

Unit - I

A] Periodic Properties

Periodic Classification of the Elements:

- Modern periodic table is based on modern periodic law.
- According to this law,
- ✓ "The elements are arranged in the increasing order of their atomic numbers.

OR

- The elements are a periodic function of their atomic number.
- As we go left to right in the periodic table, The electrons are successively added at every element with increase in atomic number.
 - It is based on electronic configuration.

Important Features of periodic Table

- It is based on Atomic number.
- It is based on Electronic configuration of an elements.
- It consist of 18 vertical columns called as groups and 7 horizontal ~~periods~~^{rows} called as periods.
- The first period consist of only two elements (Hydrogen and Helium).
- The second period (Lithium to Neon) and Third period (sodium to Argon) consist of 8 elements.
- Therefore First three periods (1, 2, & 3) are called as short periods.
- The fourth (Potassium to Krypton) and fifth (Rubidium to Xenon) consist of 18 elements.
- The sixth period (Caesium to Radon) consists of 32 elements.
- Therefore 4th, 5th and 6th periods are called as long periods.
- The last 7th period (Francium [Fr] to Dubnium [Db]) consist of 19 elements. Therefore it is called

as incomplete period.

- The elements of periodic tables are divided into four blocks: namely s, p, d, f block elements.
- The ^{elements of} extreme left of periodic table ~~are called~~ (group 1 and 2) are called as s-block elements. These elements are highly electropositive.
- The elements of right portion of periodic table (group 13 to 18) are called as p-block elements. These elements are metals, non-metals, metalloid and noble gas or rare gas elements.
- The middle portion of periodic table (group 3 to 12) are called as d-block elements, OR transition elements.
- And ^{the elements} at the bottom of periodic table are called as f-block elements OR inner transition elements.

(a) Transition elements OR d-block elements

- The elements in which last electron enters in $(n-1)d$ suborbital are called as d-block elements or transition elements.
- It consist of four series. Each contain 10 element.
- The elements in which last electron enters in $3d$ -suborbitals are called First transition series elements. It consist of elements from Sc to Zn .
- The elements in which last electron enters in $4d$ -suborbitals are called as second transition series elements. It consist of elements from Y to Cd .
- Third series consist of La , Hf to Hg and X .
- Fourth series is incomplete and contain three elements Ae , Rf & Db .

(b) Inner Transition elements OR f-block elements

- The elements in which last electron enters in $(n-2)f$ suborbital are called as f-block elements or inner transition elements.
- It consist of two series

① Lanthanides (4f-block elements):

- The elements in which last electron enters in 4f-suborbital are called Lanthanides.
- It consists of 14 elements from $_{58}\text{Ce}$ to $_{71}\text{Lu}$.
- It is present in 6th period and 3rd group.
- They are also called as rare-earth elements.
- They are present at the bottom of main body of periodic table.

② Actinides (5f-block elements):

- The elements in which last electron enters in 5f-suborbital are called Actinides.
- It also consists of 14 elements from $_{90}\text{Th}$ to $_{103}\text{Lr}$.
- It is present in 7th period and 3rd group.
- These elements are present at the bottom of main body of periodic table.

Periodic properties

① Covalent Radius:

The distance between centre of nucleus and last orbit electron in an atom of the molecule is called as covalent radius.

OR.

The half of the distance between two identical atoms in the molecule joined by covalent bond is called covalent radius.

- It is generally applied to covalent compound or non-metals.

- eg. The distance between C-C single bond is 1.54 \AA . Therefore covalent radius of carbon is $\frac{1.54}{2} = 0.77 \text{ \AA}$ [ie half of C-C distance]

② Ionic Radius:

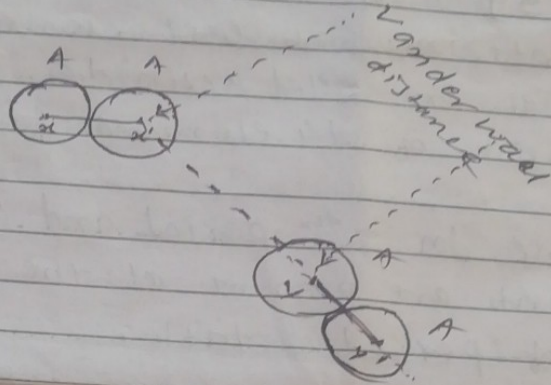
The distance between centre of nucleus and last orbit electron in an ion (cation/anion) is called ionic radius.

③ Vander Waals Radius or Collision Radius:

The half of the distance between the nuclei of two non-bonded neighbouring atoms of two adjacent molecules is called as Vander Waal radius.

eg. In CCl_4 , the CCl_4 molecules are so arranged that, the shortest distance between Chlorine nuclei in different molecule is 3.76 \AA . Therefore Vander waal radius of chlorine is

$$\frac{3.76}{2} = 1.88 \text{ \AA}$$



$$\therefore \text{Vander waal radius of atom A} = \frac{X-Y}{2}$$

Periodic variations of atomic and ionic radii

In a period:

→ As we go left to Right in the periodic table atomic and ionic radii decreases.

Generally, the elements that are present to the extreme left of periodic table (Alkali metals) have largest value of atomic and ionic radii while the elements which are present extreme right (eg halogens) have smallest atomic ~~size~~ and ionic radii.

But zero group elements have larger atomic radii than halogens due to completely filled orbital of zero group element, i.e. extra stability and inter electronic repulsion.

Explanation

As we go left to right in a period, electrons are added to same orbit. Therefore nuclear charge increases with increase in atomic number, therefore electrons experiences more and more attractive force toward nucleus. Therefore atomic and ionic radii decreases.

In group :-

As we go top to bottom in group, atomic and ionic radii increases with increase in atomic number.

Explanation

- ① As we go top to bottom in group, electrons are added to new orbit therefore distance between nucleus and last orbit electron increases. therefore atomic and ionic radii increases.
- ② As we go top to bottom, nuclear charge increases, but therefore force of attraction between nuclei.

Metallic Radius

The half of distance between the nuclei of two adjacent metal atoms in crystal lattice in which metal has a coordination number 12 is called as metallic radius.

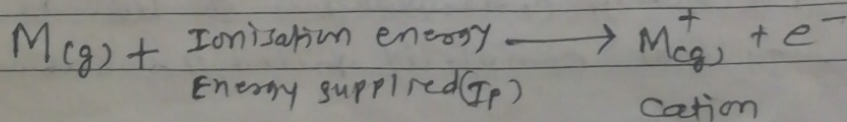
$$r_{\text{metal}} = \frac{\text{Inter nuclear distance bet}^n \text{ two adjacent metal}}{2}$$

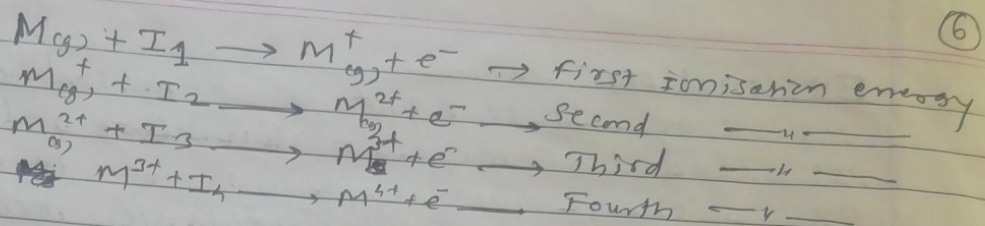
Metallic radii are ~~smaller~~ smaller than vander waal radii but larger than covalent radii (10% to 15%)

Ionisation potential or Ionisation Energy

- The minimum amount of energy required to remove the electron from last orbit, ^{from isolated gaseous atom} is called as ionisation energy.

- It is represented as TE or IP
- It is endothermic process.





The value of IP increases as $I_1 < I_2 < I_3 < I_4$.
 The successive increase in IP is due to reason that when we remove one electron from $M_{(g)}$, then $M_{(g)}^+$ ion is formed, which is smaller in size. ~~and~~ and we know that smaller is the size greater is attraction therefore more energy is required to remove the e^- from M^+ ion. Similarly M^{2+} ~~has~~ required higher energy than M^+ , M^{3+} and so on.

Periodic Variation of Ionisation Energy

In a period.

As we go left to right in period, ionisation potential increases with increase in atomic no. This can be explained as

As we go left to right,

- (1) Atomic size decreases.
- (2) Nuclear charge increases
- (3) The distance between nucleus and last orbit electron decreases.
- (4) Therefore Ionisation energy increases

Exceptions

Certain elements have high Ionisation potential that can be explain on the basis of half filled and completely filled orbitals.

If orbitals are half filled or completely filled then it achieve extra stability and ~~big~~ large amount of energy is required to remove the electrons from last orbital therefore they have high IP. eg. Be.

Electronic configuration of Be is $1s^2 2s^2$.

It has completely filled 2s sub orbital

(7)
eg. ② Nitrogen

Electronic configuration of Nitrogen is $1s^2 2s^2 2p^3$.

It has half filled p orbitals

eg. ③ Neon

Electronic configuration of Neon is $1s^2 2s^2 2p^6$.

It has completely filled p-orbitals.

The removal of electron from such atoms is difficult and large amount of energy is required to remove the electron from last orbital, and have high ionisation potential.

In Group

As we go top to bottom in group, Ionisation potential decreases with increase in atomic number.

The decrease in I.P. in group can be explain as As we go top to bottom,

(i) Atomic number increases

(ii) Nuclear charge increases

(iii) Number of orbit increases

(iv) Electrons are added into new orbits

(v) screening effect (or shielding effect) increases

(vi) Atomic size increases

(vii) Therefore Ionisation potential decreases.

In addition to above factors, the shape of orbital also affect ionisation potential.

If electron in the outermost orbital has more penetrating power then this electron approach the nucleus more ~~clatter~~ closely than other orbitals and therefore the electron in such orbital is tightly held and required more energy to remove this electron. Therefore increase in ionisation potential.

The degree of penetration of electron is in the order of $s > p > d > f$. i.e s-electron will approach the nucleus more closely than p-electron more closely than d and d more closely than f.

Therefore - s-electron will be more difficult to remove than p-electron and p-electron is more difficult than d-electron and so on.

Effect of Ionisation energy on different properties of elements

(i) Metallic and Non-metallic character:

- The metal has a tendency to loose one or more electron from its outermost orbit and forms a cation. The ability to loose electrons depends upon ionisation potential.
- As ionisation energy increases, metallic character decreases.
- As we go left to right in period, ionisation potential increases therefore metallic character decreases.
- Therefore alkali or alkaline earth ~~metal~~ elements are metallic in nature while halogens are typical non-metals.

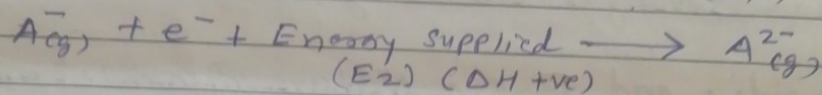
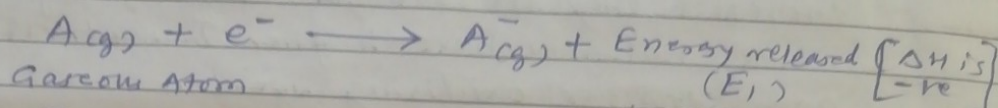
(ii) Relative reactivity of the elements:

- The elements with higher value of ionisation energy are less reactive, eg. inert gases and those having lower values are highly reactive, eg. alkali and alkaline earth metals.
- As we go top to bottom in a group, Ionisation energy decreases and therefore reactivity increases down the group.

(iii) Oxidizing and reducing power of the element

- The element which reduce other element and oxidised itself (ie loss of electron) is called as reducing agent.
- This property of element to reduce other element is called as reducing power of element.
- ~~Reducing power~~ It depends ionisation energy

repulsion between anion and electron. Therefore we have to supply energy instead of releasing and forms $A_{(g)}^{2-}$.



The process of conversion of $A_{(g)}^{-}$ to $A_{(g)}^{2-}$ is called a second electron affinity (E_2).

Periodic Variation [in Period]

As we go left to right in period, Electron affinity increases because

As we go left to right, in period,

- (i) Atomic number increases
- (ii) Atomic size ~~increases~~ decreases
- (iii) Nuclear charge increases
- (iv) Ionization energy increases
- (v) Electronegativity increases
- (vi) Therefore electron affinity increases.

Exception:

Ans

Fluorine has low Electron affinity than Chlorine. - This can be explained on the basis of smaller size of Fluorine. Because of smaller size, there is inter-electronic repulsion (electron-electron repulsion) therefore stability decreases. Therefore Fluorine has low E.A. than Chlorine.

- In Fluorine, electron is added in small and compact 2p orbital while in Chlorine, electron is added in bigger 3p orbital in which added electron is easily accommodated. Therefore Fluorine has low EA. than Chlorine.

In Group

As we go top to bottom in group, electron affinity decreases with increase in atomic number, because

- ① Atomic size increases with increase in atomic no.
- ② screening effect [shielding effect] increases with increase in inner shell.
- ③ Ionisation energy decreases
- ④ Electronegativity decreases
- ⑤ therefore electron affinity decreases.

Exception:

- ① The Electron affinity value [E] for Be and Mg is zero because for Be ($2s^2$) and Mg ($3s^2$), the s-orbital is completely filled and addition of electron in 2p and 3p orbitals have higher energy. Therefore E value for Be and Mg is zero
- ② The E-value for inert gas elements is also zero because of completely filled ns & np orbitals ($ns^2 np^6$) and addition of electron in higher ~~near~~ energy level required high^{er} energy. This is not favoured and have zero E value.
- ③ The E value for N and P have lower E value due to half filled orbitals and have extra stability and addition of electron to such atoms is difficult and hence lower E-value.

Electronegativity.

def - The tendency of atom to attract electron pair toward itself is called as electronegativity.

eg Consider HCl molecule, ~~in~~ which is formed between two dissimilar atoms, Hydrogen and chlorine. The electron pair between H & Cl does not lie exactly in the centre of the molecule but it is nearer to Cl-atom than H-atom. The reason for this equal sharing of electron pair is that, the Cl has greater tendency to attract ^{shared} electron pair than ~~hydrogen~~ toward itself than hydrogen. That means chlorine has greater electronegativity than H-atom.

- The electronegativity is denoted by X. (अणु)
- The concept of electronegativity was proposed by Pauling.

- Pauling assigned imaginary value for Fluorine is 4 which is most electronegative element.

Periodic variation

In period:

As we go left to right in period, electronegativity increases with increase in atomic number because

- ⊕ As we go left to right
- ① Atomic no. increases
- ② Nuclear charge increases
- ③ Atomic size radius decreases
- ④ Ionisation energy increases
- ⑤ Electron affinity increases
- ⑥ Therefore electronegativity increases.

In Group

As we go top to bottom in group, electronegativity decreases with increase in atomic number

because ∴ As we go top to bottom

- ① Atomic number increases
- ② Nuclear charge increases
- ③ ~~Atomic~~ Number of orbit increases
- ④ ~~the~~ shielding effect increases
- ⑤ electrons are added into new orbit.
- ⑥ Atomic size increases
- ⑦ Ionisation energy decreases
- ⑧ Electron affinity decreases
- ⑨ therefore electronegativity decreases

Determination of Electronegativity value

There are two different scales to determine the electronegativity value of elements

- ① Pauling's electronegativity scale OR Pauling Bond energy scale
- ② Mullikan's scale.

① Pauling's Electronegativity scale or Pauling's Bond Energy scale.

This method considered Bond energies (that is the energy required to break a bond to form neutral atoms).

consider bond $A-B$ between two dissimilar atoms A and B of molecule AB .

Consider E_{A-A} , E_{B-B} , E_{A-B} are the bond energies of bond $A-A$, $B-B$, $A-B$ respectively.

The bond formed between two atoms A & B is intermediate between pure covalent $A-B$ and pure ionic A^+B^- . Due to this some ionic character is developed in the $A-B$ bond therefore bond $A-B$ is somewhat strong and bond energy is increased and bond is stabilised by resonance.

For the determination of electronegativity, the following measurement are made.

- i) Actual or experimental bond energy = H
- ii) Bond energy when bond is truly covalent = Q
- iii) Resonance energy (Δ) due to ionic character of covalent bond called as ionic Resonance energy

$$\therefore \Delta = H - Q$$

where Δ is resonance energy.

The resonance energy measure partial ionic character of covalent bond and

The difference between bonded atoms is related to ionic character of covalent bond.

therefore Δ is the difference in the electronegativity of bonded atoms. If X_A and X_B are electronegativities of atom A and B and $X_A > X_B$, then

$$X_A - X_B \propto \sqrt{\Delta_{A-B}}$$

$$X_A - X_B = K \sqrt{\Delta_{A-B}} \quad \text{..... (1)}$$

where K is const. ($K = 0.208$)

$$\therefore X_A - X_B = 0.208 \sqrt{\Delta_{A-B}} \quad \text{..... (2)}$$

(14)

Pauling fixed the electronegativity value for Fluorine is 4.0. From this other electronegativity values were calculated by using above eqⁿ - i.e. $X_A - X_B = 0.208 \sqrt{\Delta_{A-B}}$ (2)

Calculation of Δ

We know that

$$\Delta = H - Q$$

The value of H can be measured experimentally and value of Q can be obtained indirectly.

If we consider the energy (E_{A-B}) of purely covalent bond between two atoms A-B then it is expected that it ~~is~~ is equal to mean value of bond energies between A-A and B-B.

Thus

$$\Delta = H - Q$$

$$= E_{A-B} - \frac{1}{2}(E_{A-A} + E_{B-B}) \quad \text{--- (3)}$$

or Combining eqⁿ (2) & (3)

$$X_A - X_B = 0.208 \left[E_{A-B} - \frac{1}{2}(E_{A-A} + E_{B-B}) \right]^{1/2} \quad \text{--- (4)}$$

According to Pauling, the Postulate of additivity of normal covalent bond is valid for large number of single bonds. Therefore ~~the~~ postulate of additivity is failure in some cases (like alkali metal hydrides) and new postulate is introduced and used geometric mean instead of arithmetic mean. (11)

Therefore eqⁿ (4) can be modified to

$$\Delta = E_{A-B} - (E_{A-A} \times E_{B-B})^{1/2} \quad \text{--- (5)}$$

\therefore eqⁿ (4) can be written as

$$\checkmark X_A - X_B = 0.208 \left[E_{A-B} - \sqrt{E_{A-A} \times E_{B-B}} \right] \quad \text{--- (6)}$$

This eqⁿ gives difference in electronegativity. It is used to calculate electronegativity of an atom A (X_A), if electronegativity of another atom B (X_B) is known, and Pauling expressed ionic resonance energy (Δ) in eV and not in kcal. [~~1 eV/bond~~ 1 eV/bond = 23 kcal/gram bond]

② Mullikan's scale :

According to Mullikan's

the electronegativity is difference between Ionisation potential (IP) and electron affinity (E.A) of atom divided by 5.6.

$$\therefore (X_A)_M = \frac{(IP)_A - (EA)_A}{5.6}$$

Where $(X_A)_M$ is the electronegativity of atom A on Mullikan's scale
1/5.6 is constant and used when IP and EA values

are expressed in eV.

on the basis of Mullikan's scale, the following three conditions for the formation of pure covalent A-B bond and ionic bonds can be given as

(i) for the formation of purely covalent A-B bond,

$$\frac{(IP)_A - (EA)_A}{5.6} = \frac{(IP)_B - (EA)_B}{5.6} \quad \text{Therefore } X_A = X_B$$

(ii) for the formation of A^-B^+ bond,

$$\frac{(IP)_A - (EA)_A}{5.6} > \frac{(IP)_B - (EA)_B}{5.6} \quad \text{Therefore } X_A > X_B$$

(iii) for the formation of A^+B^- bond,

$$\frac{(IP)_A - (EA)_A}{5.6} < \frac{(IP)_B - (EA)_B}{5.6} \quad \text{Therefore } X_A < X_B$$

But this method has following limitations

(i) The values of Electron affinity are known only for limited number of elements.

(ii) During bond formation the transfer of electron between two atomic orbitals occurs whose correct constitution may not be known.