Discipline Course-1 (DC-1)
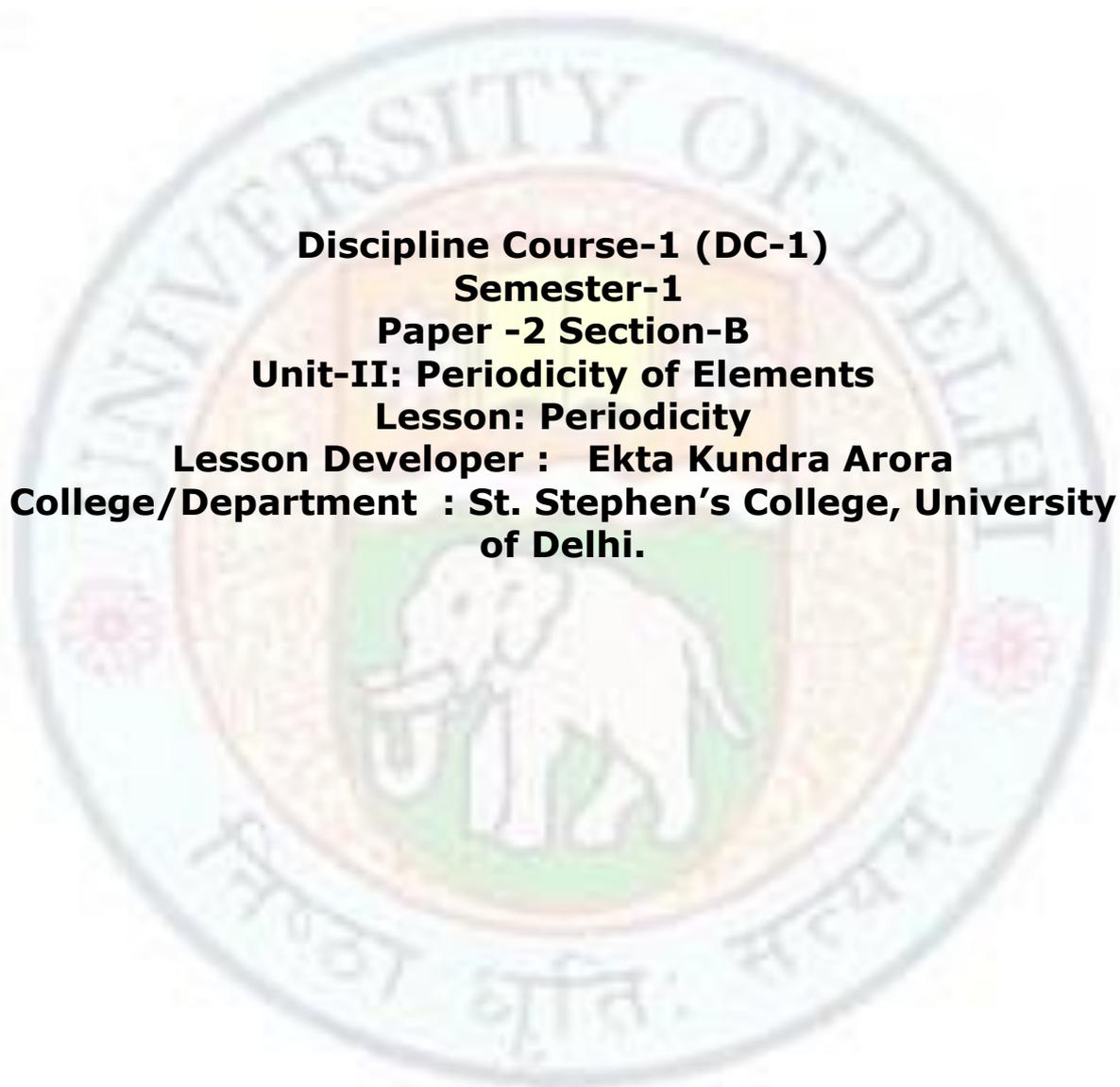**Semester-1**
Paper -2 Section-B
Unit-II: Periodicity of Elements
Lesson: Periodicity
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PERIODICITY OF ELEMENTS

1.2 PERIODICITY

Periodicity of elements

> **Variation of physical and chemical properties of elements across periods or down the groups is called periodicity.**

- ## 1.2.1 Atomic, covalent and ionic radii and their variation in groups and periods

- **Radii**: There is no practical way of measuring the radii of atoms and ions. A Mg^{2+} ion may be more tightly bound in a lattice than when present in a solvent of low polarity. There are different types of radii of atoms and ions in different bonding situations i.e. Covalent, ionic, metallic and Vander Wall radii.

- **Atomic radii**
  Wave nature of the electron does not allow us to determine the size of an individual atom as the electron density gradually fades away rather than stopping at a certain distance from the nucleus. When these atoms pack in solids or are bound in molecules they are usually present at characteristic distances from each other.

  The **atomic radii** of an element are therefore half the distance between nuclei in neighbouring atoms.

(a)   (b)

> **Fig 1**: (a) Two adjacent diatomic molecule
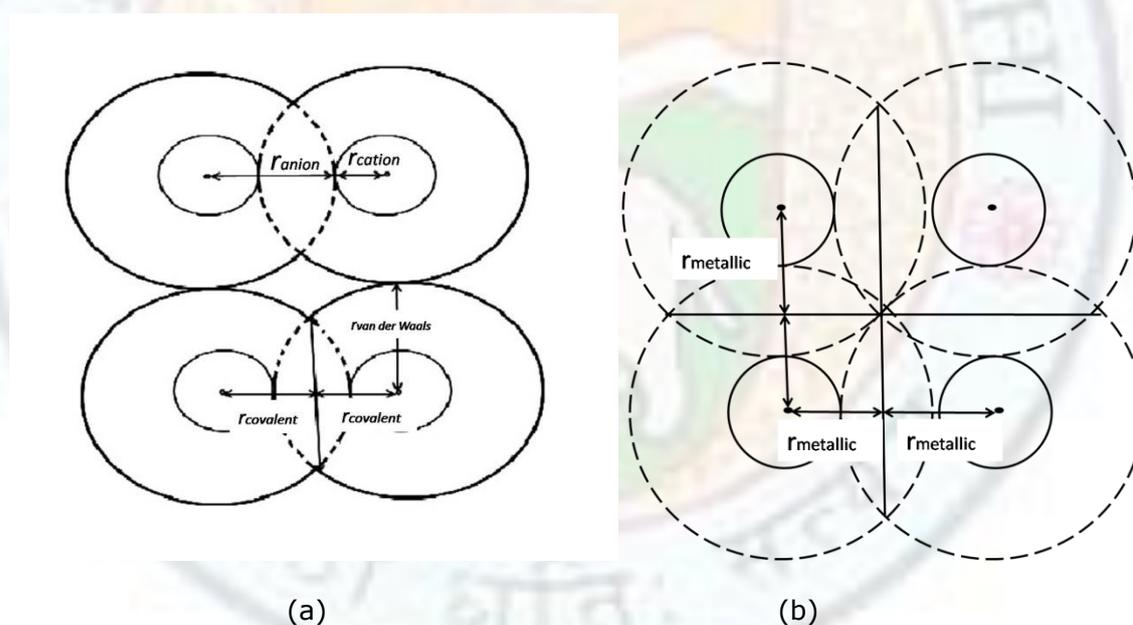>
> (b) Four adjacent atoms of a metallic Solid
> In the figures the inner circles represent core electrons and outer circles represent extent of valence electrons.

- **Covalent Radii**: In a covalent molecule the valence orbitals overlap so that the valence electron of each atom can be shared with the other. Overlap improves when atoms come closer, but ultimately we expect the

overlapping valence electrons to bump into and be repelled by the core electrons of the other atom. If the element is a non-metal than half the internuclear distance is the **covalent radii.**

- **Metallic radii**: In a **metal** each atom will have 8 or 12 nearest neighbours and all of them are at same distance from the atom under consideration. This results in a metallic distance that somewhat exceeds the covalent radii due to the large number of atoms being brought close. If the element is a metal than half the distance between the two nearest atoms is also called the **metallic radii.** Since pure covalent compounds of metals are hard to find, the single bond radii are of much use.
  This distance should be intermediate between core and valence electrons.

- **Van der Wall Radii**: The **Van der wall radii** is half the distance between two non-bonded nuclei on neighbouring atoms in the structure of the solid. If these molecules are supposed to be in a solid state in a crystal such that each molecule just touches one above and below it then distance between two non-bonded nuclei on neighbouring molecules is the Vander wall radii of the atom. This distance should be more than the covalent radii as it roughly corresponds to the distance of the valence electrons. Since there are no bonds in the atoms of this structure Vander wall radii are larger than covalent radii.

- **Ionic radii**: The ionic radii is determined from internuclear distance in ionic solids say for e.g. it is the distance between centres of sodium and chloride ions in sodium chloride crystal. The distance between centres of two ions in an ionic solid is obtained from X-ray crystallography. It is hard to determine at what point the electron density of the cation stops and the anions begins. The point of minimum electron density is used as the demarcation boundary.

1.2.2 Variations in radii

When we want to compare radii as a periodic trend, we have to keep in mind that a comparison of only similar type of radii is possible. All atoms do not participate in all types of bonding, so each type of radii for atoms may not be known. We can the work out approximate trends.

- **Variation in Covalent radii and metallic radii:**

- **Variation of radii along a period**

  For s and p block elements we observe a decrease in size from Lithium to Fluorine and from Sodium to Chlorine consistent with the increase in effective nuclear charge. This trend in decreasing radii is greatest in p block and diminishes in d block and is almost absent in f block.
  As z_{eff} increases and the principal quantum number n remains the same, electrons are pulled closer to the nucleus and atomic radius consequently decreases.
  $Z_{eff:}$ Li (1.3) Be(1.95) , B(2.60) ,C(3.25) , N(3.90), O(4.55) ,F(5.20)

  Radii :Li (1.23Å) Be(0.89Å) , B(0.80Å) ,C(0.77Å) ,N(0.74Å), O(0.74Å) ,F(0.72Å)

This trend does not continue in group 18. They are monatomic gases. They don't have covalent radii.

- **Variation of radii down the group**

  The effective nuclear charge as calculated by Slater's rule decreases slightly on going down the group and the principal quantum number n increases. With an increase in n, the most probable distance from the nuclei increases. As we go down the group, the outermost electrons are present in larger orbitals, for which maximum in radial distribution function lies further from the nucleus e.g. for Lithium the outer electron lies in 2s, for Sodium it lies in 3s and so on. Atomic radii therefore increase down the group.

  Z_{eff}: Li(1.3) ,Na(2.2) , K (2.2) , Rb (2.2) ,Cs(2.2)

  Radii: Li(1.23 Å),Na(1.57 Å), K (2.03 Å), Rb (2.16 Å),Cs(2.35 Å)

?

Do you know?

In the early part of the p block we notice two interruptions:

- Gallium and Germanium are not significantly larger than the third period elements Al and Si.

  Al: $[Ne]3s^2 3p^1$ Z_{eff}(Al)=3.50, Ga:$[Ar]3d^{10}4s^2 4p^1$,Z_{eff}(Ga) =5.00

  Gallium and Germanium follows the d block elements in the fourth period. They have completely filled 3d orbitals i.e. ten electrons have been added before the filling up of the 4s and 4p electrons. The d electrons are poor shielders. The effective nuclear charge on the outermost electrons increases and they are not significantly larger than the third period elements Al and Si.

- Similarly sixth period elements are not significantly larger than fifth period elements Indium and Tin.

- ## Variations in Ionic Radii

- Electron density is lost when atoms are converted to cations, and since the nuclear charge remains the same the cations are smaller than the neutral atoms.
- As we move from left to right in the period if the ionic charge remains constant then the decrease in radii is smooth and moderate like in the +3 cations of the lanthanides.
- In the main group elements as we move from left to right the ionic charge increases as well which causes a dramatic decrease in the radii.
  Na^+(116pm) ,Mg^{2+} (86pm), Al^{3+} (67.5pm)
- As the ionic charge on the metal increases or as the oxidation state of the metal ion in a compound increases the ionic radii decreases. The Fe(III)-Cl bond length in $FeCl_4^{2-}$ is 11pm shorter than the Fe(II)-Cl bond length in $FeCl_4^-$
- For cations as well as anions the radii increases with the increase in coordination number. With the increase in coordination number the counter ions cannot approach the central ion closely because the repulsions between the approaching counter ions increases they become more in number.

Periodicity of elements

- For isoelectronic species the ionic radii decreases very significantly as the nuclear charge increases. This is because the increased nuclear charge is acting on the same number of electrons.

  C^{4-}(2.60Å) ,N^{3-}(1.71Å) ,O^{2-}(1.40Å) ,F^-(1.36Å), Na^+(0.95Å) ,Al^{3+}(0.50Å) ,Si^{4+}(0.41Å)

- When electrons are added to atoms the electron-electron repulsion increases, the nuclear charge remains the same and anionic radii are larger than atomic radii.

☞ **Points to be remember**

- The smallest radius is the cationic radii.
- 45 to 65 pm larger than the cationic radii are the covalent and metallic radii.
- 55 to 75pm larger than the covalent and metallic radii are the anionic and Van der wall radii.
- ❖ In reality the radius of an ion varies with different compounds and different coordination number. Values of ionic radii have to be used with care!
- ❖ Simple trends as seen for atomic radii are difficult to see in ions which constantly change across s and p blocks.

1.2.3 Ionization energy and enthalpy:

Ionization energy is a measure of the ease with which the electron can be removed from the atom.

1.2.3.1 Ionization energy: The minimum energy required to remove an electron from an atom in the gaseous state at T=0K.

$$M(g) \longrightarrow M^+(g) \;+\; e^-(g) \qquad IE = E(M^+,g) - E(M,g)$$

1.2.3.2 Ionization enthalpy: The minimum energy required to remove an electron from the atom in the gaseous state at 298K. The ionization enthalpy is larger than ionization energy by 5/2 RT. This difference is not much and can be neglected.

Successive Ionization energies:

- **First Ionization Energy**: Energy required to remove the outermost electron (the electron which is least under the influence of the nucleus) from the neutral atom.
- **Second Ionization Energy**: Energy required to remove an electron from the cation resulting after removal of the first electron.

Periodicity of elements

☞

POINTS TO BE NOTED

1. Ionization energy can be assumed to be very close to the energy of the (HOMO) of the ground state atom. It is the energy difference between the highest occupied molecular orbital and that corresponding to $n = \infty$

2. **Ionization energy depends on :**

   a. The effective nuclear charge Z_{eff}

   b. The electron-electron repulsion within the same subshell:
      For an electron belonging to a shell with principal quantum number n the ionization energy can be given by $I \propto Z_{eff}/n^2$

   c. The atomic radius: Elements with small atomic radii have high ionization energy because the outermost electron is closer to the nuclei and experiences a high columbic attraction which makes it difficult to remove.
      As the radius of the atoms increases on going down the group the ionization energy decreases.
      As the radius of the atoms decreases on going from left to right in the periodic table the ionization energy increases.

   d. Electronic configuration of the atoms: Half filled and fully filled orbitals are associated with extra stability so more energy is required to ionize these electrons.

3. We may say that first ionization energy is therefore expected to increase as we go from left to right in the period in accordance with the decreasing size and increasing effective nuclear charge. The plot that we obtain is however not linear.
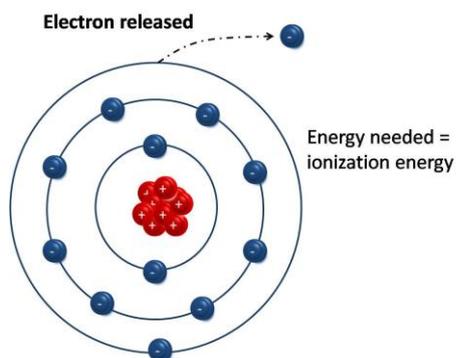
Periodicity of elements

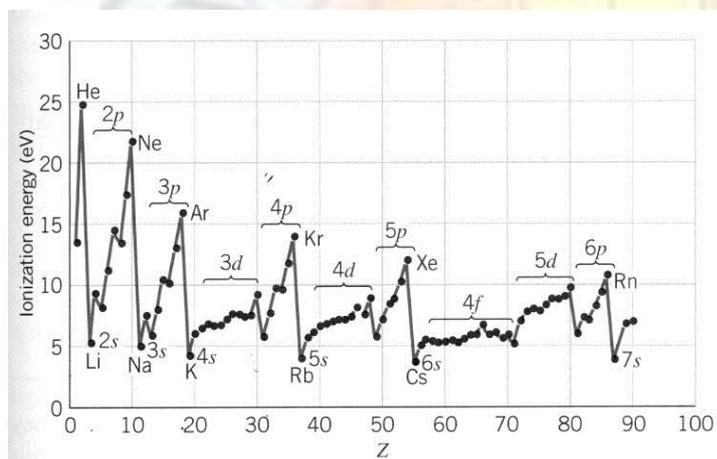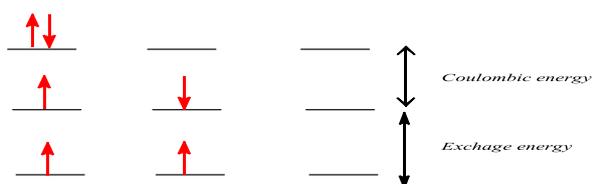

Fig2: Ionization of the valence electron in an atom.

Fig 3: The variation of Ionization Energy with Atomic Number.

The concept of half filled and fully filled orbitals:

Coulombic energy

Exchange energy

When two electrons are present in the same orbital or have to occupy the same region of space around an atom they repel each other because of the like charge. This repulsive energy called the coulombic energy favours the presence of electrons in different orbitals. There is only one possible way in which the electrons can be arranged with opposite spins in different orbitals. The coulombic energy is positive. The exchange energy which is an outcome of the quantum mechanical considerations depends on the possible exchanges between the two electrons of the *same energy and spin*. There are two possible ways in which the electrons can be arranged for the third case.

This exchange energy is *per possible exchange* E_{ex} and is **negative**. So the

Total Pairing Energy= Coulombic energy +Exchange energy

If **orbitals are degenerate** the coulombic and the exchange energy terms favour the unpaired configuration over the paired configuration.
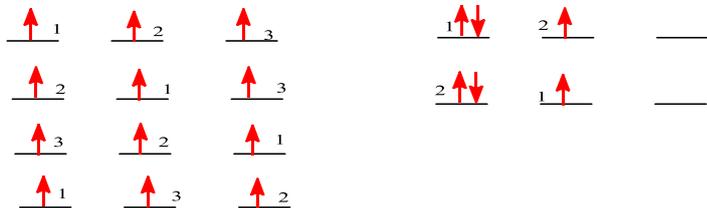
When three electrons have to fill the three degenerate p orbitals like in a nitrogen atom, two possibilities exist. If the orbitals are half-filled there are four possible arrangements of electrons and therefore three possible exchanges as shown above. The exchange energy is then $3E_{ex.}$ When we consider pairing of electrons, total energy is a combination of the positive coulombic energy term and exchange energy term. Only two arrangements are possible for electrons with the same spin in this case, the exchange energy is E_{ex} and total energy for this arrangement is higher.

 For degenerate orbitals the half filled and fully filled orbitals will have maximum stability due to minimum energy. They are therefore associated with higher ionization energies.

A word of caution:

This does not hold true in most transition metals as the 4s and 3d orbitals and the corresponding higher energy levels are close in energy and the pairing energy is very similar to the energy difference between these levels. An accurate explanation consists of considering the effect of increasing nuclear charge on energies of 4s and 3d orbitals (and corresponding higher orbitals) and interactions between electrons sharing the same orbitals.

Tell Me Why?

Q. Student: Ionization energy of Boron is smaller than Beryllium even though effective   nuclear charge is higher?

Teacher: The electronic configurations of Boron and Beryllium are (B [He]$1s^2 2s^2 2p^1$) and (Be [He]$1s^2 2s^{2.}$). In Boron the outermost electron is present in the 2p orbital and is less strongly bound than the electron present in a 2s orbital of Beryllium, which will has a higher Z_{eff} .It is easier to ionize the Boron atom.

Q. Student: Why is the ionization energy of Oxygen is less than Nitrogen

Teacher: Nitrogen has half-filled orbitals which are associated with extra stability. In Oxygen $2p_x$subshell has two electrons. The two electrons repel each other. This offsets even the higher effective nuclear charge.

N [He] $2s^2 2p_x^1 2p_y^1 2p_z^1$

O [He] $2s^2 2p_x^2 2p_y^1 2p_z^1$

Also when one electron of O gets ionized, we get the O^+ cation which has a half filled configuration associated with higher stability.
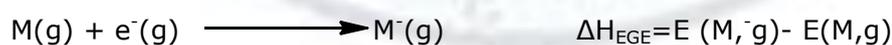
Now can you tell why?

Q1. First Ionization energy of Phosphorus is less than Sulphur?

Q2. First Ionization energy of Fluorine is less than Chlorine?

1.2.4 Electron Gain Enthalpy and Electron Affinity

1.2.4.1 Electron Gain Enthalpy

Electron gain enthalpy is the change in the standard molar enthalpy when an electron adds to the neutral   gaseous atom.

$$M(g) + e^-(g) \longrightarrow M^-(g) \qquad \Delta H_{EGE} = E(M,^-g) - E(M,g)$$

1.2.4.2 Electron affinity

The difference in energy between gaseous atoms and gaseous ions at T=0

$$EA = E(M,g) - E(M^-,g)$$

- The second electron gain enthalpy is almost always positive as the addition of an electron to an anion is not favoured due to repulsions.

- Electron affinity is the more commonly used term.

Periodicity of elements

- It is determined by the (LUMO) Lowest Unoccupied Molecular Orbital which may be unfilled or half-filled.

- An element which experiences a very strong effective nuclear charge in the outermost orbital has high electron affinity. The elements close to fluorine i.e. the top right of the periodic table have high electron affinity.

- Electron affinity depends on

  a. The effective nuclear charge $Z_{eff.}$ The electron affinity increases as the effective nuclear charge increases.
  b. Shielding effect: The electron affinity value decreases with the increase in shielding between the outer electrons and the nucleus.
  a. The atomic size: Usually the electron affinity value decreases with increasing atomic size.
  b. Half-filled and completely filled orbitals: Since the half-filled and fully filled orbitals are associated with extra stability addition of electrons is difficult.

- The electron affinity increases on going from left to right in a period as the effective nuclear charge increases.
- The electron affinity decreases on going down the group because the atomic size increases from top to bottom.

C: [He] $2S^2 2p_x^1 2p_y^1$

N: [He] $2s^2 2px^1 2py^1 2pz^1$
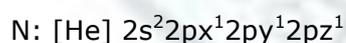
Carbon will have greater electron affinity as addition of the electron will lead to a half filled configuration associated with extra stability while addition of an electron to nitrogen will result in two electrons in the same p orbital thereby increasing the repulsion. The orbitals in this case will also no longer be half-filled.

☞ **Points to be noted**

Elements with high ionization energy are expected to have high electron affinities as well.

Fluorine is more electronegative than chlorine but chlorine has a higher tendency to accept an electron than fluorine as the addition of an electron to a small sized fluorine atom causes increased repulsions between electrons.

This effect is even more pronounced for N /P and O/S

Most of the minerals found in the earth's crust are oxides or sulphides. The acceptance of electrons by non metals like O and S to form O^- and S^- is exothermic but the formation of dinegative ions such as O^{2-} ad S^{2-} is positive i.e. endothermic . *How do these ions exist then?*

Such ions exist because of the stabilization either in the crystal lattices due to the high magnitude of lattice energy or due to solvation in the solution.

Can you account for the decrease in electron affinity as of lithium as compared to beryllium?

1.2.5 Electronegativity:

The concept of electronegativity was first introduced by Linus Pauling in 1930 as a means of describing bond energies.

- When we consider the formation of a covalent bond the attraction of the two nuclei for the electrons is not the same and the electron pair is closer to one of the nuclei.
- This tendency of a atom in a molecule to attract the electron density towards itself (or the reluctance to release the electron density) is called electronegativity.
- The electronegativity of a atom depends on the size, effective nuclear charge, oxidation state and the hybridization of the atom in the molecule. It therefore depends on the structure of the molecule and the atom.

- If the size of the atom is small and it has almost closed shell electronic configuration the tendency to attract electrons increase and the atom is highly electronegative.

1.2.5.1 Variation of electronegativity

- Electronegativity increases from left to right in a period.

- Electronegativity decreases down the group.

Many scales of electronegativity have been proposed. One of the most commonly used scale is the Pauling's scale.

1.2.5.2 Pauling's Electronegativity: For any covalent bond, the bond energy of the heteronuclear bond E(A-B) is greater than the bond energy of the sum of homonuclear bonds E(A-A) and E(B-B). This excess bond energy can be attributed to ionic contribution in the bonds. He treated this ionic contribution by the equation.

$$E(A\text{-}B) = [E(A\text{-}A) \times E(B\text{-}B)]^{1/2} + 96.48(X_A - X_B)^2$$

E(A-B) is expressed in kJ mol^{-1} and $X_A - X_B$ is the difference in "electronegativity" between the two elements. The largest electronegativity difference exists between Cs and F. The value of F was set arbitrarily at 4.0and electronegativity values of all other elements found relative to it.

> **Do you know?**
> HCl has a bond energy of 428 KJ/mol while the average bond energy of H_2 (432 KJ/mol) and Cl_2 (240 KJ/mol) molecules is 336 KJ/mol.

1.2.5.3 Allred and Rochow electronegativity: Allred and Rochow gave the electronegativity values by considering the electrostatic force exerted by effective nuclear charge, Z_{eff}, on the valence electron. They gave the equation:

$$X^{AR} = (3590 \text{ x } Z_{eff}/r^2_{cov}) + 0.744$$

1.2.5.4 Mullikan electronegativity: Mullikan proposed that two energies associated with the atom i.e. the electron affinity EA_v and the ionization potential IE_v should be a measure of electronegativity. The Mulliken electronegativity, X_M is related to the electron affinity EA_v and the ionization potential IE_v by the equation:

$$X_M = (IE_v + EA_v)/2$$

The subscript v denotes a specific valence state.

The Mulliken electronegativity X_M can be expressed on the Pauling scale by the relationship given below if the values of IE and EA are in MJ mol^{-1}:

$$X_M = 3.48[((IE_v + EA_v)/2) - 0.602]$$

1.2.5.5 Mullikan and Jaffe electronegativity : When the ionization energies and electron affinity values of atoms are plotted against the oxidation state a smooth curve results and the total energy can be described by a quadratic formula
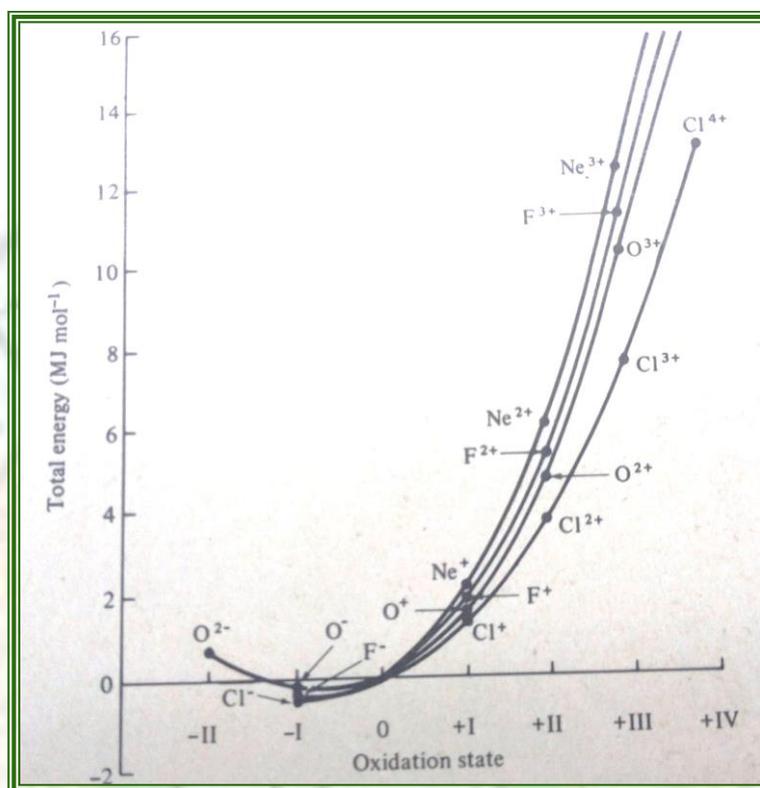
$$E = \alpha q + \beta q^2$$

Fig 4: Ionization energy and electron affinity curve for the atoms fluorine, neon, oxygen and chlorine.[1]

E is the total energy of the atom Σ_{IE} or Σ_{EA} and q is the ionic charge.

Jaffe said that the Mullikan definition of electronegativity (as given in section 1.7.4) is the slope of this curve as it passes through the origin.

$$X = dE/dq = \alpha + 2\beta q \quad (1)$$

Substituting q =+1 in the equation (1), the energy of the system corresponds to the first ionization energy and substituting q= -1 the energy of the system corresponds to the negative of electron affinity.

$$IE_V = \alpha + \beta \quad (2) \text{ and } EA_V = -\alpha + \beta \quad (3)$$

Therefore on adding equation (2) ad (3) we get $IE_V + EA_V = 2\alpha$ where **α** stands for **Mullikan electronegativity** .

Periodicity of elements

- Mullikan Jaffe electronegativity involves valence state ionization energy and electron affinities (calculated for atoms in the valence state as they exists in a molecule)
- It takes into account the electronegativity of partially charged atoms emphasising the effect the partial charge can have on the electronegativity of the atom.

χ = a +bδ where δ is the partial ionic charge

where a = inherent or neutral electronegativity and b= charge coefficient (rate of change of electronegativity with charge)

1.2.5.6 Hybridization and electronegativity

Hybridization has a profound effect on electronegativity.

- The s orbitals have lower energy hence greater electron attracting power therefore **greater the s character greater the electronegativity**.


The factor affecting the acidity of hydrogen is the difference in electronegativity between hydrogen and the atom to which it is bonded .Acetylene has highly acidic hydrogen as the carbon atom is sp hybridized (50% s character) and has almost the same electronegativity as chlorine atom. This is in contrast to methane in which the carbon atom is sp^3 hybridized (25% s character) and is not reactive .

Periodicity of elements

As the s character in hybridization of nitrogen increases the basicity of nitrogen will decrease. In ethane nitrile N is sp hybridized and hence very electronegative. The more electronegative the nitrogen atom less is the tendency to share the lone pair of electron. The basicity therefore decreases.

$$N \equiv C - CH_3 \quad + \quad H{-}O{-}H \quad \longrightarrow \quad \text{No reaction}$$
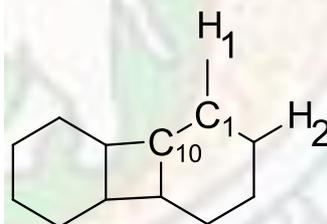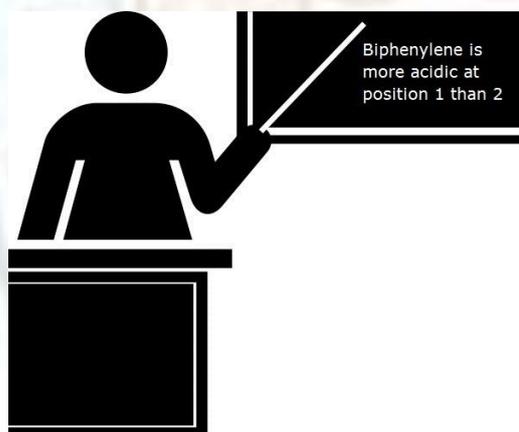
Biphenlene

Biphenylene is a strained ring system with 90° angles in the four membered rings. The strain in the 4 membered ring results in more of p character in the bond of carbon C_{10} within the four membered ring. This results in an increased s character in the bond to C_1 which causes C_{10} to be highly electronegative and this in turn induces a positive charge on C_1 which enhances the acidity of hydrogen 1 (H_1).

1.2.5.7 Electronegativity and partial charge

The electronegativity of an atom varies with the partial charge due to substituent groups on it.

- Methyl iodide hydrolyses as expected but trifluoromethyl iodide gives unusual products.
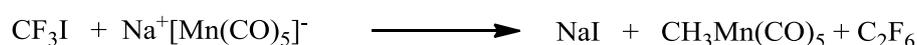
Periodicity of elements

Methyl iodide hydrolysis as shown to give methanol but trifluoromethyl iodide gives trifloromethane. The negative hydroxide ion attacks the most positive atom in the organic iodide i.e. the carbon atom in methyl iodide and the iodine atom in trifluoromethyl iodide. The fluoro groups increase the positive charge on carbon which increases the electronegativity of carbon atom to such an extent that it is greater than that of iodine and thus iodine acquires a positive charge and is attacked by the hydroxide ion.

$$CH_3I \quad + \quad OH^- \quad \longrightarrow \quad CH_3OH \quad + \quad I^-$$

$$CF_3I \quad + \quad OH^- \quad \longrightarrow \quad CF_3H \quad + \quad IO^-$$

？ Do you know?

Based on the polarity of the C-I bond (which varies with the substituent on carbon) the reaction between carbonylate anions with methyl iodide and trifluoroiodo methane gives the following products.

$$CH_3I \quad + \quad Na^+[Mn(CO)_5]^- \quad \longrightarrow \quad NaI \quad + \quad CH_3Mn(CO)_5$$

$$CF_3I \quad + \quad Na^+[Mn(CO)_5]^- \quad \longrightarrow \quad NaI \quad + \quad CH_3Mn(CO)_5 + C_2F_6$$

- The ionic character in the bond increases as the electronegativity difference between the bonded atoms increases. This will also result in an increased bond energy in a covalent bond eg. H-Cl>H-Br>H-I. The acid strength therefore increases in the reverse order. HI is the most acidic.
- As we move from left to right in the periodic table the acidic nature of the oxides of the elements increases with increase in electronegativity of the atom. This is in accordance with increasing covalency of the oxides due to increasing ease of polarizability of the oxygen. On moving to the right.

$$Na_2O > MgO > SiO_2 > P_2O_5 > SO_3 > Cl_2O_7$$
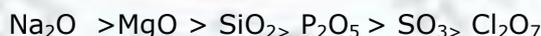
- The percentage ionic character for a polar bond can be determined using the electronegativity values

$$\% \text{ IC of a bond } AB = 16(X_A - X_B) + 3.5 (X_A - X_B)^2$$

- The basic character of NH_3 and NF_3 Ammonia and nitrogen trifluoride are both pyramidal in nature. They have three bond pairs and one lone pair each, with the ∠HNH and ∠FNF angles as 107º and 102º. Due to the electron withdrawing nature of the fluorine group the electron density on nitrogen decreases and the lone pair is present in an orbital with more s character. Nitrogen being more electronegative than hydrogen attracts the electron density of the bond pairs

toward itself in ammonia and the lone pair of electrons lies in a approximately sp^3 hybridized orbital making nitrogen in ammonia a better electron donor.

- Acid strength of oxyacids H_2SO_4 and H_2SeO_4. Sulphur and Selenium belong to group sixteen in the periodic table. Sulphur is more electronegative than selenium and can polarize and weaken the O-H bond to a greater extent than selenium in their respective oxyacids, making sulphuric acid a stronger acid.
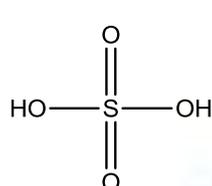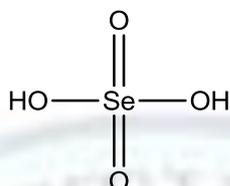
Sulphuric acid   Selenic acid

1.2.5.8 Group electronegativity

Electronegativity of the central atom in a group due to the substituent on the atom is called group electronegativity.

Group electronegativity X_G depends on

a. The inherent group electronegativity, a_G which is the average of the inherent atomic electronegativities.
b. The charge coefficient b_G which is an average but inversely proportional to the number of atoms in the group

$$X_G = a_G + b_G \delta_G$$

Groups are therefore super atoms capable of absorbing large amounts of positive or negative charges.

- Methyl group is a better electron donor than hydrogen though it is more electronegative than hydrogen.

- It has greater charge capacity which results from the ability to spread charge around that allows the methyl group to donate more electron density than smaller hydrogen atom.

1.2.5.9 Sanderson Electronegativity

- As the effective nuclear charge increases the size of the atom decreases.
- Sanderson suggested that the extent to which an atom or ion attracts the electron density to itself will depend on the effective nuclear charge felt by the outermost valence electrons. He suggested that "electronegativity, S, should be proportional to the compactness of an atom.

S = D/D$_a$

Where D is the electron density of an atom and D$_a$ is the expected electron density of an atom which is calculated from extrapolation to the noble gas elements."

Sanderson's Principle of Electronegativity Equalization:

When a bond is formed between two atoms differing in their electronegativity then electron density shifts till electronegativities become equal within the compound. The intermediate electronegativity is given by the geometric mean of the individual electronegativities of the component atoms.

- The electron density shifts towards the more electronegative atom from the more electropositive atom, generating a partial positive charge on the electropositive atom and a partial negative charge on the electronegative atom.
- As the positive charge on the atom which is losing electrons increases, its electronegativity increases. The reverse happens for the electronegative atom till the electronegativities reach the same values.
- Sanderson reached the conclusion that the partial ionic charge and ionic radius of ions are not constants, but vary depending upon the electronegativity of the surrounding atoms.

Summary

Chemist now do not have to memorize physical properties and chemical reactions of the known elements. We can now understand the properties and predict the behaviour of the elements reasonably well because of our understanding of the periodic table. When elements are arranged in order of increasing atomic numbers periodic variations in properties are observed.
The trends of physical and chemical properties across periods or down the groups are called periodicity. We can easily predict the variation in radii, Ionization energy, Electron Affinity, and Electronegativity. When we want to compare radii as a periodic trend, we have to keep in mind that a comparison of only similar type of radii is possible.

Exercise

Q1. For the following pairs of atoms which has the highest first ionization energy

a. Na and Mg
b. Mg and Al
c. Mg and Ca

Q2. Rank the 3s, 3p, 3d orbitals in order of

a. Increasing shielding ability
b. Increasing penetration ability

Q3. The single bonded metallic radii of sodium is 157 pm. Give a reasonable estimate of the following radii assuming the increment between different radii is 60 pm.

Periodicity of elements

   a. Covalent radii
   b. Van der Wall radii

Q4. Describe the main periodic trends in

   a. Electronegativity of atoms across the period and down the group.
   b. Radii of atoms across the period and down the group.

Q5. Why does Potassium have lower ionization energy than Lithium?

Q6. What is the significance of large increase in third ionization energy of calcium and fifth ionization energy of Silicon?

Q7. Why do the noble gases have large radii?

Q8. The increase in size between Lithium and Beryllium is much greater than sodium and Magnesium or Potassium and Germanium. Explain.

Q9. Which of the following atoms or ions are larger in size? Give reason.

   a. K^+ or Cs^+
   b. Ca^{2+} or Zn^{2+}
   c. Cl or Br

Q10. Which of the following atoms have the highest electron affinity and why?

   a. Li or Cs
   b. Li or F
   c. F or Cl
   d. S or Se

Q11. PtF_6 has an electron affinity even higher than fluorine. Explain.

Q12. Calculate the electronegativity of carbon from the following data

$E_{H-H}=104.2$, $E_{C-C}=83.1$, $E_{C-H}=98.8$, $X_H=2.1$

Q13. Calculate the electronegativity of silicon using the Allred and Rochow method. Covalent radius of silicon is 1.175 Å.

Q14. Why is fluorine a stronger oxidising agent than chlorine in solution?

Q15. Arrange the oxides in order of increasing acid strength giving reason

   Al_2O_3, B_2O_3, CO_2, NO_2
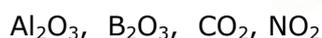
Glossary

1. **Atomic Orbitals**: The electron in the hydrogen atom is represented by a wave function that is obtained from the Schrödinger wave equation. The region in space described by the wave function is called the atomic orbital.

2. **Electron gain enthalpy**: The change in the standard molar enthalpy when an electron adds to the neutral   gaseous atom.

$$M(g) + e^-(g) \longrightarrow M^-(g) \qquad \Delta H_{EGE}=E\ (M,^-g)- E(M,g)$$
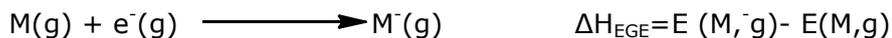
3. **Electronegativity**: The tendency of an atom in a molecule to attract the electron density towards itself (or the reluctance to release the electro density) is called electronegativity

4. **Ionization enthalpy**: The minimum energy required to remove an electron from the atom in the gaseous state at 298K. The ionization enthalpy is larger than ionization energy by 5/2 RT

5. **Periodicity**: Trends of physical and chemical properties across periods or down the groups is called periodicity.

6. **Radial probability distribution diagrams**: The radial probability distribution function is related to the probability of finding a electron in a spherical shell of radius r and thickness dr. The maxima in the radial distribution function represent the most probable distance for the electron from the nucleus.

7. **Radii:** There is no practical way of measuring the radii of gaseous atoms.There are different types of radii of atoms and ions in different bonding situations i.e. Covalent, Ionic, Metallic and Van der Wall .

8. **Shielding**:In a multi-electron system each electron acts as a shield or screen for electron further away from the nucleus, reducing the attraction between the nucleus and distant electron. This effect is called the shielding effect.

References **and weblinks**

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