MODERN ENGINEERING
&
MANAGEMENT STUDIES

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LECTURE NOTES
B.TECH 1st YEAR – SEM- II (2024-2025)

DEPARTMENT OF BASIC SCIENCE
AND
HUMANITIES

Periodic properties :-

Effective Nuclear charge (Zeff)

→ In multi Electron atoms the electrons in the valency shell experience can attractive force from the nucleus and repulsive force from the electrons in the inner shell.

→ The attractive force absorb by the nucleus on the valency shell electron is somewhat reduced by the repulsive force exerted by electron present in the inner shell.

→ The valency shell electrons do not feel the full charge of the nucleus.

→ The actual charge felt by the valency electrons is called effective nuclear charge.

→ The repulsive force felt by the valency electrons from the electrons present in the inner shell is called Shielding effect or Screening Effect.

→ Therefore the Effective Nuclear Charge

$$Z_{eff} = \text{Total Nuclear charge}(Z) - \text{Screening Constant}(S)$$

→ The Greater the number of electrons in the inner shell the larger will be Screening Effect.

→ As Screening effect increases the effective nuclear charge decreases.

→ The force of attraction by the nucleus for the valency ectrons decreases as the Ionisation Energy decreases.

Eg :- $Z_{eff}(1s) > Z_{eff}(2s)$, $Z_{eff}(4p) < Z_{eff}(3s)$

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Penetration of orbitals:

→ The ability of an electron to get close to nucleus is called the penetration of electron.

→ For the same shell (l) the penetration power of an electron in orbitals (subshell) is $s > p > d > f$ and for the different values of shell and subshell the penetrating power of an electron in orbitals is given as $1s > 2s > 2p > 3s > 3p > 4s > 3d > 4p > 5s > 4d > 5p > 6s > 4f$.

Periodic trends due to penetration and Sliding:-

(a) Effective nucleus charge (Z_{eff}):

The effective nucleus charge increase from left to right and decreases from top to bottom in a group.

(b) Atomic radius:

The atomic radius decreases from left to right in a period and increases from top to bottom in a group.

(c) Ionisation Energy:

The ionisation Energy increases from left to right and decreases from top to bottom in a group.

(d) Electronegativity:

The Electronegativity increases from left to right and decreases from top to bottom in a group.

$_3Li$ $_4Be$ $_5B$ $_6C$ $_7N$ $_8O$ $_9F$ $_{10}Ne$

$[He]_2 2s^1$ $[He]_2 2s^2$ $[He]_2 2s^2 2p^1$ $[He]_2 2s^2 2p^2$ $[He]_2 2s^2 2p^3$ $[He]_2 2s^2 2p^4$ $[He]_2 2s^2 2p^5$ $[He]_2 2s^2 2p^6$

$3-2=1$ $4-2=2$ $5-2=3$ $6-2=4$ $7-2=5$ $8-2=6$ $9-2=7$ $10-2=8$

I,

Screening constant remains unchanged from left to right across a period.

The amount of energy which is required to remove an outermost electron is known as Ionisation Energy.

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Variation of s, p, d & f orbital Energies:

The properties like valency, atomic size, ionisation energy, electron affinity and electronegativity are directly related to the electronic configuration of the atoms.

(I) Variation in a period:

On moving from left to right across a period the number of valency electrons increases from 1 to 8. Consiquently the ~~usual~~ usual valency of the elements increases from 1 to 4 and then decreases to 1 for the elements of second period.

(II) Variation in a Group:

On moving down a group the number of valency electrons remains the same therefore all the elements in a group have same valency.

e.g: All the elements of group 1 have valency 1 and Group 2 have valency 2.

* The transition elements have generally 1 to 2 e^- in their outer most energy level. They exhibit variable valency but there most common valency is 2.

Atomic and Ionic Sizes:

Atomic radius is defined as the distance from the centre of the nucleus to the outermost shell containing the electrons

(I) Variation of atomic radii in a period:

In General the atomic radii decrease with increase in atomic number as we move from Left to right in the periodic table. Along a period the e^- is being added in to the same principal shell and effective nuclear charge increases therefore the nuclear attraction on the valency electrons increases and the radii of the atoms decreases.

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(II) Variation of atomic radii in a Group:

The atomic radii of elements increase with increasing in atomic number as we move from top to bottom in a group. As we move down in a group a new Energy shell is added at each ~~Sub~~ Succeeding elements though the number of electrons in the valency shell remains to be the same.

Ionic radii:

(i) When an atom donate e^- it becomes positive ion and it is called as Cation & when an atom accepts e^- it becomes negative ion which is called as anion.

$Na \longrightarrow Na^+$
$(2,8,1) \quad (2,8)$ (Cation)

$Cl \quad Cl^-$
$(2,8,7) \longrightarrow (2,8,8)$ (Anion)

The size of cation is smaller than a neutral atom whereas the size of anion is greater than a neutral atom as it accepts ~~neutron~~ e^-.

(II) Variation of Ionic radii in a period:

In General the Ionic radii decreases with increase in atomic number as we move from left to right in the periodic table.

(III) Variation of Ionic radii in a Group:

The Ionic radii of elements increases with increase in atomic numbers as we move from top to bottom in a Group.

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Ionisation Energy:

Ionisation Energy of an element is defined as the amount of Energy required to remove the most loosely bound e^- from an Isolated gaseous atom.

$$M(g) + I.E. \longrightarrow M^+(g) + e^-(g)$$

→ Unit of Ionisation Energy is Kcal/Mole or KJ/Mole.

Factors affecting Ionisation Energy are :-

(i) Size of atoms
(ii) charge on the nucleus
(iii) Screening effect of the Inner electrons
(iv) Penetration effect of e^-
(v) Electronic configuration

(i) <u>Size of atoms</u>:- Ionisation Energy decreases with the increase in the size of the atoms because the outermost electrons are less strongly attracted by the nucleus.

(ii) <u>charge on the nucleus</u>: With the increase in nuclear charge it becomes more difficult to remove an electron and hence Ionisation Energy increases.

(iii) <u>Screening effect of the inner electrons</u> : If the number of e^- is more electron force will be less and hence the ionisation Energy will decreases.

(iv) <u>Penetration effect of e^-</u>: The ionisation Energy increases with the increase in penetration power of e^-.

As $\boxed{s > p > d > f}$

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(v) Electronic configuration: The half-filled and completely filled shells have extra stability associated with them so it is difficult to remove electrons from these stable configuration and Ionisation Energy is high.

E.g:- Be - $1s^2 2s^2$

Mg - $1s^2 2s^2 2p^6 3s^2$ (completely filled shell) so I.E is high.

N - $1s^2 2s^2 2p^3$

P - $1s^2 2s^2 2p^6 3s^2 3p^3$ (half filled shell so the I.E is high).

Variation along a period :-

→ Generally the Ionisation Energy increases with increase in atomic number in a period.

→ The values of Ionisation Energy of the Second row elements can be Explained as follows:-

Li to Be

On moving from Lithium to Beriliam there is an increase in Ionisation Energy and this is due to the increased nuclear charge and smaller atomic size.

Be to B

(a) Although the nuclear charge of Boron is more than Beryliam but there is a slight decrease in Ionisation Energy from Be to B. This is due to the fact that In Boron last e^- goes to 2p orbital which is at a slightly highere Energy than 2s and is easy to be removed.

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(b) The Electronic configuration of Boron ($1s^2\ 2s^2 2p^1$) is less stable than that of Beridium ($1s^2\ 2s^2$) which has completely filled orbitals.

B to C to N:

As we move from B to C to N, the Ionisation Energy keeps on increasing due to increasing nuclear charge and decreasing atomic size.

N to O:

O, the element next to N, has slightly smaller Ionisation Energy as compared to that of N. It is due to the fact that the e.c of N-atom ($1s^2\ 2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^1$) in which each 2p-orbital is half filled and is more stable, that of O-($1s^2\ 2s^2\ 2p_x^2\ 2p_y^1\ 2p$. Therefore I.E of N is more than than of O.

O to F to Ne:

The Ionisation Energy increases from O to F to Ne because of the Increased Nuclear Charge and decrease in size. Ne, the nobel gas has the Maximum I.E in the period due to the stable (~~$ns^2\ np^5$~~ $ns^2\ np^6$) Electronic Configuration.

Variation down a Group:

Within a Group there is a gradual decrease in I.E when we move from top to bottom.

Considering the I.E values of the elements of the 1st Group :-

(a) In going from top to bottom in a Group the nuclear charge increases.

(b) There is a gradual increase in atomic size due to an additional principal shell.

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(c) There is an increase in Shielding effect on the outermost e^- due to an increase in the number of inner electrons.

The effect of increase in atomic size and the Shielding effect is much more than the effect of increase in nuclear charge. As a result the e^- becomes less ~~and~~ held to the nucleus as we move down the group. Hence, there is a gradual decrease in the Ionisation Energy in a Group.

Electron affinity:

The amount of Energy released when an e^- is added to an Isolated gaseous atom is called electron affinity.

$$X(g) + e^- \longrightarrow X^- + \text{Energy}$$
$$Cl(g) + e^- \longrightarrow Cl^- + \text{Energy}$$

} Electron affinity

→ It's unit is K cal / mole or KJ / mole.

Factors on which electron affinity depends:

Some important factors on which it mostly depends :-

(a) Nuclear charge
(b) Size of the atom
(c) Electronic configuration

(a) Nuclear charge:

The electron affinity increases as the nuclear charge increases. This is due to greater attraction for the incoming electron if nuclear charge is high.

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(b) Size of the atom:

with the Increase in size of the atom the distance between the nucleus and the incoming e⁻ increases. This results in lessere attraction. Consequenty the electron affinity value will decreases.

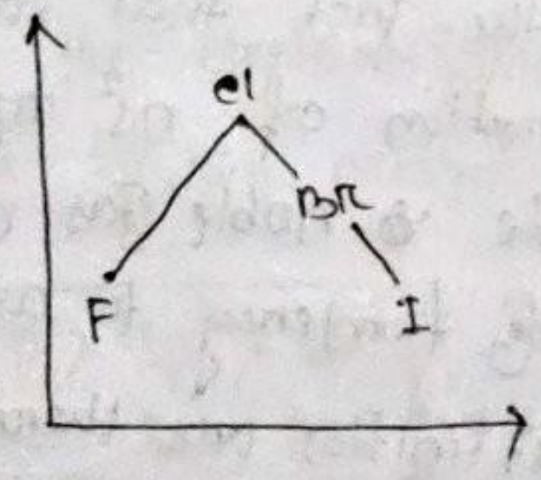
(c) Electronic configuration:

The element having stable electronic configurations of half and completely filled valency sub shells show very small tendency to accept additional e⁻ and thus electron affinities are low and or almost zero in certain cases.

Variation of electron affinity:

(a) Variation down a Group: On moving down a Group the atomic size and the nuclear charge increases but the effect of Increase in atomic size is much more than ~~the top~~ ~~nuclear~~ that off nuclear charge So, electron affinity decrea E.A decreases on going from Cl to Br and to I.

Graphically,



(b) Variation along a period: On moving across a period the size of the atom decreases and nuclear charge increases. Both these factor result in to Greater attraction for the incoming e⁻ therefore E.A increases in a period from Left to right.

(Q) (i) Electron affinity of F is unexpectedly less than that of Cl. The Low value of E.A of F-atom is due to the very small size of the F atom. For this there are strong inter electronic ~~Configuration~~ repulsions in the relatively 2p sub shell of F and

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thus the incoming e^- does not fill much attraction. But the Cl-atom is larger than F-atom where the e^- is added to 3p orbital which can easily captured the additional e^-.

Q) (ii) Electron affinity of nobel gases is zero while of Be, Mg, N & P is almost zero.

→ The E.A of nobel gases is zero because they have stable electronic configuration of $ns^2\ np^6$ and thus they have no tendency to take an additional e^-. The low or almost zero E.A value for Be, Mg, N, P can be explained due to the Extra stability of fully filled 2s and 3s orbitals in Be ($2s^2$) and Mg ($3s^2$) respectively, And of half filled 2p and 3p orbitals in N ($2p^3$) and P ($3p^3$) respectively. Therefore, their configurations show little tendency to gain any e^- and hence, their E.A value is almost zero.

Q) (iii) Halogens have the highest E.A

The Electron affinities of the halogens are the highest. This is due to the fact that halogens have the general electronic configuration of $ns^2\ np^5$ and Have only 1 e^- lasks than the stable noble gas ($ns^2\ np^6$) configuration. Thus, they have very strong tendency to accept an additional e^- and their electron affinities are therefore high.

Electronegativity:

→ The tendency of an atom to attract the share e^- pair in a molecule towards itself is called electronegativity.

→ Greater the ability of an atom to attract e^- in a bond, the larger is the value of it's electronegativity.

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Factors affecting electronegativity:

(a) oxidation state: The electronegativity of an atom varies from one bonding state to another depending upon the oxidation state of the atom of the molecule.

→ In General the electronegativity increases as the positive oxidation state of the atom increases.

→ This is because with the increase in the oxidation state the tendency to attract to the e^- will increase.

→ For anions, the electronegativity decreases with the increase in -ve charge of the ion. This is due to the fact that a more negativity charge ion will attract electrons less than a less negativity charge or neutral ion.

(b) Types of Hybridisation:

→ The types of hybridisation affect the electronegativity of an atom.

→ The S orbitals will have greater electron attractive power or electronegativity. So the electronegativity increases with the increases in S character of hybrid orbital.

$Sp > Sp^2 > Sp^3$
50% 33% 25%

→ Eg: C_2H_2 (Acetylene) (Sp)

C_2H_4 (Ethylene) Sp^2

CH_4 (Methane) Sp^3

(c) Size of the atom:

→ Atoms with small size have higher values of electronegativities.

This is due to the fact that the small atoms have

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higher effective nuclear charge therefore the shared pair of e^- is pulled more strongly by the nucleus and the electronegativity is high.

Trends in Electronegativity:

(i) Variation along a period: On moving along a period the electronegativity increases as we move from left to right, the atomic size decreases and the nuclear charge increases.

(ii) Variation in a Group: While going down in a group Zeff decreases and hence electronegativity decreases along the group because with the elements have a new principal shell is added and the size increases which overcomes the increases in nuclear charge.

Application of Electronegativity:

It helps in determine -

(a) Bond type & Bond order

(b) Tentative bond Energies

(c) Qualitative thermal stabilities

(d) Logic behind similarities & differences observed in chemical behaviour of molecules.

Polarizability:

Neutral, non polare species has spherically symmetry arrangement of electrons in their e^- clouds in the presense of an electric field their electrons clouds can be distorted.

polarizability is a measure of the ease by which an electrons clouds get distorted by an electric field.

e.g. - Large negatively charged ions I^- & Br^- are highly polarizable.

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Small positively charged ions such as Mg^{2+} & Al^{3+} have low polarizability but they have high power to polarize polarizable species such as I^- & Br^-.

Factors that influence polarizability:

(i) The greater the no. of electrons, the lesser control by the nuclear charge on charge distribution, Thus the increased polarizability of the atom.

(ii) The greater the distance of e^- from the nuclear charge, the less control by the nuclear charge on the charge distribution and Thus the increase polarizability of atom.

Oxidation States:

- The transition elements show variable valency so they exhibit different oxidation states.
- Eg- Fe show oxidation states +2 & +3 and Cu shows oxidation state +1 & +2.
- s block elements where the oxidation states is always equal to the group number and the p- block elements where the oxidation state is either group or 8 group number.
- For the 1st 5 elements of the 1st transition series in which the 3d subshell is not more than half filled, The minimum oxidation state is given by the number of electrons in the outer 's' subshell and the maximum oxidation state given by the sum of outer 's' & 'd' electron.
- The outer electronic configuration of 'Sc' is $[Ar]\ 3d^1\ 4s^2$. It shows an oxidation state Equal to +3 because after the ~~lost~~ lose of two 's' e^- and one 'd' e^- it acquire 'Ar' configuration.

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- Titanium (Ti) shows an oxidation state equal to +2 if both 's' e^- are used and +4 when two 's' and two 'd' e^- are used.
- Vanadium (V) shows oxidation states +2), +3, +4 and +5 depending upon whether it uses the two 's' e^- or in addition one, two or three 'd' e^- also. ($3d^3\ 4s^2$).
- Cromium (Cr) ($3d^5\ 4s^1$) by using the single 's' electron for bonding we get an oxidation number of +1, Hence by using varying number of 'd' e^- oxidation states like +2, +3, +4, +5, +6 are also possible.
- Manganese (Mn) ($3d^5\ 4s^2$) oxidation states +2, +3, +4, +5, +6 & +7.

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