B.Sc-I(Hons.), Paper-IB(Inorganic Chemistry)

Group-A, Unit-3 Classification of Elements & Periodicity (Contd.)

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⇒ **Ionisation enthalpy/energy:**

Ionisation energy/enthalpy is measure of tendency to loss electron by an element/atom. It is defined as "the least amount of energy required (absorbed) to remove one electron from an isolated gaseous atom (element) or ion is called ionisation energy/enthalpy of that element/ion". It is denoted by symbol IE or $\Delta_i H$, and expressed in kcal mol^{-1} or KJ mol^{-1}.

e.g; $Li(g) \xrightarrow{-e} Li^+$, $\Delta_i H$ or $IE_1 = 521$ KJ mol^{-1}
(atom) (Cation)

Since it is possible to remove one, two or three or more electrons from atoms, there is 1st, 2nd or 3rd ionisation enthalpies ($IE_1, IE_2, IE_3 \cdots$)

$M(g) \xrightarrow{-e} M^+(g) - IE_1$; $M^+(g) \xrightarrow{-e} M^{2+} - E_2$; $M^{2+} \xrightarrow{-e} M^{3+} - E_3$.

If one electron has been removed from an atom, it becomes increasingly difficult to remove the 2nd & subsequent electron from resulting cation on account of increase of effective nuclear charge and hence electrostatic attraction. Thus, the above processes: $IE_1 < IE_2 < IE_3 \cdots$

Lower the value of IE, the easier it is for the neutral atom to change into cation.

* **Factors affecting IE value:** The following factors affect the IE value:

(i) **Size of atoms or No. of orbit(n):** $\boxed{IE \propto \frac{1}{\text{size or } n}}$ IE value decrease with the increase of atomic radius/size/number of orbit(n) due to decrease of nuclear attraction on outermost electron, so easier to remove it. e.g; IE_1 of Na > IE_1 of K [Na_{11}: 2,8,1; n=3; K_{19}: 2,8,8,1; n=4]

(ii) **Nuclear charge(Z) or Effective nuclear charge(Z/e):** $\boxed{IE \propto Z \text{ or } Z/e}$

IE value increases with the increase of nuclear charge/effective nuclear charge due to increase of nuclear attraction on outermost electron and so more difficult to remove it.
e.g. IE_1 of Mg > IE_1 of Na. [Na_{11}: Z=+11, n=3 ; Mg_{12}: Z=+12, n=3]

(iii) **Shielding/Screening effect:** $\boxed{IE \propto \frac{1}{\text{Screening effect}}}$ I.E value decreases with the increase of Screening effect(σ) which decreases the nuclear attraction and so more easier to remove the outermost electron e.g. IE_1 of Cu > IE_1 of K, due to more Z term.

(iv) **Type of Suborbit/orbital:** IE value is also influenced by probability of finding electron, i.e; type of orbital. Closer the probability of finding electron (orbital) to the nucleus, more the IE value. Order of closeness of orbitals to nucleus: s>p>d>f. Hence, order of IE values: s>p>d>f (for same n value). e.g; IE_1 of Be > IE_1 of B. [Be_4: $1s^2 2s^2$; B_5: $1s^2 2s^2 2p^1$]

(v) **Symmetry of Electronic Conf:** Greater the symmetry of ele. conf. more the stability and hence more IE value. Order of IE values: Completely filled orbital > Half filled orbital > Incompletely filled orbital. e.g; $Ne_{10}(2s^2 2p^6) > N_7(2s^2 2p^3) > O_8(2s^2 2p^4)$.

* **Periodicity:** **In group**, IE values decrease in downward direction (top to bottom) due to increase of number of orbit(n)/size. e.g; In group-1 order of IE values is H > Li > Na > K > Rb > Cs > Fr.

In period: IE values increase (with some exceptions) from left to right direction due to increase of nuclear charge, and hence increase of nuclear attraction. e.g; In period-2, order of IE_1 values: Li < Be > B < C < N > O > F. (Exceptions cases)

n=	1	2	3	4	5	6	7

* Element of highest IE value: He, lowest IE value: Cs

⇒ **Electron affinity or Electron gain enthalpy:** This is measure of tendency of one element to gain or accept electron. It is defined as "The amount of energy released (sometime absorbed) when an electron is added to an isolated gaseous atom or ion is called electron affinity".

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e.g; $Cl(g) + e^- \longrightarrow Cl^-(g) + 348\ KJ$ or, $\Delta_{eg}H = -348\ KJ\ mole^{-1}$.

It's denoted by symbol EA or $\Delta_{eg}H$ & expressed in $Kcal\ mole^{-1}$ or $KJ\ mole^{-1}$.

The amount of energy released when an electron is added to an isolated g aseous atom to form an anion is called first electron affinity (EA_1 or $\Delta_{eg}H_1$) while the amount of energy sufficient when an electron is added to an anion(X^-) against electrostatic repulsion between electron being added and negative charge on anion to form $X^{2-}(g)$ is called second electron affinity (EA_2 or $\Delta_{eg}H_2$).

e.g; $O(g) + e^- \longrightarrow O^-(g)$; $\Delta_{eg}H_1 = -141\ KJ\ mole^{-1}$

$O^-(g) + e^- \longrightarrow O^{2-}(g)$; $\Delta_{eg}H_2 = +780\ KJ\ mole^{-1}$ (endothermic)

* Elements have normally $\Delta_{eg}H$ values -ve, Anions and elements with symmetrical electronic configuration (ns^2np^6) have $\Delta_{eg}H$ values +ve (endothermic process).

* The greater the energy released during electron gain by atom, greater is the electron affinity (EA) and easier to gain electron, i.e; formation of anion.

* Factors affecting EA value: The magnitude of EA value is influenced by following factors:

(i) Atomic size or No. of orbits (n): $EA \propto \frac{1}{size\ or\ n}$ Electron affinity (EA) values decrease with the increase of atomic size or, no. of orbits (n) due to decrease of nuclear attraction on adding electron e.g; EA of Cl > EA of Br [Cl_{17}: 2,8,7, n=3; Br_{35}: 2,8,18,7, n=4]

(ii) Nuclear charge (z) or Effective nuclear charge (Z/e): $EA \propto Z$ or Z/e

EA values increase with the increase of nuclear charge or effective nuclear charge due to increase of nuclear attraction on adding electron. e.g; EA of F > EA of O (F_9=2,7; O_8=2,6)

(iii) Screening effect: EA value increase with the decrease of screening effect of inner electrons, and so more nuclear attraction on adding electron

(iv) Symmetry of electronic conf: Order of EA values: Incompletely filled orbital > Half filled orbital > Completely filled orbital, due to increase of stability and so do not have any urge to take up extra electron. e.g. C(-122KJ) < O(-141KJ) > N(+31KJ) > Ne(+116 KJ)

(Incompletely filled $2s^2p^3$ or $2s^2p^4$ conf. — Half filled ($2s^2p^3$) conf. — Completely filled ($2s^2p^6$) conf.

(v) Type of suborbit/orbital: EA value is greatest for an electron entering in s-orbital and decrease for p, d & f-orbitals. This factor is not practical.

* Periodicity: In group, EA values decrease (with some exceptions) in downward direction, i.e; top to bottom due to increase of numbers of orbits (n) or size of atom.

e.g; In group 17, order of EA values: Cl > F > Br > I > At. (* exception case)

EA: -349 -328 -325 -295 -270 KJ

In period; EA values increase (with some exceptions) from left to right due to increase of nuclear charge and so more nuclear attraction on adding electron.

e.g; In period-2, Order of EA values: Ne < Be < N < Li

+116 +66 +31 -38

Elements of highest electron affinity: Cl (Group 17 element)

" lowest " : Rn (Group 18 element)

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