
3. The electron affinity of chlorine is 349 KJ/mole. How much energy in KJ is released when 1 gm of chlorine is converted completely into $Cl^-_{(g)}$ ions?
4. Calculate the electronegativity of carbon atom from the data given as E_{H-H}=104.2 Kcal/mole, E_{C-C}= 83.1 Kcal/mole, E_{C-H}= 98.8 Kcal/mole and χ_H=2.1
5. Calculate the electronegativity of a lead following Allred-Rochow procedure. Covalent radius of lead = 1.53 Å and atomic number of Lead = 82.
6. Calculate the electronegativity of fluorine atom given that ionization energy of F-atom = 17.41 eV and electron affinity of F-atom = 3.45 eV.
7. Calculate the electronegativity of Cl- atom. Given that ionization energy of Cl-atom = 13.0 eV and electron affinity of Cl-atom = 4.0 eV.
8. On the basis of Pauling equation, calculate the percentage of ionic character in HF molecule.
9. On the basis of Hannay and Smith equation calculate the percentage ionic character in gaseous HF, HCl and HBr molecules.
10. Calculate the H-F bond length in HF molecule by Schonmker and Stevenson's equation.

    Given: r_F= 0.72 Å, r_H = 0.37 Å, χ_F = 4.0 and χ_H = 2.2.
11. Calculate the H-Cl bond length in HCl molecule by Schonmker and Stevenson's equation.

    Given: r_{Cl} = 0.99 Å, r_H = 0.37 Å, χ_{Cl} = 2.83 and χ_H = 2.2.
12. Using Pauling's equation, calculate the heat of formation of $BeCl_2$ molecule.

    Given: χ_{Be} = 1.6 and χ_{Cl}= 3.2.

******* ***By Dr. K. D. Patel***