Chapter 17

Classification of Elements and Periodicity in Properties

PERIODIC TRENDS IN PROPERTIES

A. Atomic Size (or atomic radius)

Atomic radius is the size of the atom of an element. Atomic radius is defined as "the distance from the centre of the nucleus upto the centre of outermost electron." It is measured in Angstrom unit (Å). It is not possible to measure exact atomic radius as an atom is unstable and it cannot be isolated to get its radius. Moreover, the exact position of the outermost electron is uncertain. The values for radii are obtained from X-ray measurements. Following points are to be noted in this context :

(a) The size of an atom or ion decreases in a horizontal period as we move from left to right.

(b) The atomic radius increases in a group with the rise in atomic number.

(c) **A positive ion (cation) is smaller than the corresponding atom :** A positive ion or cation is formed by the loss of one or more electrons from an atom and the number of protons remains the same in the nucleus. Thus the ratio of the positive charge in the nucleus to the number of electrons *i.e.*, effective nuclear charge increases. Hence the force of attraction of nucleus to the outer electrons increases thus decreasing the size of cation. In case of alkali metals, the removal of an electron removes the entire outermost shell.

(d) **A negative ion (anion) is bigger than the corresponding atom :** In the formation of negative ion (anion) one or more electrons(s) are added to the atom. This results in the expansion of the size of the nuclear charge, which in turn decreases the force of attraction and increases the size of an anion or the pull exercised by the nucleus on the electron becomes less *i.e.*, they move a little farther resulting in an increase in the ionic size.

Note : ***Size of Iso-electronic ions :*** *These are such cations or anions which carry the same number of electrons. The size of such ions depends upon the effective nuclear charge. Greater the nuclear charge of an ion, greater will be the force of attraction for same number of electrons. As a result, the size of the ion decreases. For example :*

N^{3-}, O^{2-}, F^{-}, Na^{+}, Mg^{2+} *and* Al^{3+} *are isoelectronic ions, among these* N^{3-} *is largest* (1.71 A) *and* Al^{3+} *is smallest* (0.50 A).

B. Ionization Enthalpy

It is the amount of energy required to remove most loosely held electron from the ground state of an Avogadro number of the isolated atoms, ions or molecules in the gaseous state. The ion formed by loss of first electron may lose further electrons and thus we may have successive ionization energies for removal of 2nd, 3rd and 4th electrons in the gaseous state.

Ionization is always an endothermic process and ionization energies are therefore always assigned positive values.

Factors influencing Ionization energy

(1) Successive Ionization - Generally ionization energy increases for successive ionizations.

(2) Atomic size - Ionization energy decreases as the size of atom increases.

(3) Value of Z (atomic number) - Higher the value of Z, higher is the I.E.

(4) Distance of electron from the nucleus - Smaller the distance of the electron from the nucleus, larger is the ionization energy

(5) Shielding effect - Higher is the shielding of the electron to be removed, lower is the I.E. Shielding effect of the electrons of different orbitals follows the order $s > p > d > f$.

(6) Penetration effect - Higher the penetration power of the electron to be removed higher is the I.E. The penetration power of electrons of various orbitals follow the order $s > p > d > f$.

(7) Nature of shell - Ionization energy increases if the electron to be ionized from the species belongs to a half filled shell or a completely filled shell. The relative stability of these configurations follows the order $d^5 < p^3 < d^{10} < p^6$.

(8) Changes in the quantum shell - During the successive ionization, the electron to be ionized belongs to the lower quantum shell the I.E. therefore increases many folds. It is the combined effect of (a) effective nuclear charge (b) stability of completely filled shells (c) closer proximity of the lower shell to the positively charged nucleus.

Note : $I.E_1$: Li < B < Be < C < O < N < F < Ne

$I.E_1$: Na < Al < Mg < Si < S < P < Cl < Ar

$I.E_2$: O > F > N > C.

C. Electron affinity and Electron gain Enthalpy (ΔH_{EG})

It is defined as the energy released when electron is added to the valence shell of the one mole of isolated gaseous atoms or ions and the enthalpy change accompanying the process is defined as the electron gain enthalpy ($\Delta_{eg}H$). Electron gain enthalpy provides a measure of the ease with which an atom adds an electron to form anion, $X_{(g)} + e^- \rightarrow X^{\ominus}_{(g)}$. It may be considered to be same as I.E. of corresponding anion. The first E.A. of active non metals is negative. But the addition of a second electron to an already formed anion makes the reaction , ($X^- + e^- \rightarrow X^{2-}$) endothermic. At the time of formation of oxide or sulphide ion, the effect of 2nd E.A. is so much that the overall E.A. for the formation of oxide and sulphide ions is **endothermic**.

Variation of electron affinity

(1) Elements which have higher I.E. have higher E.A. also.

(2) The E.A. values of the second period elements are lower in comparison with the values of third row elements. This is due to increase in the interelectronic repulsions which are more for the smaller elements because of higher electron densities.

(3) Effective nuclear sheilding by the '*s*' electrons and the necessity of using higher energy orbitals to accept electrons turn the E.A. of group IIA elements negative.

(4) Au because of very high effective nuclear charge has higher electron affinity.

(5) The electron gain enthalpy of the elements having $d^{10}s^2$ configuration are positive as electron is to be accommodated into the higher energy *p* orbital.

Note : EA_1 : Cl > F > Br > I

EA_1 : S > Se > Te > Po > O

EA_1 : C > B > Li > Be

EA_1 : Si > Al > Na > Mg

EA_1 : F > O > N > Ne.

D. Electronegativity

It may be defined as : "The tendency of an atom to attract shared electron pair towards itself in a molecule". The small atoms attract electrons more strongly than larger ones, hence they are more electronegative.

The numerical value of electronegativity depends upon the ionisation potential and electron affinity. Higher ionisation potential and higher electron affinity both imply higher electronegativity. To measure electronegativity, an arbitrary scale was developed by Linus Pauling which is known as electronegativity scale. On this scale fluorine has maximum electronegativity of 4.0 and Li has a value of 1.0 while inert gas have no value of electronegativity.

The value of electronegativity show periodic variations as given below

Generally, in a group electronegativity decreases from top to bottom due to increase in size of atom.

F	Cl	Br	I	At
4.0	3.0	2.8	2.5.	2.2

In a period, electronegativity increases from left to right

Li	Be	C	N	O	F
1.0	1.5	2.5	3.0	3.5	4.0

Some Important Points

1. Melting point of alkali metal halides follow following order

   $M - F > M - Cl > M - Br > M - I$

   NaF > NaCl > NaBr > NaI
2. The order of melting point of chlorides of alkali metals is as follows :

   LiCl < CsCl < RbCl < KCl < NaCl
3. The melting point of LiCl is lowest because it is with highest covalent character.
4. The solubility of alkali metal carbonates in water at 298 K increases down the group from Lithium to Caesium.
5. The basic character of oxides and hydroxides of group 1 and group 2 increases down the group because metallic character increases down the group *e.g.*, LiOH is least basic whereas CsOH is most basic. $Be(OH)_2$ is amphoteric, $Mg(OH)_2$ is a weak base, $Ca(OH)_2$ and $Sr(OH)_2$ are moderately strong bases, $Ba(OH)_2$ is strong base.
6. The solubility of hydroxides of Group 1 and Group 2 in water increases down the group.
7. The solubility of sulphates, carbonates and phosphates decreases down the Group 2 because lattice energy dominates over hydration energy in Group 2, for example $MgSO_4$ is soluble in water whereas $BaSO_4$ is insoluble in water.
8. Li_2CO_3 is thermally unstable whereas other alkali metal carbonates are thermally stable.
9. Thermal stability of carbonates of Group 2 increases down the group. All are thermally unstable.
10. Properties of Li almost similar to that of Mg; Be is almost similar to that of Al and B is almost similar to that of Si due to diagonal relationship.

❑ ❑ ❑