SHAHID MATANGINI HAZRA GOVT. COLLEGE FOR WOMEN

TOPIC : CHEMICAL PERIODICITY

Lecture : 2

Discipline : B.Sc (H)

Subject : Chemistry

Semester : II

Course Code : CCT3

prepared

Basudev Mandal

Asst.Professor

Department Of Chemistry

LANTHANIDE CONTRACTION

- **Lanthanide Contraction :**
- lanthanide contraction is the gradual decrease in the atomic and ionic size of lanthanoids ($_{Ln}^{3+}$) from Ce_{58} to Lu_{71} with an increase in atomic number.
- **Causes of lanthanide contraction :**
- With an increase in the atomic number, the positive charge on nucleus increases by one unit and one more electron enters same 4f subshell.

  The electrons in 4f subshell imperfectly shield each other. Shielding in a 4f subshell is lesser than in d subshell.

  With the increase in nuclear charge, the valence shell is pulled slightly towards the nucleus. This causes lanthanide contraction.

INERT PAIR EFFECT

- **Inert pair effect :**
  Two electrons present in the valence s-orbital become inert and are less available for bonding. This is known as inert pair effect. It increases down the group.
- A chemical consequence is the occurrence of oxidation states which are two units less than the group oxidation
- **Examples:**
- 1) In 13^{th} group, thallium can exhibit +1 and+3 oxidation states but it is stable in +1 oxidation state only due to inert pair effect
- 2) In 14^{th} group, lead shows both +2 and +4 oxidation states but it is stable in +2 oxidation state due to inert pair effect.

IONIZATION ENERGY

- **Ionization Energy :**

  The **ionization energy** (IE) is qualitatively defined as the amount of **energy** required to remove the most loosely bound valence electron of an isolated gaseous atom in its lowest energy state to form a cation.

- It is also sometimes referred to as ionization potential (IP) and is usually an endothermic process.
- It is measured either in units of electronvolts (eV) or kJ/mol.
- Examples :

i. IP for Mg is greater than Al
ii. IP for N is greater than O
iii. IP from H to He increases but decreases from noble gases to alkali

IONIZATION ENERGY TREND IN THE PERIODIC TABLE

- **Variation of IP in a period :**

Along a period from left to right IP increases due to increasing nuclear charge and decreasing atomic radius. As a result, attraction force between nucleus and the valence electron increases. hence it is very difficult to Remove a valence electron.

Variation of IP in a group :

Along a period from top to bottom IP decreases due to increasing shielding effect as number of inner shell increases and atomic radius increases .As a result attraction force decreases between nucleus and the valence electron . Hence it is easier to remove a valence electron.

FACTORS AFFECTING IONIZATION ENERGY

- **Factors Affecting Ionization Energy :** There are several factors that govern IE.

i.Charge Of The Nucleus :

If the nucleus is positively charged then the electrons are strongly attracted to it. The ionization energy is high as it will be more difficult to remove an electron.

ii.Size Of The Atom :

If an electron lies near or close to the nucleus then the attraction will be greater than the one when the electron is further away. Therefore IP increases with decreasing size.

iii.Electronic Arrangement : Half filled or full filled stable electronic arrangement gives high IE.

ELECTRON AFFINITY

- **Electron Affinity :** The amount of energy released when an electron is added to an isolated gaseous atom in its lowest energy state to produce an anion is called electron affinity (EA).
- It is usually an exothermic process.
- It is measured either in units of electronvolts (eV) or kJ/mol.
- **Examples :**

i. EA of noble gas atoms are zero or positive.

ii. EA of halogens are in the order Cl>F>Br>I

ELECTRON AFFINITY TREND IN THE PERIODIC TABLE

- **Variation of EA in a period :**

Along a period from left to right EA increases due to increasing nuclear charge and decreasing atomic radius .As a result attraction force between nucleus and the outer most electron increases. hence it is easier to add an electron in its outer most shell.

Variation of EA in a group :

Along a period from left to right EA decreases due to increasing shielding effect as number of inner shell increases and atomic radius increases .As a result attraction force decreases between nucleus and the outer most electron . Hence it is very difficult to add an electron in its outer most shell .

FACTORS AFFECTING ELECTRON AFFINITY

Nuclear Charge :

- Greater the nuclear charge, greater will be the attraction for the incoming electron and as a result larger will be the value of electron affinity.

Atomic Size :

- Larger the size of an atom, larger will be the distance between the nucleus and the incoming electron. Thus, smaller will be force of attraction felt by incoming electron and hence smaller will be the value of Electron affinity.

Shielding or Screening Effect :

- Greater the number of inner lying state, less will be the electron affinity between nucleus and incoming electron

Electronic Configuration :

- If an atom has fully filled or half filled orbitals, its electron affinity will be zero or low as lesser will be its tendency to accept incoming electron.

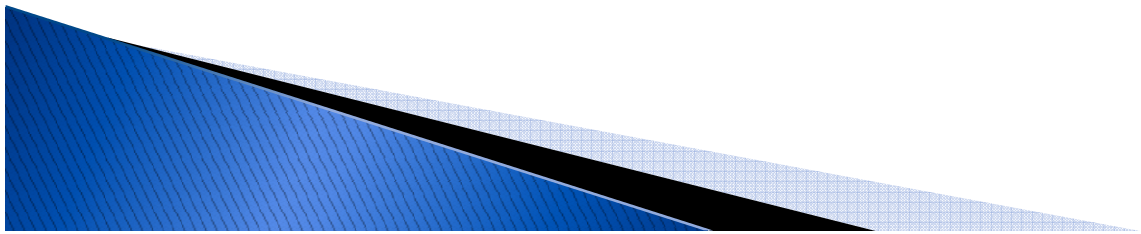
ELECTRONEGATIVITY

- Electronegativity: There are three scale to define electronegativity-

1. Pauling Scale :

According to Pauling , The Electronegativity is a measure of the tendency of an atom to attract a bonding pair of electrons towards itself.

- The Pauling scale is the most commonly used.
- It is symbolized by X (pronounced Kai for Greek alphabet Chi).
- It is a dimensionless property



PAULING SCALE AND MULLIKEN SCALE

Pauling Scale :

$$X_A - X_B = 0.102\sqrt{E_{AB} - (E_{AA}.E_{BB})^{\frac{1}{2}}}$$

- X_A , X_B = Electronegativity of element A and B , such that $X_A > X_B$; E_{AA} =Bond energy of the A-A bond; E_{BB} =Bond energy of the B-B bond;
- E_{AB} =Bond energy of the A-B bond;

2. Mulliken Scale :

According to Mulliken, The Electronegativity of an atom in a molecule is directly proportional to the average of its IP and EA.

This is done by dividing the **Mulliken** electronegativity value by 2.8.

In other words (IE + EA)/2x2. 8 or (IE + EA)/5.6 yield E.N values in Pauling **Scale**.

ALLRED AND ROCHOW SCALE

- **3.Allred and Rochow Scale :**
- According to Allred and Rochow Electronegativity is the electrostatic force exerted by effective nuclear charge, Z_{eff} , on valence electron.

$$\chi^{AR} = \left(\frac{3590 \times Z_{eff}}{r_{cov}^2}\right) + 0.744$$

r_{cov} is the covalent radius.

Allred and Rochow added certain perimeters so that it would more closely correspond to Pauling's electronegativity scale

ELECTRONEGATIVITY TREND IN THE PERIODIC TABLE

- **Variation of EN in a period :**

  Along a period from left to right EN increases due to increasing nuclear charge and decreasing atomic radius . As a result , attraction force between nucleus and bonding electron pairs increases . Hence it is easier to accept sharing pair of elrctrons towards itself.

- **Variation of EN in a group :**
- Along a group from top to bottom EN decreases due to increasing shielding effect as the number of inner shell increases as well as atomic size increases .As a result attraction force between nucleus and bonding electron pairs decreases . Hence it is very difficult to accept sharing pair of elrctrons towards itself.

FACTORS AFFECTING ELECTRONEGATIVITY

- **Atomic Size :** The smaller the size of an atom, greater is its tendency to attract shared pair of electron towards itself and hence Electronegativity increases.
- **Oxidation state of the ion :** The element in higher O.S has more value of EN than in the lower O.S. Thus the value of EN of Fe3+ is higher than that of Fe2+.
- **Type of hybridization :** The magnitude of EN inereases as the s character in hybrid orbitals increases.
- **Ionisation Energy and Electron Affinity :**

According to Mulliken, EN increases with increasing IP and EA.

Effective Nuclear Charge : According to Allred and Rochow,EN increases with $Z_{eff.}$